chapter 4

MAGNETOCALORIC EFFECT IN THE VICINITY OF PHASE TRANSITIONS

A.M. TISHIN

Faculty of Physics
M.V. Lomonosov Moscow State University
Moscow, 119899
Russia
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1. Introduction

During recent decades an essential interest in investigations of magnetothermal properties of materials was demonstrated due to their significance for the development of fundamental and applied magnetism on the whole. These phenomena have a strong influence on the character of the behavior of such fundamental physical quantities as the entropy, specific heat, and thermal conductivity, and could lead to a number of extra anomalies in the dependencies of the above mentioned material properties on temperature, magnetic field and some other external parameters.

Warburg (1881) first discovered the magnetocaloric effect (MCE) as an important manifestation of magnetothermal properties. About 120 years ago, he was the first of currently known scientists to observe heat evolution in iron under the application of a magnetic field. Soon after, Edison (1887) and Tesla (1890) suggested their thermomagnetic generators of electrical power, using materials with a sharp temperature dependence of magnetization. If the effect of the field takes place under adiabatic conditions, it can result in an increase or in a reduction of the original temperature of a magnetic material. This is a consequence of the variation, under the field, of the internal energy of the material possessing a magnetic structure.

Currently, the authors of most papers define the magnetocaloric effect as the change of the initial temperature of a magnetic material as an external magnetic field is applied under conditions of constant total entropy of the material (adiabatic magnetization). However, in our meaning the term MCE should be considered more widely. Thus, we will use it to describe processes of entropy variation of the magnetic subsystem.

MCE investigations were shown to yield the kind of information that is hard to obtain by other techniques. In recent years the interest in investigations of the MCE and the influence of the magnetic field on the entropy has become renewed for the following reasons: first, the possibility to obtain information on magnetic phase transitions, and, second, by the prospect of using some of the materials in magnetic cooling machines (magnetic refrigerators).

Up to the present, the MCE has not been reviewed completely enough anywhere. At the same time, in accordance with our estimation, about 400 papers about the MCE and related questions have been published. Some recent MCE data in lanthanide materials have been reviewed by Tishin (1997). A comprehensive review of the MCE properties of some transition metals and some alloys can be found in the papers of Kuz'min and Tishin (1991, 1993a).

This chapter presents the attempt of giving an overview of the investigations made in this field over the past years and mostly deals with MCE physics. The author gives special
emphasis to the character of the MCE behavior in different magnetic materials and comprehensively reviews the studies of this effect. This review will embrace materials with magnetic moments of either band or localized origin, and materials where the magnetic ordering can have collinear, as well as more complicated character, such as helical.

Since space does not permit to discuss the details of all questions of concern, we concentrate on the focal points giving the main theoretical concepts and experimental findings. The thermodynamic approach is the most elaborate one for understanding the observed phenomena. Also often used are Landau's theory of second-order phase transitions and mean-field approximation (MFA), proposed by Rosing (1892, 1896) and Weiss (1907). Both models well describe the behavior of a number of magnetic quantities, but are inapplicable in the vicinity of the transition point because of critical fluctuation effects. In the low temperature region the spin-wave theory is used to describe temperature dependencies of magnetization, MCE and specific heat in ferro- and antiferromagnets (Akhiezer 1961). Scaling theory is used in certain cases to describe the MCE in magnetic materials in the vicinity of the phase transition points (Mathon and Wohlfarth 1969; Stauffer 1970; and Kamilov and Aliev 1983).

A notable part of the chapter is dedicated to the description of experimental techniques used by various investigators to study MCE. Consideration is given to both quasi-stationary and pulse field setups.

For the first time a detailed discussion of experimental and theoretical studies of a great number of magnetic systems is given. The emphasis is put on understanding the physical essence of the observed phenomena. Results of calculations of the field effect on the entropy and specific heat are reported and systematized for a number of magnetic materials. Contributions to the entropy change from the exchange interaction and magnetic anisotropy are discussed. The problem of the maximum value of the effects under consideration is also addressed. It is shown, in particular, that in heavy rare earth metals the maximum MCE value at the magnetic phase transition from the ordered to the paramagnetic state can be as high as hundreds of Kelvins (e.g., in terbium it is 254 K under saturation field) and that it is proportional to the product of the transition temperature and the atomic magnetic moment (Tishin 1990a).

The magnetocaloric effect is utilized in magnetic refrigeration machines. At the beginning of the century Langevin (1905) demonstrated for the first time that the changing of a paramagnet magnetization would generally result in a reversible temperature change. The idea of utilizing reversible temperature changes in paramagnetic salts is well known to belong to Debye (1926) and Giauque (1927), over 20 years after Langevin's work appeared. The first experiments to put this idea into practice were carried out in 1933–1934 (Giauque and MacDougall 1933; de Haas et al. 1933; Kurti and Simon 1934). Investigation in the wide temperature region (from 4.2 K to room temperature and even higher) were encouraged by Brown (1976). Technologically the current interest in the MCE is connected with the real possibility to employ materials with large MCE values in the phase transition region in magnetic refrigerators (see, for example, Barclay 1994). The current extensive interest is to give birth to magnetic refrigeration as one of the most efficient methods of cooling at room temperatures and even higher. For instance, recently the Ames Laboratory (Iowa State University) and the Astronautics Corporation of America have been collaborating to create an advanced industrial prototype of a magnetic refrigerator operating in the
room temperature region (Zimm et al. 1998). In principle, such type of refrigerators could be used in hydrogen liquefiers, infrared detectors, high speed computers, SQUIDs, frozen food processing plants, large building air conditioning, motor vehicles, waste separation and treatment (see, for example, Gschneidner and Pecharsky 1997a). There is a number of surveys dealing with the problem of magnetic refrigeration. From the whole range of questions concerning this problem, we consider here only the aspect of working materials, leaving out most of the technical questions of refrigerator design and operation. Results are reported on a broad class of rare earth (and some other) materials promising from the viewpoint of magnetic refrigeration. In this part of the work the author puts accent primarily on the exploration of the physical mechanisms leading to the evolution of significant amounts of heat under a magnetic field.

2. Elements of thermodynamic theory

2.1. General thermodynamic formalism

Let us consider the general thermodynamic equations which can be used for description of magnetothermal effects in magnetic materials.

The internal energy $U$ of the system can be written down as a function of the entropy $S$, the volume $V$ and the magnetic field $H$:

$$ U = U(S, V, H), \quad (2.1a) $$

or as a function of $S$, $V$ and magnetic moment $M$:

$$ U = U(S, V, M). \quad (2.1b) $$

Accordingly, the total differential of $U$ can have the forms:

$$ dU = T \, dS - p \, dV - M \, dH, \quad (2.2a) $$

$$ dU = T \, dS - p \, dV - H \, dM, \quad (2.2b) $$

where $p$ is the pressure, $T$ is the absolute temperature.

Below, we will use the magnetic field $H$ as mainly an external parameter in the free energy $F$ and Gibbs free energy $G$.

The free energy $F$, which is a function of $T$, $V$ and $H$ is used for systems with constant volume and has the form:

$$ F = U - TS \quad (2.3) $$

and its total differential has the form:

$$ dF = -S \, dT - p \, dV - M \, dH. \quad (2.4) $$
The Gibbs free energy $G$ is used for systems under constant pressure and is a function of $T$, $p$ and $H$:

$$G = U - TS + pV - MH$$  \hspace{1cm} (2.5)

with the total differential:

$$dG = V \, dp - S \, dT - M \, dH.$$  \hspace{1cm} (2.6)

For $F$ the internal parameters $S$, $p$ and $M$ (generalized thermodynamic quantities), conjugate to the external variables $T$, $V$ and $H$, can be determined by the following equations of state:

$$S(T, H, V) = -\left(\frac{\partial F}{\partial T}\right)_{V,H},$$  \hspace{1cm} (2.7a)

$$M(T, H, V) = -\left(\frac{\partial F}{\partial H}\right)_{T,V},$$  \hspace{1cm} (2.7b)

$$p(T, H, V) = -\left(\frac{\partial F}{\partial V}\right)_{T,H}.$$  \hspace{1cm} (2.7c)

Accordingly, for the Gibbs free energy the following equations are valid:

$$S(T, H, p) = -\left(\frac{\partial G}{\partial T}\right)_{V,H},$$  \hspace{1cm} (2.8a)

$$M(T, H, p) = -\left(\frac{\partial G}{\partial H}\right)_{T,V},$$  \hspace{1cm} (2.8b)

$$V(T, H, p) = -\left(\frac{\partial G}{\partial p}\right)_{T,H}.$$  \hspace{1cm} (2.8c)

If the magnetic moment $M$ is chosen in $G$ as an external variable instead of the magnetic field $H$, then:

$$H = \left(\frac{\partial G}{\partial M}\right)_{T,p}.$$  \hspace{1cm} (2.8d)

From eqs (2.8a) and (2.8b), (2.8a) and (2.8c) and (2.8a) and (2.8d) one can derive the Maxwell equations:

$$\left(\frac{\partial S}{\partial H}\right)_{T,p} = \left(\frac{\partial M}{\partial T}\right)_{H,p},$$  \hspace{1cm} (2.9a)

$$\left(\frac{\partial S}{\partial p}\right)_{T,H} = -\left(\frac{\partial V}{\partial T}\right)_{H,p},$$  \hspace{1cm} (2.9b)

$$\left(\frac{\partial S}{\partial M}\right)_{T,p} = -\left(\frac{\partial H}{\partial T}\right)_{M,p}.$$  \hspace{1cm} (2.9c)
The heat capacity $C$ at constant parameter $x$ is defined as:

$$C_x = \left( \frac{\delta Q}{\delta T} \right)_x. \quad (2.10)$$

When using the second law of thermodynamics

$$dS = \left( \frac{\delta Q}{T} \right) \quad (2.11)$$

it can be given as:

$$C_x = T \left( \frac{\partial S}{\partial T} \right)_x. \quad (2.12)$$

The bulk thermal expansion coefficient $\alpha_T(T, H, p)$ can be defined as:

$$\alpha_T(T, H, p) = -\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{T, H, p} \quad (2.13a)$$

or, using eq. (2.9b):

$$\alpha_T(T, H, p) = -\frac{1}{V} \left( \frac{\partial S}{\partial p} \right)_{T, H, p} \quad (2.13b)$$

Let us consider the total entropy of the system $S(T, H, p)$. Its total differential can be written down as:

$$dS = \left( \frac{\partial S}{\partial T} \right)_{H, p} dT + \left( \frac{\partial S}{\partial H} \right)_{T, p} dH + \left( \frac{\partial S}{\partial p} \right)_{T, H} dp. \quad (2.14)$$

For an adiabatic process (where $dS = 0$) one can obtain from eq. (2.14) using eqs (2.9a), (2.12) and (2.13b):

$$\frac{C_{H, p}}{T} dT + \left( \frac{\partial M}{\partial T} \right)_{H, p} dH - \alpha_T V dp = 0, \quad (2.15)$$

where $C_{H, p}$ is the heat capacity under constant magnetic field and pressure.

For an adiabatic-isobaric process ($dp = 0$), eq. (2.15) gives the following expression for the temperature change due to the change of the magnetic field (the magnetocaloric effect):

$$dT = -\frac{T}{C_{H, p}} \left( \frac{\partial M}{\partial T} \right)_{H, p} dH. \quad (2.16)$$
Let us consider the adiabatic–isochoric process \((dV = 0)\). The total differential of \(V(T, H, p)\) has the form:

\[
dV = \alpha T V \, dT + \left( \frac{\partial V}{\partial H} \right)_{T, p} \, dH - V \kappa^{-1} \, dp.
\]  

(2.17)

Here eq. (2.13b) and the expression for the bulk elastic modulus \(\kappa\):

\[
\frac{1}{\kappa} = - \frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_{T, H}
\]  

(2.18)

were used. By means of eqs (2.15) and (2.17) the following equation can be derived for an adiabatic–isochoric process:

\[
\left\{ \frac{C_H}{T} - \alpha_T^2 \kappa V \right\} \, dT + \left[ \left( \frac{\partial M}{\partial T} \right)_{H, p} - \alpha_T \kappa \left( \frac{\partial V}{\partial H} \right)_{T, p} \right] \, dH = 0.
\]  

(2.19)

The second term between the brackets is small and can be neglected, which leads to the equation (Kuz’min and Tishin 1992):

\[
dT = - \frac{T}{C_H, p} \left[ \left( \frac{\partial M}{\partial T} \right)_{H, p} - \alpha_T \kappa \left( \frac{\partial V}{\partial H} \right)_{T, p} \right] \, dH.
\]  

(2.20)

The second term in eq. (2.20) appears due to the internal magnetostriction tensions arising from the change in magnetic state of the system keeping the volume constant.

From eq. (2.14) the general expression for the temperature change \(dT\) of a magnetic material during adiabatic magnetization by a field \(dH\) under isobaric conditions can be obtained:

\[
\frac{dT}{dH} = - \frac{(\partial S/\partial H)_{T, p}}{(\partial S/\partial T)_{H, p}}.
\]  

(2.21)

If the entropy change is considered as a function of \(T, M, \) and \(p\), then its total differential can be written down as:

\[
dS = \left( \frac{\partial S}{\partial T} \right)_{M, p} \, dT + \left( \frac{\partial S}{\partial M} \right)_{T, p} \, dM + \left( \frac{\partial S}{\partial p} \right)_{T, M} \, dp.
\]  

(2.22)

Using this equation and eqs (2.12) and (2.9c), one can obtain an expression for the temperature change caused by an adiabatic–isobaric change of magnetization:

\[
dT = \frac{T}{C_{M, p}} \left( \frac{\partial H}{\partial T} \right)_{M, p} \, dM.
\]  

(2.23)

The finite temperature change \(\Delta T = T_2 - T_1\) (where \(T_2\) and \(T_1\) are the final and the initial temperatures, respectively) under adiabatic magnetization can be obtained by integration of the corresponding equation eqs (2.23) or (2.16).
The thermodynamic equations obtained above are sufficiently general, since no assumptions as to the structure of the considered system were made. To obtain more concrete results one should know the form of the functions \( F \) or \( G \) of a specific system, which requires some model assumptions.

Let us consider the nonequilibrium thermodynamic potential \( \Phi(T, H, M, p, V) \) in which the internal parameters \( M \) and \( V \) or \( p \) are regarded as independent variables. To obtain the equilibrium Gibbs free energy \( G \) or equilibrium free energy \( F \) one should minimize \( \Phi \) with respect to \( M \) and \( V \) or \( M \) and \( p \):

\[
G(T, H, p) = \min_{M,V} \Phi(T, H, M, p, V),
\]
\[
F(T, H, V) = \min_{M,p} \Phi(T, H, M, p, V).
\]

Then, with the help of the thermodynamic eqs (2.7) and (2.8) the equilibrium internal parameters of a system can be obtained. The form of the nonequilibrium potential \( \Phi \) can be determined by symmetry and microscopic consideration.

It is known that in ferromagnets a second order phase transition takes place at the Curie point \( (T_C) \). Belov (1961a) adopted the Landau theory of second order phase transitions (Landau and Lifshitz 1958) to magnetic transitions. According to this theory, near the Curie point the potential \( \Phi \) of a ferromagnet can be expanded in a power series of an order parameter, the latter becoming zero at the Curie point. In ferromagnets the order parameter is the magnetization and for a single domain, isotropic ferromagnet in the absence of magnetic field, the expansion takes the form:

\[
\Phi = \Phi_0 + \frac{\alpha}{2} I^2 + \frac{\beta}{4} I^4 + \cdots,
\]

where \( \Phi_0 \) is a part of the potential not connected with the magnetization, \( I \) is the magnetization \( (I = M/V) \), \( \alpha \) and \( \beta \) are thermodynamic coefficients.

At the Curie temperate \( \alpha \) becomes zero and in the vicinity of the Curie temperature it can be presented as:

\[
\alpha = \alpha_0 (T - T_C) + \cdots.
\]

Above \( T_C \) \( \alpha > 0 \) and below \( T_C \) \( \alpha < 0 \). The coefficient \( \beta \) near \( T_C \) is not dependent on \( T \); \( \beta = \beta(T_C) \). Minimizing eq. (2.25) with respect to \( I \), one can obtain from the equation \( \partial \Phi / \partial I = 0 \) the equilibrium value of spontaneous magnetization \( I_s \):

\[
I_s^2 = -\frac{\alpha}{\beta} = -\frac{\alpha_0 (T - T_C)}{\beta}.
\]

By substitution of \( I_s \) into eq. (2.25) the equilibrium thermodynamic potential can be obtained.
For a ferromagnet in which the magnetoelastic interaction is taken into account, and which is brought into a magnetic field $H$, the potential $\Phi$ has the form:

$$\Phi = \Phi_0 + \frac{\alpha}{2} I^2 + \frac{\beta}{4} I^4 + \frac{1}{2} \gamma I^2 p - HI.$$  \hfill (2.28)

Minimization of eq. (2.28) with respect to $I$ leads to the equation describing the magnetization near the Curie point (Belov 1961a):

$$(\alpha + \gamma p) I + \beta I^3 = H.$$  \hfill (2.29)

Since the condition of the Curie temperature implies vanishing of the coefficient in the first term of eq. (2.29), the displacement of $T_C$ under pressure can be calculated by the equation:

$$\frac{\Delta T_C}{\Delta p} = -\frac{\gamma}{\alpha\Theta}.$$  \hfill (2.30)

From eq. (2.29) we can calculate the derivative $$(\partial H/\partial T)_I$$, which after substitution into eq. (2.23) gives the values of the MCE near the Curie temperature:

$$dT = \frac{\alpha\Theta T}{C_{M,p}} dI^2.$$  \hfill (2.31)

From eq. (2.31) it follows that the temperature change due to the change of magnetization is proportional to the squared magnetization: $\Delta T = k I^2$, where $k$ is a coefficient of proportionality. Then from eq. (2.29) one can obtain an expression describing the MCE field dependence near the Curie temperature (Belov 1961a):

$$\frac{\alpha + \gamma p}{k^{1/2}} + \frac{\beta}{k^{3/2}} \Delta T = \frac{H}{\Delta T^{1/2}}.$$  \hfill (2.32)

Equations (2.16) and (2.23) obtained in this section are sufficiently general and include the contribution from paraprocesses and magnetocrystalline anisotropy. However, they are usually used for description of the MCE in the region of the paraprocess which is characterized by a simple relation between $M$ and $H$. By paraprocess we mean the magnetization in the field region where the processes of domain wall displacement and magnetization vector rotation are completed and the field acts against thermal agitation and exchange interactions (in antiferromagnetic and ferrimagnetic materials). Other contributions to the MCE (such as the contribution from the magnetocrystalline anisotropy) will be discussed below.

Above we have considered the magnetocaloric effect in relation to a reversible process of magnetization. Nonreversible magnetothermal effects can arise due to such processes of magnetization as displacement of domain walls and nonreversible rotation of the saturation magnetization, or to first order magnetic phase transitions. These effects are characterized by a hysteresis in the magnetization cycle. The net magnetic work applied on the magnetic material in this case, proportional to $\int H \, dM$, is dissipated as heat which leads to the additional temperature rising.
Another source of additional heating is the Foucault currents which are induced in metals during applying of the magnetic field. According to the estimations made by Tishin (1988) in the case of rare earths this reason can give remarkable contribution (of about 0.1 K for rapid change of the field from 0 to 60 kOe) only in low temperature region. The nonreversible effects can decrease the sample cooling under adiabatic demagnetization.

2.2. A simple model of a magnetic material

According to the statistical theory, free energy of a system can be calculated as:

$$ F = -k_B T \ln Z(x), $$

(2.33)

where \( k_B \) is the Boltzmann constant and \( Z(x) \) is the statistical sum or partition function. Then, using eq. (2.7), one can obtain the internal parameters of the system. The partition function of the system is determined as (Smart 1966):

$$ Z = \sum_n e^{-E_n/(k_B T)} = \text{Sp}(e^{-\hat{H}/(k_B T)}), $$

(2.34)

where \( \hat{H} \) is the Hamiltonian of the system and \( E_n \) are its eigenvalues.

Let us consider first a quantum mechanical case for a paramagnet. The Hamiltonian (for one atom) in this case has the form:

$$ \hat{H} = -\hat{M}_J \hat{H}, $$

(2.35)

where \( \hat{H} \) is the vector of magnetic field, \( \hat{M}_J = g_J \mu_B \hat{J} \) the atom magnetic moment operator. The partition function for one atom is given by the equation (Smart 1966):

$$ Z_J(x) = \sum_{m=-J}^J \exp \left[ \frac{g_J \mu_B m H}{k_B T} \right] = \sum_{m=-J}^J \exp \left[ \frac{m x}{J} \right], $$

(2.36)

where \( g_J \) is the g-factor of the atom, \( J \) is the total angular momentum quantum number, \( m = J, J - 1, \ldots, -J \), and \( x \) for a paramagnet has the form:

$$ x = \frac{M_J H}{k_B T}, $$

(2.37)

\( M_J = g_J \mu_B J \) is the magnetic moment of an atom.

After summation eq. (2.36) takes the form:

$$ Z_J(x) = \sinh \left( \frac{2J}{2J} x \right) / \sinh \left( \frac{1}{2J} x \right). $$

(2.38)

For the system consisting of \( N \) atoms the free energy (its part related the magnetic subsystem) has the form:

$$ F_M = -k_B T \ln (Z_J(x))^N. $$

(2.39)
Then, the magnetic moment can be calculated by eq. (2.7b):

\[ M = N M_J B_J(x), \]  

(2.40)

where \( B_J(x) \) is the Brillouin function:

\[ B_J(x) = \frac{2J + 1}{2J} \tanh \left( \frac{2J + 1}{2J} x \right) - \frac{1}{2J} \tanh \left( \frac{x}{2J} \right). \]  

(2.41)

For \( k_B T \gg M_J H \) (or \( x \ll 1 \)) (this case is usually realized in an experiment) \( B_J(x) \) can be expanded as:

\[ B_J(x) = \frac{J + 1}{3J} x - \frac{[J(J+1)^2 + J^2(J+1)]}{90J^2} x^3 + \ldots. \]  

(2.42)

So, in the case of \( x \ll 1 \), eq. (2.38) leads to the Curie law:

\[ M = \frac{C_J}{T} H, \]  

(2.43)

where \( C_J = N \mu_B^2 g_J^2 J(J+1)/3k_B \) is the Curie constant.

From eq. (2.16) the MCE of a paramagnet can be obtained:

\[ dT = \frac{T}{2C_{H,p} C_J} \delta (M^2)_{T,p}, \]  

(2.44)

where \( \delta (M^2)_{T,p} = (\partial M^2/\partial H)_{T,p} dH \) is the isothermobaric variation of squared magnetization.

The Hamiltonian of an isotropic ferromagnet has the form:

\[ \mathcal{H} = - \sum_{i>j} \mathcal{J}_{ij} (\hat{j}_i \hat{j}_j) - \sum_i \hat{M}_{i,j} \hat{H}, \]  

(2.45)

where \( \mathcal{J}_{ij} \) is the exchange integral for the interaction between the \( i \) and \( j \) ions, \( \hat{J}_i \) is the total angular momentum operator of the ion. In the mean field approximation (MFA) eq. (2.45) becomes:

\[ \mathcal{H} = - \sum_j \mathcal{J}_{ex} z J (\hat{j}_j \hat{n}) - \sum_i \hat{M}_{ji} \hat{H}, \]  

(2.46)

where \( z \) is the number of the nearest neighbor magnetic ions, \( J \) is the quantum number of the total angular momentum, \( \hat{n} \) is the unit vector determining the orientation of the total magnetic moment of the ion, \( \mathcal{J}_{ex} \) is the exchange integral (it is supposed in MFA that the exchange interaction for every pair of the nearest neighbors has the same value \( \mathcal{J}_{ex} \)). In MFA the external magnetic field in eq. (2.36) should be replaced by the sum (Smart 1966):

\[ H + H_m = H + wM, \]  

(2.47)
where $H_m = wM$ is the molecular field, $w$ is the molecular field coefficient, related with the exchange integral. Equations (2.38)–(2.42) are valid in this case $x$ takes the form:

$$x = \frac{M_j(H + wM)}{k_BT}.$$  \hfill (2.48)

The field and temperature dependences of $M$ can be obtained by simultaneous solution of eqs (2.40) and (2.48).

In the absence of magnetic field for $T > T_C$ the equations have only one stable solution $M_s = 0$. When the temperature is less and/or close to the $T_C$ a stable nonzero solution appears, corresponding to the spontaneous magnetic moment:

$$M_s^2 = M_{s0}^2 \frac{10(J + 1)^2}{3((J + 1)^2 + J^2)} \left(1 - \frac{T}{T_C}\right).$$  \hfill (2.49)

where $M_{s0} = NM_j$ is the spontaneous magnetic moment at $T = 0$ K.

In the paramagnetic region, where $x \ll 1$, only first term in eq. (2.42) may be taken into account and the magnetization equation takes the form of the Curie–Weiss law:

$$M = \frac{C_JH}{T - T_C},$$  \hfill (2.50)

where $T_C$ is the Curie temperature:

$$T_C = \frac{NM_{J}^2w}{3k_B} = \frac{2(J + 1)}{3Jk_B}zT_{ex}.$$  \hfill (2.51)

$M_{\text{eff}} = g_J(J(J + 1))^{1/2}\mu_B$ is the effective magnetic moment of an atom. Using eq. (2.16), one can obtain for MCE of a ferromagnet in the paramagnetic region ($T > T_C$) the equation which has the same form as eq. (2.44).

For $T < T_C$ and nonzero magnetic field analysis of eqs (2.40) and (2.48) is substantially complicated. For $x \ll 1$ the following expression for MCE was obtained (Kuz'min and Tishin 1992):

$$dT = \frac{T_C}{2CH_pC_J} \frac{1}{\delta(M^2)}_{T,p}.$$  \hfill (2.52)

In the classical case a magnetic material is regarded as consisting of particles with a magnetic moment $\mu$, which can have an arbitrary orientation in space. The magnetic moment of such a system is given by the formula (Smart 1966):

$$M = N\mu L(x),$$  \hfill (2.53)

where

$$x = \mu H/(k_BT)$$  \hfill (2.54)
MAGNETOCALORIC EFFECT

for paramagnets:
\[ x = \mu (H + w M)/(k_B T) \]  
(2.55)

for ferromagnets, and
\[ L(x) = \coth x - \frac{1}{x} \]  
(2.56)
is the Langevin function. For \( x \ll 1 \) \( L(x) \) can be expanded as:
\[ L(x) = \frac{x}{3} - \frac{x^3}{45} - \cdots . \]  
(2.57)

Equations (2.43), (2.44), (2.50), (2.52) in this case are valid with the Curie constant:
\[ C_J = \frac{N \mu^2}{3k_B} \]  
(2.58)

and the Curie temperature:
\[ T_c = \frac{N \mu^2 w}{3k_B} \]  
(2.59)

2.3. Magnetic entropy, heat capacity and free energy

An important characteristic of a magnetic material is the entropy of its magnetic subsystem \( S_M \) (magnetic entropy). It can be changed by variation of the magnetic field, temperature and others thermodynamic parameters. In the most of works available in literature and concerning magnetothermal properties, the isothermal variation of magnetic entropy, \( \Delta S_M \), induced by the magnetic field change is considered. \( S_M \) and \( \Delta S_M \) are closely related with MCE value and magnetic contribution to the heat capacity. \( \Delta S_M \) is also used to determine the characteristics of magnetic refrigerators, such as the refrigerant capacity (see section 11).

The total entropy of a magnetic material can be presented as (Tishin 1990a):
\[ S(H, T, p) = S_M(H, T, p) + S_L(T, p) + S_e(T, p), \]  
(2.60)

where \( S_M \) is the magnetic entropy, \( S_L \) is the entropy of the lattice subsystem and \( S_e \) is the entropy of conduction electron subsystem. This formula is correct for rare earth magnetic materials, but in the case of intermetallic and 3d magnetic materials 3d-electrons form the magnetic moment having an itinerant nature and their contribution to the conductivity is comparable with p- and s-electron contributions. Separation, for example, of the lattice entropy in this case is possible only if electron–phonon interaction is not taken into account. In eq. (2.60) it is assumed that \( S_e \) and \( S_L \) do not depend on a magnetic field.
The lattice entropy can be calculated by Debye interpolation formula:

\[ S_L = R \left[ -3 \ln \left(1 - e^{\frac{T_D}{T}}\right) + 12 \left(\frac{T}{T_D}\right)^3 \int_0^{\frac{T_D}{T}} \frac{x^3 \, dx}{e^x - 1} \right], \]  

(2.61)

where \( R \) is the gas constant, \( T_D \) is the Debye temperature. The calculations by eq. (2.61) show that \( S_L \) decreases when \( T_D \) increases.

The electron entropy can be obtained by the standard relation:

\[ S_e = a_e T, \]  

(2.62)

where \( a_e \) is the electronic heat capacity coefficient.

As it follows from eq. (2.60), the total heat capacity of the magnetic material has the form:

\[ C = C_M + C_L + C_e, \]  

(2.63)

where \( C_M, C_L \) and \( C_e \) are the magnetic, lattice and electron contributions, respectively.

The heat capacity can be calculated using eq. (2.12). The lattice heat capacity under constant pressure \( C_L \) for temperatures substantially lower than \( T_D \) has the form:

\[ C_L = \frac{12\pi^4}{5} Nk_B \left(\frac{T}{T_D}\right)^3. \]  

(2.64)

It should be noted that difference between the heat capacity at constant pressure \( C_p \) and at constant volume \( C_V \) is given by the well known equation:

\[ C_p - C_V = \frac{9a_e^2}{\kappa} VT \]  

(2.65)

and for solids below room temperature it is small and usually may be neglected.

The electronic heat capacity \( C_e \) at constant pressure is defined as:

\[ C_e = a_e T. \]  

(2.66)

As one can see from eq. (2.16), the contributions to the total heat capacity from the lattice and conduction electron subsystems act as an additional heat load, reducing MCE.

The magnetic entropy \( S_M \) of a spin subsystem is related to the free energy of the magnetic subsystem by eq. (7a). Using eq. (2.39) one can obtain (Smart 1966):

\[ S_M(T, H) = Nk_B \left[ \ln \frac{\sinh \left(\frac{2J+1}{2} x\right)}{\sinh \left(\frac{2J}{2} x\right)} - xB_J(x) \right]. \]  

(2.67)
For \( x \ll 1 \) (high temperature, low field) the statistical sum \((Z_j(x))^N\) in eq. (2.39) can be expanded in a power series of \( x \), which leads to the following formula for \( S_M \) of a paramagnet (Vonsovskii 1974):

\[
S_M(T, H) = Nk_B \left[ \ln(2J + 1) - \frac{1}{2} \frac{C_J H^2}{T^2} \right],
\]  

(2.68)

where \( C_J \) is the Curie constant.

For a ferromagnet above the Curie temperature the analogous equation is valid:

\[
S_M(T, H) = Nk_B \left[ \ln(2J + 1) - \frac{1}{2} \frac{C_J H^2}{(T - T_C)^2} \right].
\]  

(2.69)

In completely disordered state \((H = 0, T \to \infty)\) the magnetic entropy in a system with localized magnetic moments reaches its maximum value which, according to eq. (2.68) and (2.69), is equal to:

\[
S_M = Nk_B \ln(2J + 1) \equiv R \ln(2J + 1).
\]  

(2.70)

The magnitude of the magnetic entropy change \( \Delta S_M \) (as well as the total entropy change \( \Delta S \)) with the change of magnetic field \( \Delta H = H_2 - H_1 \) can be calculated from the Maxwell relation (2.9a) on the basis of magnetization data as:

\[
\Delta S_M = S_M(H_2, T) - S_M(H_1, T) = \int_{H_1}^{H_2} \left( \frac{\partial M(H, T)}{\partial T} \right)_H \, dH.
\]  

(2.71)

Equations (2.71), (2.43) and (2.50) give for a paramagnet and a ferromagnet above \( T_C \), respectively:

\[
\Delta S_M = -\frac{1}{2} \frac{C_J \Delta(H)^2}{T^2},
\]  

(2.72)

\[
\Delta S_M = -\frac{1}{2} \frac{C_J \Delta(H)^2}{(T - T_C)^2},
\]  

(2.73)

where \( \Delta(H)^2 = H_2^2 - H_1^2 \). As one can see from eqs (2.72), (2.73) large heat values of \( \Delta S_M \) are expected in magnetic materials with large \( M_{\text{eff}} \) and in a temperature range close to 0 K for paramagnets, and close to \( T_C \) for ferromagnets.

Oesterreicher and Parker (1984) in the framework of MFA obtained for the field dependence of \( \Delta S_M \) of a ferromagnet in the vicinity of \( T_C \) the following expression:

\[
\Delta S_M = -1.07 \, R \left( \frac{g_J \mu_B J H}{k_B T_C} \right)^{2/3},
\]  

(2.74)
where $R$ is the gas constant. This equation yields the field dependence of the MCE near $T_C$ as: $\Delta T \sim H^{2/3}$ (see eq. (2.77) below).

For the entropy change due to the field change from zero to $H$, we have:

$$\Delta S_M = S_M(H, T) - S_M(0, T) = S(H, T) - S(0, T) = \Delta S$$  \hspace{1cm} (2.75)

with $H_1 = 0$ in eq. (2.71). In this formula the isothermal contributions $\Delta S_e$ and $\Delta S_L$ in the isothermal change of the total entropy $\Delta S$ are neglected.

The magnetic entropies $S_M(H, T)$ ($H \neq 0$) and $S_M(0, T)$ ($H = 0$) can be calculated on the basis of eq. (2.12) as:

$$S_M(H, T) = \int_0^T \frac{C_M(H, T)}{T} dT,$$  \hspace{1cm} (2.76)

where $C_M(H, T)$ is the magnetic heat capacity which may be determined with the help of eqs (2.63), (2.64) and (2.66).

Another method for the evaluation of $\Delta S_M$ is based on the fact that the temperature dependence of the total entropy in the presence of a magnetic field $S(H, T)$ is shifted on the temperature axis relative to the zero-field total entropy $S(0, T)$ to the higher temperature region by the value of MCE for the magnetic material under adiabatic conditions. The $S(0, T)$ dependence can be determined on the basis of total heat capacity data by an equation analogous to (2.76). Then $\Delta S_M$ is calculated as the difference between $S(H, T)$ and $S(0, T)$ (other field-dependent contributions less than $S_M$ contribution are not taken into account). The method requires experimentally measured $\Delta T(H, T)$ dependences and does not need experimental $C(H, T)$ dependences. It was used, for example, to evaluate $\Delta S_M$ in Gd (Brown 1976; Tishin 1990b).

Let us consider as an example the ferromagnetic compound EuS. Hashimoto et al. (1981) calculated the total temperature and field dependences of its entropy. First, on the basis of eq. (2.71) the magnetic entropy change $\Delta S_M$, induced by various $\Delta H$, was calculated. The necessary data on magnetization was determined by MFA for $T_C = 13$ K and $J = 7/2$. Then, using the heat capacity measurements of Moruzzi and Teaney (1963) and eq. (2.76), Hashimoto et al. (1981) calculated $S_M(0, T)$ and $S_M(H, T)$. The lattice entropy was determined by eq. (2.61), which allowed to evaluate the total entropy $S = S_M + S_L$. The results are shown in fig. 2.1. As one can see from fig. 2.1(b), $S_M(0, T)$ is saturated at high temperatures well above $T_C$.

The infinitesimal change $dT$ of the sample induced by the adiabatic change of magnetic field is related with the infinitesimal total entropy change $dS$ by the relation:

$$dT = -\frac{T dS_M}{C_{p,H}}.$$  \hspace{1cm} (2.77a)

It can be derived with the help of eqs (2.12) and (2.14) for adiabatic–isobaric process. To obtain the magnetocaloric effect $\Delta T$ (the finite temperature change) one should integrate eq. (2.77a). This task is quite difficult because in general case all quantities are field and/or temperature dependent. In supposition that $C_{p,H}$ does not depend on magnetic field
Fig. 2.1. The temperature dependences of: (a) the magnetic entropy change $\Delta S_M (T, H)$ induced by the magnetic field change $\Delta H$; (b) the calculated magnetic entropy $S_M (T, H)$; (c) the total entropy $S(T, H) = S_M + S_L$ for EuS (Hashimoto et al. 1981).
and $\Delta S/C_{p,H}$ is small, the following equation relating $\Delta T$ and corresponding magnetic entropy change $\Delta S_M$ can be derived:

$$
\Delta T = -\frac{T \Delta S_M}{C_{p,H}}. \quad (2.77b)
$$

As was noted by Tishin (1997), the suppositions made above are valid only in the region far from the transition point and/or in relatively weak fields.

Druzhinin et al. (1975, 1977, 1979) took into account in Hamiltonian (2.45) the contribution from the one-ion hexagonal magnetocrystalline anisotropy in the form:

$$
\hat{H}_a = -\sum_i \left( a \hat{j}_z^2 + b \hat{j}_z^4 + c \hat{j}_z^6 + d \left( \hat{j}_1^6 - \hat{j}_z^6 \right) \right), \quad (2.78)
$$

where the coefficients $a, b, c, d$ are related to the crystal field coefficients $A_i^n$ (Taylor and Darby 1972). The magnetic entropy $S_M$ was determined by the Boltzmann equation:

$$
S_M = -k_B N \sum_n \frac{\exp(-E_n/(k_B T))}{Z} \ln \left[ \frac{\exp(-E_n/(k_B T))}{Z} \right]. \quad (2.79)
$$

The $S_M(T)$ dependences were calculated for the case of $H = 0$ for Tb and Dy (Druzhinin et al. 1977). The results show some better agreement with experimental data in comparison with calculations made on the basis of isotropic MFA (see Hamiltonian (2.45)). The experimental $S_M(T)$ dependences were obtained from magnetization data by the equation:

$$
S_M(T) = \int_0^{I_s(0)} \left( \frac{\partial H}{\partial T} \right)_I dI - \int_0^{I_s(T)} \left( \frac{\partial H}{\partial T} \right)_I dI, \quad (2.80)
$$

where the first term is the magnetic contribution for $T > T_C$, equal to $k_B N \ln(2J + 1)$.

Bennett et al. (1993) considered theoretically the dependence of magnetic entropy of a ferromagnet with an axial anisotropy (the first term in the Hamiltonian (2.78)) on the magnetic field. The total Hamiltonian had the form:

$$
\hat{H} = -\sum_{i>j} T_{ij} \hat{s}_i \hat{s}_j - \mu_B \sum_i \left( \hat{s}_i \hat{H} + a \hat{s}_i^2 \right), \quad (2.81)
$$

where $\hat{s}_i$ is the spin angular momentum operator and the magnetic field is directed along the $z$ axis.

In this case for $a > 0$ the preferred directions of the spins are $\pm z$ and for $a < 0$ they lie in the $x$-$y$ plane. The magnetic moment was calculated by the Monte Carlo method for a $20 \times 20 \times 20$ fcc lattice using Hamiltonian (2.81), and $\Delta S_M$ was obtained by eq. (2.71) with $H_1 = 0$ and $H_2 = 10$ kOe. The calculations showed that for $a > 0$ increase of the anisotropy coefficient $a$ lead to a sharpening and increase of $\Delta S_M$ peak height in the vicinity of $T_C$, but in the rest temperature range the curves were effectively identical. For
\( a < 0 \) \( \Delta S_M \) essentially increased near \( T_C \) and decreased above \( T_C \) in the paramagnetic region with increasing of \( a \) in the absolute value.

For first-order magnetic phase transitions the magnetic Clausius–Clapeyron equation is valid:

\[
\frac{dH}{dT} = -\frac{\Delta S_M}{\Delta M},
\]

(2.82)

where \( \Delta S_M = S_M(2) - S_M(1) \) and \( \Delta M = M_2 - M_1 \) are the differences in magnetic part of the entropy and the magnetic moment between the magnetic states 2 and 1 at the temperature of the transition. This equation makes it possible to calculate the entropy change (and consequently, MCE) at the transition on the basis of magnetization data and the magnetic phase diagram \( H-T \). From eqs (2.77), (2.82) one can obtain the formula for the magnetocaloric effect at the first-order transition (see, for example, Tishin 1994):

\[
\Delta T = \frac{T}{C_{p,H}} \left( \frac{\partial H}{\partial T} \right) \Delta M.
\]

(2.83)

In the classical limit the partition function, magnetic free energy and entropy of the system consisting of \( N \) particles with magnetic moments \( \mu \) have the form (see McMichael et al. 1992):

\[
Z_{\infty}(x) = 4\pi \frac{\sinh x}{x},
\]

(2.84)

\[
F = -k_B T \ln \left( Z_{\infty}(x) \right)^N,
\]

(2.85)

\[
S_M = Nk_B \left[ \ln \left( 4\pi \frac{\sinh x}{x} \right) - x \ln(x) \right] \\
= Nk_B \left[ 1 - x \coth x + \ln \left( 4\pi \frac{\sinh x}{x} \right) \right],
\]

(2.86)

where \( x \) is determined by eqs (2.54) and (2.55).

The magnetic entropy change under magnetization in magnetic fields from \( H_1 \) to \( H_2 \) can be calculated by the formulae, analogous to eqs (2.72) and (2.73) (see also eq. (2.58) for the Curie constant):

\[
\Delta S_M = \int_{H_1}^{H_2} \left( \frac{\partial M}{\partial T} \right)_H dH = -\frac{N\mu^2}{6k_B} \frac{\Delta(H)^2}{T^2}
\]

(2.87)

for a paramagnet; and

\[
\Delta S_M = -\frac{N\mu^2}{6k_B} \frac{\Delta(H)^2}{(T - T_C)^2}
\]

(2.88)

for a ferromagnet at \( T > T_C \).
A more general expression for $\Delta S_M$ for a magnetic field increasing from zero to $H$ in the classical limit has the form (see McMichael et al. 1992):

$$\Delta S_M = S_M(T, H) - S_M(T, 0) = Nk_B \left[ 1 - x \coth x + \ln \frac{\sinh x}{x} \right]. \quad (2.89)$$

In ferromagnets the magnetic entropy change due to the occurrence of the spontaneous magnetization below $T_C$ in the absence of a magnetic field can be described in the framework of the Landau theory of the second-order phase transitions (Landau 1958). As it was shown in section 2.1, the spontaneous magnetization is determined by eq. (2.27). Substituting eq. (2.27) into eq. (2.25) one can obtain the equilibrium thermodynamic potential $\Phi$ and then, using equation $S = -\partial \Phi / \partial T$ the following formula (Belov 1961a):

$$\Delta S_M = -\frac{\alpha \Theta}{2} I_s^2 = -\frac{(\alpha \Theta)^2}{2 \beta} (T - T_C). \quad (2.90)$$

The change in magnetic heat capacity, related to the change of magnetic entropy can be obtained by eq. (2.12), which gives:

$$\Delta C_M = T \frac{\partial \Delta S_M}{\partial T}. \quad (2.91)$$

From eqs (2.90), (2.91) it follows, that in the framework of the Landau theory the heat capacity anomaly $\Delta C_M$ at the Curie point in a ferromagnet has the form (Belov 1961a):

$$\Delta C_M = T \alpha \Theta \frac{\partial (I_s^2)}{\partial T} = T \frac{(\alpha \Theta)^2}{2 \beta}. \quad (2.92)$$

The mean field approximation predicts the heat capacity anomaly as (Smart 1966):

$$\Delta C_M = -\frac{1}{2} w \frac{d(I_s^2)}{dT}. \quad (2.93)$$

Using eq. (2.49) for $M_s$, one can obtain:

$$\Delta C_M = k_B N \frac{5(J + 1)}{J^2 + (J + 1)^2}. \quad (2.94)$$

Calculations made by means of eq. (2.94) show that the maximum value of $\Delta C_M$ per atom is $5k_B/2$ (Foldeaki et al. 1995).

The heat capacity anomaly can also be calculated from the magnetization data by using the thermodynamic equation:

$$\Delta C_M = C_H - C_M = -T \left( \frac{\partial H}{\partial T} \right)_M \left( \frac{\partial M}{\partial T} \right)_H = T \left( \frac{\partial M}{\partial T} \right)_H \left( \frac{\partial H}{\partial M} \right)_T, \quad (2.95)$$
where $C_H$ and $C_M$ are the heat capacities at constant magnetic field and magnetic moment, respectively.

Kohlhaas et al. (1966) have shown, that the influence of magnetic field on the heat capacity can be determined by means of the relation:

$$ C_H(T, H) = C_H(T_0, 0) \frac{T}{T_0} \left[ 1 - \frac{\partial \Delta T}{\partial T} \right], \quad (2.96a) $$

where $\Delta T = T - T_0$ is the MCE caused by the magnetic field change from $H_0$ to $H$. Equation (2.96a) allows to obtain the heat capacity in a magnetic field on the basis of zero-field heat capacity and MCE data. However, the formula presented by Kohlhaas et al. (1966) can not be used for real calculations due to the fact that the $(H, T)$ coordinates of a point of calculation of the derivation of the MCE are unknown.

The approach, analogous to that proposed by Kohlhaas et al. (1966) (based on the consideration of reversible closed thermodynamic cycle), was used by Tishin et al. (1999) to investigate the magnetic-field and temperature dependences of $\Delta T$ in the vicinity of magnetic phase transitions. It was shown that in this region the MCE can be described by the following equation:

$$ \Delta T(T_0, H) = -T_0 \left[ \Delta C(T, H) - \frac{\partial \Delta T(T_0, H)}{\partial T} \frac{C(T, H)}{C(T_0, H)} \right], \quad (2.96b) $$

where

$$ \Delta C(T, H) = \frac{C(T_0, 0) - C(T, H)}{C(T_0, 0)}, $$

and $T_0$ and $T$ are the initial and final temperatures, respectively. It follows from eq. (2.96b) that at the temperature $T_M(H)$, where the peak (maximum or minimum) MCE occurs (here $\partial \Delta T/\partial T = 0$), the heat capacity of a magnetic material is not affected by the magnetic field. This temperature lies higher than the temperature of the zero magnetic field heat capacity peak and approaches the magnetic ordering temperature when the magnetic field decreases. According to the consideration of Tishin et al. (1999), one would also expect in a ferromagnet the caret-like shape of MCE temperature dependence with a single maximum near the magnetic ordering temperature. A simple antiferromagnetic material should exhibit a reverse caret-like behavior with a single minimum for weak magnetic fields not high enough to quench antiferromagnetism and convert it to a field induced ferromagnetism. The experimental measurements of the specific heat and MCE of high purity Gd, Dy, GdPd and (Dy$_{0.25}$Er$_{0.75}$)Al$_2$ made in the work of Tishin et al. (1999) confirmed the conclusions derived from the theoretical model.

The magnetization data also can be used for the calculation of the free energy change arising from the magnetic ordering by the expression (Ponomarev and Moreva 1975):

$$ \Delta F(T) = - \int_0^{T_c} \left[ \int_0^{h(T')} \frac{dH}{dT} \frac{dH}{dI} \right] dT'. \quad (2.97) $$
2.4. Superpara- and ferromagnetic nanocomposite systems

The enhancement of MCE in nanocomposite magnetic materials was discussed by Koko-rin et al. (1984), Bennett et al. (1992), McMichael et al. (1992, 1993a, 1993b), Shull et al. (1993), Shull (1993a, 1993b), Shao et al. (1996a, 1996b), Chen et al. (1994, 1995).

In the works of McMichael et al. (1992) and Shull (1993a, 1993b) a superparamagnetic system was taken to consist of monodispersed and noninteracting magnetic clusters uniformly dispersed in a nonmagnetic matrix. Each cluster contains certain number of magnetic atoms. Such a system can be described by the mean field approximation in the classical limit.

The magnetic entropy change of a classical system due to the change of external magnetic field from zero to \( H \) can be calculated by eq. (2.89) and for weak fields and high temperatures \( (x \ll 1) \) by eq. (2.87):

\[
\Delta S_M = -\frac{N\mu^2 H^2}{6k_B T^2},
\]  

(2.98)

where \( N \) is the number of magnetic moments in the system and \( \mu \) is the size of magnetic moment. As it is seen from eq. (2.98), \( \Delta S_M \) (and consequently MCE) can be made larger if \( \mu \) is made larger and \( N \) is simultaneously made smaller (to keep the saturation magnetic moment \( M_0 = N\mu \) constant), because of the squared dependence of \( \Delta S_M \) on \( \mu \) and only a linear dependence on \( N \). So, for a superparamagnet one can write (Shull 1993a):

\[
\Delta S_M = -\frac{n((N/n)\mu)^2 H^2}{6k_B T^2},
\]  

(2.99)

where \( n \) is the number of clusters and \( (N/n)\mu = \mu_c \) is the magnetic moment of the cluster. The factor \( n((N/n)\mu)^2 \) in eq. (2.99) may be much larger than \( N\mu^2 \) in eq. (2.98).

The limit of the MCE enhancement follows from eq. (2.89), according to which \( \Delta S_M \) will decrease at high \( x \), and has a maximum at (McMichael et al. 1992):

\[
x_{\text{max}} = \frac{\mu_c H}{k_B T} \approx 3.5,
\]  

(2.100)

where \( \Delta S_M \) is given by:

\[
\Delta S_M = -0.272 \frac{M_0 H}{T}.
\]  

(2.101)

Equation (2.100) determines an optimum cluster size for given \( H \) and \( T \).

By means of eq. (2.71), integrating from zero to \( H \) and from \( T = 0 \) to \( T = \infty \) (where \( M = 0 \)), McMichael et al. (1992) derived a sum rule:

\[
\int_0^\infty \Delta S_M \, dT = -M_0 H.
\]  

(2.102)
Equation (2.102) determines the form of the $\Delta S_M(T)$ curve and implies that for materials with the same saturation magnetic moment $M_0$ those with higher $\Delta S_M$ at a particular temperature will have lower $\Delta S_M$ in the rest of the temperature range.

McMichael et al. (1992) calculated the magnetic entropy change due to removal of a magnetic field of 10 kOe for different arrangements of Gd atoms (spin equal to 7/2). For the calculations the mean field quantum mechanical expression (see eq. (2.67)) was used. In fig. 2.2 the results for systems consisting of individual atoms and of magnetic clusters of various sizes (10, 30, and 100 atoms) are presented. The accuracy of the calculations is confirmed by the closeness of the calculated curve for the individual atoms to the experimental one measured on a gadolinium gallium garnet (Shull et al. 1993). One can see an obvious enhancement of $\Delta S_M$ at high temperatures in clustered systems. The behavior of $\Delta S_M(T)$ is in accordance with the sum rule (2.102).

Equation (2.99) was obtained for the case of cluster magnetic moments independent of the temperature. If $\mu_c = \mu_c(T)$, eq. (2.99) becomes (Kokorin et al. 1984):

$$\Delta S_M = -\frac{n\mu_c^2 H^2}{6k_B T^2} \left( 1 - \frac{T}{\mu_c} \frac{\partial \mu_c}{\partial T} \right).$$  (2.103)

The second term in the parentheses in eq. (2.103) can have a substantial value in the vicinity of the Curie point of magnetic cluster materials and lead to an additional contribution to $\Delta S_M$ in this region.

As follows from eq. (2.100) there is an optimum cluster size for a given $H$ and $T$, which corresponds to a maximum value of $\Delta S_M$. For the typical values $T = 300$ K and $H = 10-50$ kOe this size lies in the nanometer range (Chen et al. 1994). Chen et al. (1994) considered the process of nanocomposite system formation by deposition of magnetic and
nonmagnetic particles on a substrate. They took into account the possibility of formation of chains in the nonmagnetic matrix, consisting of magnetic particles (clusters) touching each other. These chains increase the effective magnetic cluster size, causing a deviation from the optimum value and a reduction of $\Delta S_M$. The number and length of the chains forming in a nanocomposite during the random deposition process was numerically simulated by a simple computer model. These data were used for the calculation of the magnetic entropy change by means of the equation:

$$\frac{T \Delta S_M}{M_0 H} = \sum_i \frac{n_i}{n} \frac{1}{x} \left[ 1 - m_i x \coth (m_i x) + \ln \frac{\sinh (m_i x)}{m_i x} \right],$$

where $m_i$ is the number of clusters per chain, $n_i$ is the number of $m_i$ type chains, $n = \sum_i n_i m_i$ is the total number of clusters.

It was shown, that the formation of chains reduces the magnetic entropy change. The value of this reduction depends on the dilution of the nanocomposite by the nonmagnetic particles, which is determined by the ratio of the number of nonmagnetic particles in the composite to the number of magnetic particles. The general dependence is such, that for large clusters $\Delta S_M$ increases with increasing dilution and the opposite situation takes place for small clusters. The cluster size (and the value of $x$), corresponding to the maximum magnetic entropy change increases with increasing dilution. These results are illustrated in fig. 2.3.

Later Chen et al. (1995) took into account the ability of particles to migrate on the substrate during the deposition and considered the influence of the substrate temperature on the chain formation. To simulate the process of nanocomposite fabrication the event driven Monte Carlo technique was used. It was shown that low substrate temperature presents difficulties to chain formation, thus leading to larger values of $\Delta S_M$ for a given
value of dilution. Another way to reduce the effect of chain formation, proposed by Chen et al. (1995), was to use unipolar electrostatic charging of the magnetic particles. The results of calculations showed that this method can substantially reduce the decrease of $\Delta S_M$ due to chain formation.

Let us consider systems with interacting magnetic clusters. Such systems display behavior similar to that of ferromagnets, with an effective interaction temperature $T_I$, analogous to the Curie temperature $T_C$, and were called "superferromagnets" (Mørup et al. 1983). Above $T_I$ the material is superparamagnetic and below $T_I$ long-range order between the clusters occurs. In the superparamagnetic region, $\Delta S_M$ induced by a field change from 0 to $H$ can be obtained, analogous to eq. (2.88) (Shull 1993), by the equation:

$$\Delta S_M = \frac{n((N/n)\mu)^2 H^2}{6k_B(T - T_I)^2}. \quad (2.105)$$

Analogous to the superparamagnetic case, the factor $n((N/n)\mu)^2$ in eq. (2.105) may become much larger than $N\mu^2$ in eq. (2.88). The latter is valid for a ferromagnet consisting of single magnetic atoms. This implies, that $\Delta S_M$ above $T_I$ in a system with magnetically interacting clusters can become substantially larger than in a simple ferromagnet above $T_C$. The maximum value of $\Delta S_M$ is observed at $\mu_c H/(k_B T) \approx 3.5$, as in the case of a superparamagnet.

MFA calculations (Bennett et al. 1992; McMichael et al. 1993a, 1993b) show that, at $T = T_I$ and below $T_I$, $\Delta S_M$ is smaller in clustered systems than in simple ferromagnets. Bennett et al. (1992) made calculations in the framework of the Monte Carlo method, which is more correct near the Curie temperature than MFA. The theoretical results of $\Delta S_M$ induced by the removal of a magnetic field of 10 kOe are shown in fig. 2.4. $\Delta S_M(T)$
was calculated for a ferromagnetic system consisting of individual moments of $8\mu_B$ and for interacting magnetic clusters of 30 and 100 atoms. MFA and Monte Carlo results are in good agreement, although in MFA an adjusting of the ordering temperature was needed. The decrease of $\Delta S_M$ near the ordering temperature in the 100-atoms cluster system was about 3.6 times lower than for a simple ferromagnet. In the paramagnetic region $\Delta S_M$ in the clustered system was much larger than that in the ferromagnet, in accordance with the sum rule (2.102). A broader maximum in the $\Delta S_M(T)$ curve is observed for the systems with larger cluster sizes.

The magnetization measurements of ultrafine magnetic particles consisting of a metastable iron–mercury alloy in Hg have been used to calculate the $\Delta S_M(M, T)$ (Pedersen et al. 1997). It is shown that obtained values of $\Delta S_M$ are much larger than those theoretically calculated for a paramagnet system. Application of the model with interparticular magnetic interaction permitted authors to get better description of the experimental results. It is necessary to note that the investigations of the MCE in nano-scaled systems is promising direction which needs additional theoretical and experimental efforts.

2.5. Inhomogeneous ferromagnet

Belov (1961a) developed the Landau theory of the second order phase transitions (which was considered in section 2.1) for the case of spatially inhomogeneous ferromagnets. The inhomogeneity is one of the reasons of the appearance of magnetization "tails" above the Curie temperature.

The main idea in Belov's model was a spatially inhomogeneous distribution of the local Curie temperature $T_C(\vec{r})$. Using this model, Wagner et al. (1996) and Silin et al. (1995) calculated the mean magnetization $\langle I \rangle$ as a function of the field and temperature in the region of the magnetic phase transition. The maximum value of $T_C^\text{max}(\vec{r}) = T_C$ was considered as the temperature of ferromagnetism arising and the minimum value $T_C^\text{min}(\vec{r}) = T_C - \Delta T_C$ as the temperature of the heat capacity peak.

The thermodynamic potential (its magnetic part) was chosen by Wagner et al. (1996) in the following form:

$$\Phi_M(T, M) = \int_0^1 ds \ W(s) \left\{ \frac{d_0}{2} (T - T_C(s)) M^2 + \frac{\beta}{4} M^4 \right\},$$

(2.106)

where $s$ is the parameter responsible for the value of the local Curie temperature, $W(s)$ is the distribution function of the $s$ parameter, $I$ is the local magnetization and it was established, that $T_C(s) = T_C - s \Delta T_C$. The potential (2.106) yielded the equation for the local magnetization:

$$H = \alpha \varphi (T - T_C - s \Delta T_C) I + \beta I^2,$$

(2.107)

which was then used to calculate the mean magnetization of the material:

$$\langle I \rangle = \int_0^1 ds \ W(s) I(s).$$

(2.108)
Using the results of Wagner et al. (1996) for (I), Romanov and Silin (1997) calculated by eqs (2.71) and (2.77) (the dependence of heat capacity on $H$ and $T$ was neglected) the temperature and field dependences of MCE in the region of magnetic phase transition for an inhomogeneous ferromagnet. The equations obtained were rather complex. Therefore we only show in fig. 2.5 the results of numerical calculations, made under assumptions that $W(s) = 1$ and $\Delta T_C$, characterizing the length of magnetization tails, is equal to 0.1 $T_C$. In fig. 2.5 the quantity $\Delta T_\beta 10^2/(\alpha^2 T_C)$, characterizing the MCE, is plotted against $T/T_C$ and the strength of magnetic field is characterized by the dimensionless parameter $t_0 = [3\beta/(2T_C)](H/2\beta)^{2/3}$. The curves marked 1 were obtained for the simple Landau theory and the curves marked 2 for an inhomogeneous ferromagnet.

As one can see from fig. 2.5, the $\Delta T(T)$ dependences for an inhomogeneous ferromagnet are more gradual and the MCE is weaker than for a homogeneous one. In the first case the $\Delta T$ peak is observed in the temperature region of the magnetization tail $T_C - \Delta T_C < T < T_C$ and in the second case at $T = T_C - \Delta T_C$. An increase in magnetic field leads to a shift of the MCE maximum to higher temperatures and increases the difference in the $\Delta T(T)$ behavior. Calculations showed that the nature of the $W(s)$ function had only a slight effect on the $\Delta T(T)$ behavior for the case of strong fields but had a stronger effect for relatively weak fields.

### 2.6. Magneto- elastocaloric effect

The heat generation and absorption in magnetic materials during adiabatic processes (magneto- and elastocaloric effects) was discussed by Tishin (1998b). The general thermodynamic relations for the elastocaloric effect was derived, and numerical values for the rare earths Gd and Ho were calculated.

An elastocaloric effect (ECE) in magnets has not been introduced correctly enough in the available literature. In our opinion, the ECE is a heat emission or absorption at a constant applied magnetic field (in a simple case at zero field) and value changing external pressure, $p$ (Tishin 1998b). If a pressure change takes place under adiabatic conditions then the ECE (like MCE) manifests itself as heating or cooling of a magnet by a temperature $\Delta T_{ECE}(p, T)$. In the case of ECE, eq. (2.14) for adiabatic processes takes the form:

$$\frac{C_{H,p}}{T} dT - \left(\frac{\partial V}{\partial T}\right)_{H,p} dp = 0, \quad (2.109)$$

where $V$ is the volume. Thus, for the ECE we can write (Tishin 1998b):

$$dT_{ECE} = \frac{T}{C_{H,p}} \left(\frac{\partial V}{\partial T}\right)_{H,p} dp. \quad (2.110)$$

The general form of this formula is close to the thermodynamic equation for a temperature change of a gas in a reversible adiabatic expansion process. Because each real gas has a positive value for $\partial V/\partial T$, the gases may cool down under adiabatic expansion ($dT < 0$ at $dp < 0$). In thermodynamics this phenomenon, well known as the Joule–Thomson effect,
Fig. 2.5. Dependence of the dimensionless magnetocaloric effect $y = \Delta T \beta H \times 10^2/(\alpha^2 T_C)$ on reduced temperature $T/T_C$ for different values of the parameter $t_0 = \frac{36}{a} \left( \frac{\beta H}{\Delta T_C} \right)^{2/3}$ characterizing the strength of magnetic field: (a) $t_0 = 0.3$; (b) $t_0 = 1$; (c) $t_0 = 3$ (Romanov and Silin 1997).
is at present widely used to liquefy gases. Using the bulk thermal expansion coefficient, $\alpha_T(T, H, p)$, eq. (2.110) can be transformed into:

$$dT_{ECE} = \frac{\alpha_T VT}{C_{H, p}} dp.$$  \hspace{1cm} (2.111)

The sign of the ECE is determined by the coefficient $\alpha_T$. In regular solids the value of $\alpha_T$ is positive and lies in the range $10^{-3}$–$10^{-6}$ K$^{-1}$. A negative value of $\alpha_T$ occurs, for example, in water at temperatures up to $4^\circ$C. In accordance with eq. (2.111), it means that in this temperature interval water should cool down under adiabatic stress. For example, this effect, in principle, could lead to freezing of water in micro-pores of road surface under quick pressing of this water (at temperature close to zero) by vehicle tires.

As distinct from eq. (2.16) the ECE value is proportional to the temperature derivative of the volume, and to the pressure change. Thus, a nonzero value of the ECE could be found in any materials for which $(\partial V/\partial T)_p \neq 0$ (with the exception of a case when $T = 0$). From this viewpoint, the ECE could have a non-zero value in materials without any magnetic structure. This is the first and main difference between the ECE and the MCE.

The second distinction is the sign of the ECE. The volume of most materials increases with increasing temperature $(\partial V/\partial T)_p > 0$. Thus, under the action of pressure $(dp > 0)$ the sign of the ECE should be positive in most cases, in accordance with eq. (2.110). It is well known, that nonmagnetic solids without electronic or magnetic phase transitions have an almost constant value of $(\partial V/\partial T)_p$ in the temperature region above the Debye temperature, $T_D$. Therefore, at $T > T_D$ the value of the $dT_{ECE}$ is proportional to the temperature $T$. Obviously, the ECE will have a small absolute value in temperature regions where $(\partial V/\partial T)_p$ is close to zero. In accordance with eq. (2.111), irregular behavior of the ECE could be found in the vicinity of temperatures where marked changes of $\alpha_T(T)$ and $C_{H, p}(T)$ take place. Near a phase transition the ECE could change its sign, for example, from negative to positive, which could result in a variation of the sign of the coefficient $\alpha_T(T)$ (Tishin 1998b).

Up to the present, the ECE has not been widely studied in different materials. However, simplified thermodynamic equations for the ECE in the case of a steel bar have been obtained by Sychev (1986). It is shown that in the first approximation the value of the ECE in the bar does not depend on its length and cross section. However, in a steel wire an ECE value of $-0.16$ K was reached under a rapidly applied stress up to $2 \times 10^8$ Pa (Sychev 1986).

An experimental investigation of the ECE has been made in the work of Annaorazov et al. (1996). The heat generation measurements in Fe$_{49}$Rh$_{51}$ occur under pulsed linear stress of the ingot applied by a couple of hawsers that were attached via two holes to the sample. It was shown that at the temperature of the antiferromagnetic (AFM)–ferromagnetic (FM) phase transition, $T_{AFM-FM} \sim 315$ K, the cooling of the ingot is about 5 K under a tensile stress of $5.29 \times 10^8$ Pa (Annaorazov et al. 1996). However, the nature of the negative sign of the ECE has not been interpreted. The duration of the stress pulses (adiabaticity of the process) and total accuracy of these measurements are unknown. The results of the work of Annaorazov et al. (1996) mostly have a fundamental meaning because the compound Fe$_{49}$Rh$_{51}$ can not be used in any commercial applications due to the
extremely high price of Rh. So, the search of other compounds with a large elastocaloric effect is a significant task. From this viewpoint, lanthanide metals and compounds are of great interest.

In rare earth metals the coefficient $\alpha_T(T)$ has large value in the vicinity of structural or magnetic phase transitions. In holmium the phase transition from the ferromagnetic conical phase to the antiferromagnetic spiral structure occurs at about 19 K. The specific volume change, $dV/V$, at this transition is equal to $-2.2 \times 10^{-4}$ in a temperature interval of $\sim 0.5$ K (Steinitz et al. 1987). The atomic volume of La changes by 0.5% and 4% at the transitions from dhcp to fcc and from fcc to bcc, respectively. The thermal expansion coefficients of Eu$^{2+}$ and Yb$^{2+}$ are three times larger than in other rare earth elements (Taylor and Darby 1972). The fcc crystalline form of Sm transforms to dhcp by applying $7 \times 10^8$ Pa at room temperature. This structure transformation is accompanied by volume decrease of about 8% (Jayaraman 1991). The thermodynamic data for structural transitions of lanthanide metals are summarized in table 9.2 of the report of Jayaraman (1991). Thus, the rare earth elements could be considered as a favorable basis for creating materials with large ECE values (Tishin 1998b).

Let us estimate the ECE value in the rare earth metals gadolinium and holmium in the vicinity of magnetic phase transitions. According to the experimental data of Dan'kov et al. (1998) the transitions from the paramagnetic to the ferromagnetic phase occurs in Gd at $T_C = 294$ K. Below the spin reorientation temperature, $T_{SR} = 227$ K, the easy magnetization vector departs from the [0001] crystallographic axis. The temperature dependence of the atomic volume in Gd has been studied by Finkel et al. (1971) and Finkel (1978). Near these magnetic phase transitions the value of bulk thermal expansion coefficient is close to zero. Thus, the ECE value at the Curie point $T_C$, as well as around $T_{SR}$ should be approximately equal to zero. (It is necessary to note that the MCE reaches its maximum value at the Curie point of Gd.) At the same time, the gadolinium has a negative value of $\alpha_T$ (and, therefore, a negative ECE value) in the temperature region between $T_C$ and $T_{SR}$. Based on the data of Dan’kov et al. (1998), Finkel et al. (1971) and Finkel (1978) it is possible to estimate that at $T = 285$ K and $dp = 10^8$ Pa the value of the ECE is negative and approximately close to $-0.61$ K (Tishin 1998b). Thus, the estimated $d\tau_{ECE}$ value of Gd has the same order as the ECE value of Fe$_{49}$Rh$_{51}$, $d\tau_{ECE} \sim -1.7$ K, at pressure $\sim 10^8$ Pa (Annaorazov et al. 1996).

The experimental data concerning the heat capacity and bulk thermal expansivity at the ferromagnetic–antiferromagnetic phase transition at about 19.5 K can be found in the reports of Steinitz et al. (1987), Lounasmaa and Sundstrom (1966), Stewart and Collocott (1989) and White (1989). However, experimental values of the heat capacity presented by Lounasmaa and Sundstrom (1966), Stewart and Collocott (1989) and White (1989) are different at this phase transition. Taking $C_{HP} \approx 14.1$ J/mol K and $\alpha_T \approx -4.4 \times 10^{-4}$ K$^{-1}$, we could obtain a value of the ECE close to $-1.1 \times 10^{-2}$ or $-1.2$ K at pressure values of $9.8 \times 10^5$ Pa ($\sim 10$ bar) and $10^8$ Pa ($\sim 1$ kbar), respectively (Tishin 1998b). The pressure $1 \times 10^8$ Pa could be compared with pressure of a middle weight man on a magnetic material with a cross section about 7–8 mm$^2$. However, it is necessary to note that according to data of the work of Baaazov and Manjavidze (1983), this pressure is close to the value of $\sim 1.7 \times 10^8$ Pa (17 kg/mm$^2$) which determines a limited durability of the rare earth metals under tensile strain.
For these estimations we neglected any influence of pressure on the values of $\alpha_T$ and $C_{H,H,p}$. Actually, due to the effect of pressure on the elastic and magnetic properties of the rare earth metals (see Jayaraman 1991), the above calculated ECE values should be considered as the first approximation only. In rare earth elements the shifts of magnetic phase transition temperatures reach a few K under pressure of $5 \times 10^8$ Pa (Jayaraman 1991). However, at present, experimental information about the values of $\alpha_T$ and $C_{H,H,p}$ at different pressures is unavailable and therefore, more accurate calculations of the ECE are impossible.

As shown above, in accordance with thermodynamics, a heat generation and/or absorption in magnets can arise at $dp = 0$ (MCE) as well as at $dH = 0$ (ECE). We have estimated the value of the ECE for the magnetic phase transitions in Gd and Ho. However, it is possible to reach large values of the ECE and MCE in cases where magnetic and structural phase transitions coexist. For example, the crystal structure of Dy transforms at about 90 K from the $P6_3/mmc$ to the Cmcm type. This transition involves large changes of the interatomic distances and accompanies the transition from a spiral antiferromagnet to a ferromagnet (Taylor and Darby 1972). If in an adiabatic process the pressure and the magnetic field change simultaneously, the total heat evolution can be written down as (Tishin 1998b):

$$dT = dT_{MCE} + dT_{ECE} = -\frac{T}{C_{H,H,p}} \left[ \left( \frac{\partial I}{\partial T} \right)_{H,H,p} dH - \left( \frac{\partial V}{\partial T} \right)_{H,H,p} dp \right].\quad (2.112)$$

The joint magneto-elastocaloric effect (MECE) has not previously been studied by experiment. The MCE and ECE can have positive as well as negative signs. So, the general behavior of the temperature dependencies of the MECE could be complicated. The nature of the MECE is close to the MCE in an adiabatic-isochoric process. The equations for the MCE under adiabatic-isochoric conditions have been derived by Kuz'min and Tishin (1992).

Currently, in the construction of magnetic refrigerators only the MCE (the first term of eq. (2.112)) is utilized. The second term (ECE) is neglected. In our opinion, the possibilities to use both effects at the same time under adiabatic and/or adiabatic-isochoric conditions should be analyzed. It is possible to propose, for example, a design of magnetic cryocooler in which a refrigerant is both affected by a magnetic field and also by a contraction or expansion of the refrigerant owing to the magnetostriction (Tishin and Kuz'min 1991; Tishin 1997). The benefit of a technical utilization of the ECE is that nonmagnetic materials with giant volume expansion or linear thermal expansion could be used.

2.7. MCE in the vicinity of magnetic phase transition

Tishin (1998a) discussed adiabatic magnetization processes (magnetocaloric effect) in the region of magnetic phase transitions. His discussion is based on the known experimental data about magnetic phase diagrams and magnetocaloric effects of the rare earth metals Gd and Dy. A correlation was assumed between the arrangement of the curves describing the magnetic phase transitions in $H-T$ diagrams and the corresponding value of the magnetocaloric effect (Tishin 1998a).

The heavy rare earths are metals with well-studied magnetic properties (see, for example, the reviews of Jensen and Mackintosh (1991) and by McEwen (1991)). The magnetic
phase diagrams of these magnetic materials have been intensively studied by different techniques (see, for example, the reports of Bohr et al. (1986), Tindal et al. (1993), Gschneidner and Pecharsky (1997b)). The general form of the phase diagrams strongly depends on the used experimental techniques as well as on the method employed for the determination of the phase change point from the experimental curves. Most of currently practiced setups give different values of the phase transition points for the same sample. A comparison of the different procedures for determining the position of the phase transition point of gadolinium has been presented by Dan’kov et al. (1998).

Practically, experimentalists operate under either isothermal or adiabatic conditions when studying $H-T$ magnetic phase diagrams of different magnetic materials. The isothermal conditions can be easily achieved by static and/or quasi-static magnetic field measurements. For example, this is the case for a very slowly increasing field in a situation where a material has the possibility to keep its zero field temperature due to heat exchange with the surrounding. At the same time, under adiabatic conditions, the temperature of the magnetic material under investigation could be changed by the magnetocaloric effect. For experimental measurements this situation is often observed when a sample is located inside a vacuum and/or in pulsed field studies. Up to the present, the experimental circumstances necessary for exact realization of the quasi-adiabatic conditions in non-vacuum are unknown. In accordance with the data published by Levitin et al. (1997) the transition between isothermal and quasi-adiabatic circumstances occurs in a range of fields increasing with rates from 200 kOe/s to 2 MOe/s (for situations where the sample is located in liquid nitrogen or helium). It is shown (Dan’kov et al. 1997) that in a nitrogen gas surrounding a field sweep rate of about 900 kOe/s clearly corresponds to the adiabatic condition.

Let us consider the $H-T$ phase diagram of a magnetic material under atmospheric pressure. Under the isothermal conditions the concrete magnetic state in the $H-T$ diagram is determined by the values of the zero field temperature and the applied magnetic field. In the adiabatic cases, when the initial temperature for a magnetization process can be changed due to MCE, the visualization of the $H-T$ coordinates requires also the MCE value. In the case that an initial magnetic state of a sample under adiabatic conditions can be changed by applying a magnetic field (for example, from an antiferromagnetic to a ferromagnetic phase) the situation is more complicated. Especially, if the magnetic material can cross the curve of the first-order phase transition and/or if the rate of increasing field is too large (for example, 650 MOe/s as in the report of Nojiri et al. (1995)).

Tishin’s (1998a) consideration refers directly to the MCE, since the measurement of the temperature change practically occurs when the magnetic field changes from zero to $H$. The analysis makes it possible to assume: first, the value of the MCE in the vicinity of the Curie point is limited by the shift of the Curie point as the field increases; second, under adiabatic conditions (without heat exchange with the surrounding) Gd can not change its initial magnetic state. Gd is a regular ferromagnet and, in our view, the above conclusions should also be applicable to other ferromagnets. Thus, the extent of heating of a ferromagnet during an adiabatic magnetizing process is determined by the behavior of the phase transition line.

The magnetic phase diagram of Dy is very complex. For example, Herz and Kronmüller (1978) and Nikitin et al. (1991b) denote the phase transition from the FM to the PM state, by the vertical line in the $H-T$ diagram which starts from zero magnetic field and the
Néel temperature, $T_N \sim 180$ K. In other diagrams this line is shifted to the region of low (Gschneidner and Pecharsky 1997b) or high (Alkhafaji and Ali 1997) temperatures from the zero field transition point. Tishin's (1998a) scheme of the magnetic phase diagram of Dy is based on the experimental results described in these reports.

Tishin's (1998a) results were obtained under the assumption that in the vicinity of the zero field transition point the MCE in Gd and Dy could not lead to changes of the initial FM and/or AFM phases to other magnetic states. It may be stated for ferromagnetic Gd (based on the experimental results of Dan'kov et al. (1998)). In the case of Dy this result should be verified more thoroughly on the basis of new experimental measurements of the magnetic phase diagram and MCE on the same single crystalline sample of Dy.

The character of the behavior of the MCE in a magnetic field, when $H$ becomes equal to the critical value, $H_{cr}$, could be explained in the framework of the thermodynamic relation for the magnetic entropy, $S_M$, which can be easily obtained from Maxwell's formula (see eq. (2.9a)) (Bailyn 1994).

In conclusion, Tishin (1998a) have assumed that the FM and/or AFM states of magnetic materials can not be changed under adiabatic magnetizing conditions due to the non-zero MCE value that leads to an additional shift of the initial temperature. The MCE can not exert any influence on the initial magnetic phase state. At atmospheric pressure the latter can be transformed just by applying a magnetic field of the corresponding value, $H \geq H_{cr}$. From the other side, it is known that the curves describing AFM–FM and FM–PM phase transitions of antiferro- and ferromagnets may become shifted with increasing field to the high and low temperature regions, corresponding to negative and positive signs of the derivative $dH_{cr}(T)/dT$, respectively. In our opinion, for fields close to the critical field, the sign of $dH_{cr}(T)/dT$ determines the MCE value. It is negative or close to zero MCE for the AFM state and positive for the FM phase.

The results obtained by Tishin (1998a) are especially important for experimental studies of magnetic materials with a large MCE value in the vicinity of the magnetic phase transition. It should be noted, however, that in the case of antiferromagnets these assumptions require further careful experimental verifications.

3. Methods of MCE measurements

3.1. Direct methods

3.1.1. Pulse techniques

The method of direct measurements of the change in material temperature during the application or removal of a magnetic field by an electromagnet (switch-on technique) was proposed by Weiss and Forer (1926). The first measurements in strong magnetic fields (up to 110 kOe) were made by this method on yttrium iron garnet by Clark and Callen (1969). The temperature of the sample was measured by a thermocouple.

Kurth et al. (1985) used a differential thermocouple, which gave more accurate result for the MCE measurements, see fig. 3.1. Here the differential thermocouple (3) measures the temperature difference between a massive copper body (2), (4) and the sample (6), which is the MCE value. Thermocouple (5) measures the average temperature of the sample.
MCE measurements in siderite FeCO₃ in pulsed magnetic fields were made by Borovikov et al. (1981). The samples were shaped as parallelepipeds with linear dimensions of several millimeters. A compact solenoid produced a pulsed magnetic field of 270 kOe with a pulse duration of 2 ms in a working space of 5.5 mm diameter and 20 mm long. The temperature change was measured by the thermocouple or by a magneto-optic technique allowing an instant temperature measurement (Litvinenko et al. 1973). The latter method is based on the observation of the absorption band series in the region of 24 000 cm⁻¹ and can be used for measuring of the sample temperature above 21 K with an accuracy of 0.5 K.

A further development of the pulsed-field method was made by Ponomarev (1983, 1986). He studied the MCE in polycrystalline gadolinium in pulsed fields up to 80 kOe (with a total pulse length of 0.5 s) in the temperature range from 80 to 350 K. The copper-constantan thermocouple, made of strips ~ 20 μm thick and 1 mm wide, was placed in the center of a sample that was 6 mm diameter wide and 15 mm long. The solenoid used had a length of 200 mm and a bore diameter of 50 mm. It was shown that for the given pulse duration, sample dimensions and thermocouple configuration any errors due to heat exchange between the sample, thermocouple and environment can be neglected.

Let us consider as an example the pulsed field setup, as described by Dan’koy et al. (1997). The principal scheme of this setup is shown in fig. 3.2 and the scheme of its low temperature part is displayed in fig. 3.3.

Changes of the sample temperature were measured by a copper-constantan thermocouple made of small diameter wires (~ 0.05 mm). This provide a small mass of thermocouple
The Gd sample, measured by Dan'kov et al. (1997) was shaped as a parallelepiped with dimensions $4 \times 4 \times 10$ mm and cut into two equal parts along the long axes. The thermocouple was placed between the parts in the center of the sample. The experimental tests showed, that during the period of time required by the magnetic field to reach its maximum value (0.08 s) the heat exchange with environment lowers the sample temperature by less than 2%. That is why the sample was not insulated by a vacuum layer.

The low temperature insert (fig. 3.3) was assembled from thin-walled tubes made of non-magnetic stainless steel. The sample temperature was regulated by simultaneous operation of the electric heater (2) (fig. 3.3) controlled by feeding block (9) (fig. 3.2) and cooling by flowing of nitrogen or helium gas through the insert.

The magnetic field was created by the solenoid $L$ under the discharge of a battery of capacitors $C$. The battery had a total capacity of $0.035 \, F$ and was charged up to $1000 \, V$, which provided a total pulse duration of 0.2 s. A thyristor driven by the starting signal from the control desk 1 (fig. 3.2) was used as a power switch for the battery discharge. Simultaneously the starting signal triggered the pulse memory oscilloscope (8). The signal from thermocouple was fed into one channel of the oscilloscope. The signal from the field measuring coil (3) (fig. 3.3) after passing through the integrator (6) (fig. 3.2) was fed into the second channel. This technique made it possible to determine the sample temperature change due to the change of the magnetic field, i.e., the MCE at a given field and temperature. The measurements block (5) (fig. 3.2) was used for communication with other setup blocks.
During the measurements a parasitic signal might be induced in the thermocouple wiring, which decreased the accuracy of measurements. To prevent the influence of this interference, a compensation scheme (11) (fig. 3.2) was employed, in which a signal from the field measuring coil (3) (fig. 3.3) was added as a compensation signal to the signal from thermocouple. Such a compensation scheme allowed to nearly completely exclude the influence of the interferences on the experimental results.

The solenoid L had a bore diameter of 23 mm and was wound from copper wire of a cross-sectional diameter of 1.3 mm. It was cooled by direct heat exchange with a liquid nitrogen bath, which made it possible to achieve a magnetic field up to 80 kOe. Tests showed that the solenoid possessed a small field inhomogeneity: the axial inhomogeneity was less than 5% within ±1 cm from the solenoid center, and the radial inhomogeneity was one order of magnitude smaller.

Taking into account various sources of random and systematic errors (such as induced thermocouple interferences, various heat losses, eddy currents) Dan’kov et al. (1997) concluded that the apparatus permitted to measure the magnetocaloric effect with an accuracy of 8–15%, depending on the MCE value and the temperature range.
3.1.2. Static apparatus

When the field is produced by an electromagnet the rise time has a maximum value of about a few seconds, while it can be several minutes for a superconducting solenoid. During the field rise a substantial dissipation of heat produced in the sample by the MCE can occur. Tishin (1988) considered this point and estimated, that the field rising time must not be greater than 10 s for temperatures above 30 K. In the temperature region of 10–20 K this time must be several times smaller because of the increase of the heat leak via the thermocouple. This implies that MCE measurements made by a switch-on technique are difficult in the case of a superconducting solenoid.

This is the reason why Nikitin et al. (1985a, 1985b) and Tishin (1988) used for MCE measurements in a superconducting solenoid a method in which the sample was brought quickly into the field. The measurement was done in the following sequence. First the sample was placed outside the solenoid. When the field strength in solenoid had reached a given value, the sample was brought as fast as possible (∼ 1 s) inside the solenoid. When the sample was fixed in the center of solenoid, its temperature was measured.

The scheme of the experimental set-up is shown in fig. 3.4. The sample holder (15) made of teflon, containing the sample (16) was fixed at the end of a rod (6). To minimize the heat leak between the sample and the holder mica glued on to the bottom of the holder was used.
as a gasket. The rod with the holder were placed into an evacuated tube (11) pumped to a pressure \( \approx 1 \) Pa. Vacuum jackets (13) and (14) were used to reduce helium evaporation caused by sample heating by the electric heater (12). The heater through a connector (10) was connected to the temperature control circuit. The superconducting solenoid (17) made it possible to create magnetic fields up to 66 kOe. The whole apparatus was placed into liquid helium.

A special coil (5) was used to compensate the force pulling the sample into the solenoid. This force is the product of the field gradient and the sample magnetic moment. A permanent magnet made of SmCo5 (4) and the special coil (5) prevented the sample from being pulled into the solenoid. The same coil is used to return the sample to its initial position. The sample is fixed in the upper position (out of the solenoid) by a ferrite permanent magnet (1) and begins to move after compensation of the field of the magnet (1) by another coil (2). A teflon gasket (7) on a flange (8) fixes the sample at the center of the solenoid during the measurement. When the sample reaches the center of the solenoid, the copper washer on the rod closes the contacts on the gasket (7), which leads to the turning off of the special coil (5). Coils (2) and (5) were water-cooled.

The switch-on technique for MCE measurements in a superconducting solenoid was used by Green et al. (1988). The apparatus of the latter authors employed a superconducting solenoid 12.13 cm in diameter, 25.4 cm long and 8.54 cm bore, which could produce a field up to 70 kOe. The temperature was measured after achieving the maximum field value by five thermocouples placed on the sample, which took 10 s. Together with the field rise time about 30 s the overall process had a duration of 40 s. This method was used to measure MCE in rare earth metals at the temperatures above 180 K.

3.2. Magnetization measurements

Experimental data on the magnetic field dependence of the magnetization at constant temperatures allow one to calculate the magnetic entropy change by means of eqs (2.71) and (2.75) and then the magnetocaloric effect by eq. (2.77b). Such calculations of \( \Delta S_M \) in rare earth metals were made for instance by Foldeaki et al. (1995), Dan'kov et al. (1996) and other authors.

Equation (2.16) can be also used to calculate the value \( \Delta T \) of the magnetocaloric effect from experimental data on magnetization and heat capacity (Tishin 1997):

\[
\Delta T(T, H) = \int_{T(H=0)}^{T(H)} dT = - \int_0^H \frac{T}{C(H, T)} \left( \frac{\partial I}{\partial T}(H, T) \right)_H \ dH, \tag{3.1}
\]

where \( I = M/V \), \( \Delta T(T, H) = T(H) - T(H = 0) \). In an experiment the field usually changes from \( H = 0 \) to \( H \). However, in case if the values of the magnetic field are changed from a value of \( H_1 \) up to the \( H_2 \) than these values of the fields should be taken as the limits of the integration in the eq. (3.1).

Pecharsky and Gschneidner (1996) point to the difficulties of magnetization technique: (a) possible essential errors near the temperatures of magnetic phase transitions due to the MCE and poor thermal contact between the sample and thermocouple; (b) problems related with the presence of magnetic hysteresis in some materials at low temperatures.
Another method allowing to determine the MCE from pulsed field magnetization measurements was proposed by Levitin et al. (1997). It is based on the comparison of $I(H)$ dependences measured under isothermal and adiabatic conditions. Due to the magnetocaloric effect the initial temperature of ferro- and paramagnets increases during adiabatic magnetization. That is why the adiabatic magnetization curve will intersect the isothermal curves obtained at higher temperatures. The intersection points determine the field dependence of the sample temperature under adiabatic magnetization, i.e., the magnetocaloric effect.

It was concluded that the adiabatic conditions of magnetization are preserved for field rising rate of about $10^4$ kOe/s or higher for the samples with dimensions of several mm. A decrease of the rate to $10^{-100}$ kOe/s leads practically to isothermal magnetization processes.

The possibility of the pulsed field method to measure the MCE was demonstrated on a paramagnetic Gd$_3$Ga$_5$O$_{12}$ single crystal in pulsed fields up to 400 kOe. As it was predicted, intersections between the adiabatic and isothermal curves were observed. The $\Delta T(H)$ curve obtained by this method gives $\Delta T = 46$ K for $\Delta H = 400$ kOe and $T = 4.2$ K in Gd$_3$Ga$_5$O$_{12}$. The adequacy of the obtained $\Delta T(H)$ curves was checked by MFA calculations.

3.3. Heat capacity measurements

This method was used to determine the MCE and $\Delta S_M$ by Brown (1976) and Gschneidner and coworkers (see, for example, Pecharsky and Gschneidner 1996). It allows to determine all parameters required for magnetic refrigeration design: heat capacity, $\Delta S_M$, MCE and $S(T, H)$ dependences.

On the basis of eq. (2.12) the total entropies of the material in zero and nonzero magnetic field $S(T, 0)$ and $S(T, H)$ can be calculated by the equation

$$S(T, H) = \int_0^T \frac{C(T, H)}{T} dT,$$

(3.2)

if the experimental dependences of the total heat capacity $C(T, 0)$ and $C(T, H)$ are known. Then on the basis of these data the adiabatic temperature rise (i.e., MCE) $\Delta T$ for the field change from zero to $H$ can be determined by

$$\Delta T = T(S, H) - T(S, 0),$$

(3.3)

where $T(S, H)$ and $T(S, 0)$ are the temperatures in the field $H$ and $H = 0$ at constant total entropy $S$, respectively. For $\Delta S_M$ calculations the following formula can be used:

$$\Delta S_M = S(T, H) - S(T, 0),$$

(3.4)

where $S(T, H)$ and $S(T, 0)$ are the total entropies in magnetic field $H$ and $H = 0$ at constant temperature, respectively. An analogous method was used by Tishin (1990a) to determine the $\Delta T(T)$ dependences of Gd on the basis of theoretically calculated entropies $S(T, 0)$ and $S(T, H)$. The method was tested on various magnetic materials such as RA12 (R = Er, Dy), (Dy$_{0.25}$Er$_{0.75}$)Al$_2$, Gd–Pd, Gd and Dy. The data showed good accordance
Fig. 3.5. The MCE temperature dependences of high purity polycrystalline Gd measured directly by quasistatic and pulsed techniques (filled symbols) compared with those determined from the heat capacity (opened symbols) for $\Delta H = 20$ kOe (Dan'kov et al. 1998).

with $\Delta S_M$ and $\Delta T$ results obtained by direct and magnetization measurements (Pecharsky and Gschneidner 1996).

The estimations of errors, made by Pecharsky and Gschneidner (1996), showed that the magnetocaloric parameters derived from the heat capacity method are characterized by sufficient accuracy: near room temperatures the uncertainty in $\Delta S_M$ is 100–300 mJ/mol K and the uncertainty in $\Delta T$ is 1–1.5 K. In the low temperature region the accuracy becomes substantially better.

Figure 3.5 shows the MCE temperature dependences measured on high purity polycrystalline Gd directly by pulsed-field and quasistatic (switch-on) techniques and determined from the heat capacity for a magnetic field change from 0 to 20 kOe. One can see quite good agreement between the results obtained by these three methods, especially in the temperature range from 220 to 330 K. The $\Delta S_M(T)$ curves of the single crystal Gd determined for $\Delta H$ up to 50 kOe from the magnetization measurements are also in good accordance with those calculated from the heat capacity data (Dan’kov et al. 1998).

3.4. Other methods

Bredy and Seyfert (1988) measured entropy changes in EuS induced by a magnetic field by means of an experimental set-up that consisted of a temperature control system, superconducting solenoid and thermal resistor.
The temperature control system, including carbon thermometer, electric heater and electronic system allowed to maintain the sample temperature at a constant value independently from the magnetic field variation. Magnetic fields up to 30 kOe were created by the superconducting magnet. A thermal resistor, made of brass, linked the sample holder to a liquid helium bath. The heat flux \( \frac{dQ}{dt} \), flowing through the thermal resistor, determines the sample temperature. At constant magnetic field the flux is determined by the heat power \( W_0 \), generated by the sample heater. When the magnetic field is changed, additional heat \( Q_{\text{magn}} \) is realized in the sample due to the magnetization and the heater power \( W_x \) will be decreased or increased by the electronic system in order to compensate this heat and keep the temperature constant. The process can be described by the following system of equations:

\[
\begin{align*}
\frac{dQ(T)}{dt} &= W_0, \\
\frac{dQ(T)}{dt} &= W_x + \frac{dQ_{\text{magn}}}{dt}.
\end{align*}
\] (3.5)

On the basis of this system one can, after integration, obtain the equation:

\[
T \Delta S = T \left[ S(H_2) - S(H_1) \right] = \int \left( \frac{dQ_{\text{magn}}}{dt} \right) dt \\
= \int_{H_1}^{H_2} (W_x - W_0) \, dt,
\] (3.6)

where \( H_2 = H(t_2); \, H_1 = H(t_1) \). So, measuring \( W_0 \) and \( W_x \) and integrating these signals over time, one can determine the entropy change induced by the field change, mainly related to the magnetic entropy change.

4. Magnetocaloric effect in 3d metals, alloys and compounds

4.1. Ferromagnetic 3d metals (Fe, Co, Ni)

It follows from eq. (2.16), that in a ferromagnet the MCE must display a maximum in the vicinity of the Curie temperature. For the first time such a maximum was observed by Weiss and Piccard (1918). MCE studies made in Fe, Ni and Co in fields up to 30 kOe have shown that the magnitude of the MCE near \( T_C \) is well described by eq. (2.16) and is governed by the paraprocess (Weiss and Piccard 1918; Weiss and Forrer 1924, 1926; Potter 1934; Hirschler and Rocker 1966; Kohlhaas et al. 1966; Kohlhaas 1967; Rocker and Kohlhaas 1967).

Equations (2.44) and (2.52) show that near the Curie temperature the value of the MCE in ferromagnets should be quadratic in the magnetization. This was used to determine the magnetization from the experimental data on the MCE (Weiss and Forrer 1926). For this purpose \( \Delta T(I^2) \) curves linear in the region of the paraprocess were extrapolated to the \( I^2 \) axis. In the ferromagnetic region the intersection of \( I^2 \) axis corresponds to the value of \( I_s^2 \).
TABLE 4.1
Parameters of 3d ferromagnets used in theoretical calculations, the results of the calculations of the maximum possible values of the MCE ($\Delta T_{\text{max}}$) at $T = T_C$ and the values of the magnetic field $H_{\text{max}}$ (the field varies from 0 to $H_{\text{max}}$), in which the MCE values are different from $\Delta T_{\text{max}}$ by at most 1% (Tishin 1990a).

<table>
<thead>
<tr>
<th>3d ferromagnets</th>
<th>$g_J$</th>
<th>$J$</th>
<th>$T_C, K$</th>
<th>$T_D, K$</th>
<th>$\Delta T_{\text{max}}, K$</th>
<th>$H_{\text{max}}, \times 10^4$ kOe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>2</td>
<td>1.4</td>
<td>1043</td>
<td>420</td>
<td>350</td>
<td>6</td>
</tr>
<tr>
<td>Ni</td>
<td>3</td>
<td>0.3045</td>
<td>631</td>
<td>385</td>
<td>84</td>
<td>2.9</td>
</tr>
<tr>
<td>Co</td>
<td>2</td>
<td>0.95</td>
<td>1403</td>
<td>375</td>
<td>348</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Fig. 4.1. Theoretical (solid lines) and experimental (dashed lines) temperature dependences of the MCE in Fe induced by the magnetic field changes $\Delta H$ specified near the curves (Tishin 1990a; Potter 1934).

at a given temperature. This method was used to determine the $I_s(T)$ dependence in Fe, Ni and Co by Weiss and Forrer (1926), Potter (1934) and Rocker and Kohlhaas (1967).

The Landau theory of the second order phase transitions gives eq. (2.32), which should be valid near $T_C$. The linear dependences of $H/\Delta T^{1/2}$ on $\Delta T$ was observed by Belov (1961a, 1961b) in Ni in the temperature range from 618 to 627 K.

The temperature dependence of the spontaneous magnetization in 3d ferromagnets is satisfactorily described by the mean field approximation. On the basis of this Tishin (1990a) used MFA to determine the magnetocaloric effect in Fe, Ni and Co. Equations (2.60)–(2.62), (2.67) were used to calculate the total temperature dependences of the entropy of a material in zero and nonzero magnetic fields and then by the method described in section 3.3 (see eq. (3.3)) the $\Delta T(T)$ dependences were obtained. In these calculations $g_J = 2$ was used and the values of $J$ were determined by comparison of the experimental temperature dependences of the spontaneous magnetization in the vicinity of the Curie temperature with the results of the calculations made by MFA. The values of $J$, $g_J$, $T_C$ and Debye temperature $T_D$ are given in table 4.1.
Fig. 4.2. Theoretical (solid lines) and experimental (dashed lines) temperature dependences of the MCE in Ni induced by the magnetic field changes $\Delta H$ specified near the curves (Tishin 1990a; Weiss and Forrer 1924).

Fig. 4.3. Theoretical (solid lines) and experimental (dashed lines) temperature dependences of the MCE in Co induced by the magnetic fields specified near the curves (Tishin 1990a; Kohlhaas 1967).

Figures 4.1–4.3 present the results of theoretical calculations (solid lines) made by Tishin (1990a) together with experimental curves (dashed lines) of the MCE (Weiss and Forrer 1924; Potter 1934; Kohlhaas 1967). As one can see, they are in relatively good agreement. For $\Delta H = 60$ kOe near the Curie temperature the MCE value in Fe is 9.5 K. In
Gd and Tb, having the largest values of the MCE among the rare earth metals, the magnetocaloric effect is 12 and 10.5 K, respectively (Brown 1976; Nikitin et al. 1985a, 1985b).

Figure 4.4 shows the results of calculations of MCE field dependences in Fe, Ni and Co near the Curie temperature. It follows from fig. 4.4 that the linear increase of the MCE value with the field is observed in weak magnetic fields only. The experimental values of the MCE (see fig. 4.4) are well described by the calculated dependences.

Figure 4.5 presents the temperature dependences of the MCE induced by a magnetic field of $6 \times 10^3$ kOe. Unlike rare earth metals, in 3d ferromagnets in this field the maximum of the MCE is fairly sharp. The MCE in Fe and Co exceeds that of Ni by several times. Tishin (1990a) calculated the maximum possible MCE in Fe, Co and Ni using eq. (2.77b). The maximum possible $\Delta S_M$ value was determined by eq. (2.70) for the corresponding $J$ value. The values of $\Delta H_{\text{max}}(T_C)$ in which the MCE is different from $\Delta T_{\text{max}}$ by at most 1% were calculated in the framework of MFA. The results are shown in table 4.1. $\Delta T_{\text{max}}$ in Fe and Co is larger than in rare earth metals (see table 7.3).
Analogous mean field calculations of MCE were made by Hashimoto et al. (1981), which were found to be in good agreement with experimental results for Ni (Weiss and Forrer 1926). It was found that in Ni $\Delta T \approx 1.3$ K at $T_C = 628$ K and $\Delta H = 17.8$ kOe.

Noakes and Arrott (1973) studied the MCE of a nickel single crystal in the vicinity of $T_C$ in weak fields up to 900 Oe. They found the maximum $\Delta T = 0.15$ K at $\Delta H = 900$ Oe.

The magnetocrystalline anisotropy contribution to the MCE can be found in the following way. In the general case the anisotropic part of the Gibbs energy can be written down as:

$$G_a = \sum_i K_i \psi_i,$$

where $K_i$ is the anisotropy constant, $\psi$ is a function of the orientation of the spontaneous magnetization vector. From eqs (2.8a), (2.77) and (4.1) the following formula for the MCE due to a rotation of the spontaneous magnetization can be obtained:

$$\Delta T_a = \frac{T}{C_{p,H}} \sum_i \left( \frac{\partial K_i}{\partial T} \right)_{p,H} \Delta \psi_i.$$

The MCE due to rotation of the spontaneous magnetization was investigated in Ni by Akulov and Kirensky (1940). To measure this effect a single crystal of nickel was placed in a field exceeding the value of technical saturation and then quickly turned with respect to the field. The value of temperature change was $\sim 10^{-3}$ K at 78 K. Under the conditions of measurement the energy of the magnetocrystalline anisotropy of a cubic crystal can be written down as:

$$G(T, H) \approx K_1(T) \sum_i \alpha_i^2 \alpha_j^2,$$

where $\alpha_i = H_i/|\vec{H}|$ are the direction cosines of the magnetic field $\vec{H}$ (or $\vec{I}_a$) with respect to the crystal axes, $K_1$ is the magnetocrystalline anisotropy constant. On the basis of eq. (4.3) the following expression can be derived (Akulov and Kirensky 1940):

$$\Delta T = \frac{T}{C_{p,H}} \left( \frac{\partial K_1}{\partial T} \right)_{H} \Delta \sum_i \alpha_i^2 \alpha_j^2.$$

The effect reaches its maximum value at low temperatures, where the derivative $(\partial K_1/\partial T)_H$ has high values. The results of experimental MCE measurements showed a fairly good agreement with calculations made by eq. (4.4).

The MCE due to rotation of the saturation magnetization in Co which has a hexagonal crystal structure and is characterized by an axial anisotropy was considered by Ivanovskii (1959), Ivanovskii and Denisov (1966a, 1966b). For a single crystal the following formula was obtained:

$$\Delta T = \frac{T}{C_{p,\Theta}} \left[ \left( \frac{\partial K_1}{\partial T} \right)_{\Theta} \Delta \sin^2 \Theta + \left( \frac{\partial K_2}{\partial T} \right)_{\Theta} \Delta \sin^4 \Theta \right].$$
where $\Theta$ is the angle between the $c$-axis and $\vec{I}_s$, and $C_{p,\Theta}$ is the heat capacity under constant pressure and $\Theta$. On the basis of eq. (4.3) and the assumption of a random distribution of crystallite axes, Ivanovskii (1959) derived a formula for the MCE under magnetization of Co polycrystals. Experimental measurements showed that below 500 K the MCE caused by magnetic field increase had a negative sign ($\Delta T \approx 7 \times 10^{-2}$ K for $T = 504$ K and $\Delta H = 7$ kOe) and above 600 K $\Delta T$ was positive. The sign change of $\Delta T$ took place near 565 K. Ivanovskii (1959) related this behavior with the temperature dependence of $K_1$ in Co: near 535 K $K_1$ changed its sign from positive in lower temperature region to negative at higher temperatures.

To obtain the heat capacity of Fe in a magnetic field on the basis of the zero-field heat capacity and MCE measurements, eq. (2.96a) was used by Kohlhaas et al. (1966). As one can see from fig. 4.6, where the experimental results and the results of calculations are shown, the $C_{H,p}(T)$ curve near $T_C$ becomes smooth and the maximum of $C_{H,p}$ becomes significantly lower under the influence of the magnetic field. Analogous behavior was observed in Ni, Co and Fe–Si alloys (Hirschler and Rocker 1966; Rocker and Kohlhaas 1967; Korn and Kohlhaas 1969).

4.2. Alloys and compounds

The MCE in ferromagnetic Cr$_3$Te$_4$ was investigated experimentally and theoretically using MFA by Hashimoto et al. (1981). The results are shown in fig. 4.7, where one can see a fairly good agreement between the calculations and experiment. At $T_C = 316$ K the MCE
Fig. 4.7. The MCE in Cr3Te4 induced by a magnetic field of 20 kOe. Open circles are the experimental points and the solid curve is the MFA calculation (Hashimoto et al. 1981).

TABLE 4.2
Magnetic entropy change $\Delta S_M$ induced by a magnetic field change $\Delta H$ in some 3d metal based ferromagnets (Hashimoto et al. 1982).

| Substance | $T_C$, K | $|\Delta S_M| \times 10^{-3}$ J/g K |
|-----------|----------|----------------------------------|
| $\Delta H = 10$ kOe | $\Delta H = 8$ kOe |
| MnAs      | 318      | 2.9                               | 11.4 |
| MnP       | 298      | 2.9                               | 11.4 |
| CrTe      | 333      | 1.7                               | 6.8  |

in Cr3Te4 reaches a value of $\approx 1.1$ K for $\Delta H = 20$ kOe. The results on $\Delta S_M$ in the ferromagnets MnAs, MnP and CrTe, which have Curie points near room temperature are presented in table 4.2.

MFA was successfully used to describe the MCE in ferromagnetic compound Mn5Ge3, which had at $T_C = 298$ K $\Delta T = 1.7$ K for $\Delta H = 20$ kOe (Hashimoto et al. 1982).

Figure 4.8 shows the temperature dependence of the magnetic moment in a field of 4 kOe and $\Delta T$ for $\Delta H = 6.5$ kOe in the MnAs compound (Kuhrt et al. 1985). The temperature hysteresis accompanying the first-order transition from paramagnetism (PM) to ferromagnetism (FM) is also observed for the MCE.

In MnAs$_{1-x}$P$_x$ ($x = 0.08; 0.09$) compounds complex first-order field-induced transitions between different magnetic states (FM – spiral structure – FM) were observed below the magnetic ordering temperature (for $x = 0.08$ it was $\approx 220$ K) (Kuhrt et al. 1985). The value of the MCE anomalies at these transitions was described by the Clausius–Clapeyron equation (2.82). For $x = 0.08$ at $T = 220$ K and $H = 70$ kOe $\Delta T \approx 1.2$ K. The temperature dependences of the heat capacity for MnAs$_{1-x}$P$_x$ ($0.03 \leq x \leq 0.13$) were measured by Krokozinski et al. (1982).

The MCE at the first-order transitions from ferri-(FI) or ferromagnetism to antiferromagnetism (AFM) was studied in FeRh (with Fe concentrations 0.48–0.50), Mn$_{2-x}$Cr$_x$Sb ($x = 0.03; 0.05; 0.10; 0.16$), Mn$_3$Ge$_2$, CrS$_{1.17}$ and Mn$_{0.95}$V$_{0.05}$As (Selte et al. 1977; Flippen and Darnell 1963; Ponomarev 1972; Nikitin et al. 1990; Baranov et al. 1992).
In Fe–Rh alloys the AFM–FM phase transition takes place near room temperature within the concentration range 47–53% of Rh (Kouvel and Hartelius 1962; Zaharov et al. 1964). MCE measurements on quenched and annealed Fe_{0.49}Rh_{0.51} were made by Nikitin et al. (1990) in magnetic fields up to 19.5 kOe. Magnetic fields induce the transition from the AFM structure, arising below the transition point $T_{AFM-FM} \approx 310$ K, to a ferromagnetic one. This is accompanied by sample cooling, reaching 13 K for the quenched sample at a field of 20 kOe (see fig. 4.9). It should be noted that the quenched and annealed samples display different values of the MCE and different temperature dependences of the MCE. Since the transition was of the first order, it had an irreversible character and $\approx 20–30$ kOe was required to overcome the hysteresis effects.

Ponomarev (1972) studied the magnetization of Fe_{0.58}Rh_{0.58} in pulsed fields up to 300 kOe in the temperature range from 77 to 330 K. He constructed the magnetic phase diagram $H_{ct}(T)$ (here $H_{ct}$ is the field of the AFM structure destruction) and determine the specific magnetization change $\Delta \sigma$ ($\sigma = M/m$, where $m$ is the mass) across the transition. On the basis of these data and the Clausius–Clapeyron equation (2.82) the magnetic entropy change $\Delta S_M$ at the transition temperature $T_{AFM-FM} = 333$ K was calculated ($\Delta S_M = 1.83 \times 10^5$ erg/g K), and then by eq. (2.77) the value $\Delta T \approx 20$ K was obtained.

Analogous calculations of $\Delta S_M$ were made by Baranov et al. (1992) for Mn_{1.9}Cr_{0.1}Sb and by Flippen and Darnell (1963) for Fe_{0.5}Rh_{0.5}, Mn_{2-x}Cr_{x}Sb, Mn_{3}Ge_{2}, CrS_{1.17}, Li_{0.1}Mn_{0.9}Se on the basis of the data of Heikes et al. (1961). The results are shown in table 4.3. Direct measurements of the MCE in Mn_{1.9}Cr_{0.1}Sb made by Baranov et al. (1992) gave $\Delta T = -2.7$ K for $\Delta H = 60$ kOe at $T \approx 245$ K in the vicinity of transition point.

Selte et al. (1977) studied the magnetocaloric effect in Mn_{0.95}V_{0.05}As in pulsed magnetic fields up to 210 kOe and at the temperatures from 160 K to 260 K. At the transition from a helicoidal antiferromagnetic (HAFM) state with MnP crystal structure to a ferromagnetic state with NiAs structure near 200 K a positive MCE with a maximum value of about 5 K was induced by a field change of 210 kOe.
Okazaki et al. (1993) investigated the MCE in ferromagnetic Ni–Mn alloys (66–83% Ni) characterized by partial atomic disorder in the crystalline structure. The degree of order was changed by annealing of the sample. The MCE peak was observed in the Curie temperature region and had a maximum value of about 0.5 K for $H = 6.4$ kOe in the ordered $\text{Mn}_{0.17}\text{Ni}_{0.83}$ alloy. Linear $\Delta T(I^2)$ dependences observed in this alloy system allowed to obtain the $I_s(T)$ curve. The MCE has also been studied by Sucksmith et al. (1953) in copper–nickel and by Znamenskii and Fakidov (1962) in copper–manganese alloys. An investigation of MCE in distorted triangular lattice antiferromagnet $\text{RbMnBr}_3$ has been done by Pérez et al. (1998).

4.3. Thin films

The MCE and magnetic entropy change induced by a magnetic field in thin films prepared on the basis of 3d elements was studied by Babkin and Urinov (1987, 1989) and Morelli et al. (1996). Babkin and Urinov (1989) considered the MCE due to the uniform rotation
TABLE 4.3
Change of the specific magnetization ($\Delta \sigma$) and magnetic entropy ($\Delta S_M$), and temperature derivative ($-\partial H_c/\partial T$) of the critical field at the first order transition $T_s$ in some magnetic substances based on 3d metals.

<table>
<thead>
<tr>
<th>Substances</th>
<th>$T_s$, K</th>
<th>$\Delta \sigma$, emu/g</th>
<th>$-\partial H_c/\partial T$, kOe/K</th>
<th>$\Delta S_M$, $10^4$ erg/g K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$<em>{1.97}$Cr$</em>{0.03}$Sb</td>
<td>127</td>
<td>39.6</td>
<td>1.08</td>
<td>4.28</td>
<td>[1]</td>
</tr>
<tr>
<td>Mn$<em>{1.95}$Cr$</em>{0.05}$Sb</td>
<td>211</td>
<td>32.8</td>
<td>1.97</td>
<td>6.5</td>
<td>[1]</td>
</tr>
<tr>
<td>Mn$<em>{1.90}$Cr$</em>{0.10}$Sb</td>
<td>305</td>
<td>24.3</td>
<td>2.43</td>
<td>5.9</td>
<td>[1]</td>
</tr>
<tr>
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<td>2.6</td>
<td>$\approx$6.8</td>
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<tr>
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</tr>
<tr>
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<td>2.08</td>
<td>0.72</td>
<td>[1]</td>
</tr>
<tr>
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<td>2.29</td>
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<td>[1]</td>
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<tr>
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<td>[1]</td>
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<tr>
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</tr>
<tr>
<td>Li$<em>{0.10}$Mn$</em>{0.90}$Se</td>
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<td>5.3</td>
<td>14</td>
<td>[1]</td>
</tr>
</tbody>
</table>

References:
[1] Flippen and Darnell (1963)

of the spontaneous magnetization vector in thin films. The magnetic free energy of the film was presented as:

$$F_M = K \sin^2 \Theta - IH \cos(\phi - \Theta),$$  

(4.6)

where $K$ is the film anisotropy constant including the form anisotropy and induced magnetic anisotropy, $\phi$ and $\Theta$ are the angles between the film surface and the $\vec{H}$ and $\vec{I}$ vectors, respectively.

The value of the MCE was determined with the help of eqs (2.21), (2.7a) and the expression for equilibrium magnetic free energy obtained from eq. (4.6). The following formula for the MCE was derived (Babkin and Urinov 1989):

$$\left( \frac{\Delta T}{\Delta H} \right)_S = \left\{ \frac{T}{C_H} \frac{K \sin^2 2\Theta}{I[H(2K\cos 2\Theta + IH\cos(\phi - \Theta))]} \left[ I \frac{\partial K}{\partial T} - K \frac{\partial I}{\partial T} \right] \right.$$

$$- \frac{T}{C_H} \frac{\partial I}{\partial H} \cos(\phi - \Theta) \right\}. \quad (4.7)$$

Depending on the relation between $K(T)$ and $I(T)$ the first term in eq. (4.7) gives a positive or negative contribution to the MCE. If the anisotropy is absent ($K = 0$, $\phi = 0$), eq. (4.7) transforms into eq. (2.16). If the film anisotropy is governed only by the form anisotropy ($K = 2\pi I^2$) the first term in eq. (4.7) is always negative. Figure 4.10(a) presents the results of calculations made by using eq. (4.7) for the case $H = 4\pi I$ and $K = 2\pi I^2$.

Experimental MCE measurements were made on polycrystalline ferromagnetic Ni and single crystalline ferrimagnetic dielectric $\gamma$-Fe$_2$O$_3$ films, 0.15–0.30 \mu m thick. A vanadium...
Magnetocaloric Effect

1.0 (a) S

0.16

0.08

0

-0.08

(b) ~0~ \( \sim \theta \sim \) 

Fig. 4.10. Dependence of the MCE on the angle \( \phi \) between the film surface and the magnetic field \( H \): (a) theoretical calculation using eq. (4.7) for \( H = 4\pi I \) and \( K = 2\pi I^2 \); (b) experimental data for the Ni film, \( H = 3.4 \text{kOe} \) (Babkin and Urinov 1989).

dioxide film 0.1–0.5 \( \mu \)m thick was used as a temperature-sensitive element (its resistance decreased drastically under heating near \( \approx 330 \text{ K} \)).

The experimental results for the Ni film for \( H = 3.4 \text{kOe} \) are shown in fig. 4.10(b) (analogous, but some more complicated behavior was displayed the \( \gamma \)-Fe\(_2\)O\(_3\) film). With increasing magnetic field the maximum of the MCE near the hard magnetization axis (\( \phi = 0 \)) disappears. The proposed theory contradicts the experimental results obtained for an orientation of the magnetic field near the hard axis (the region of negative MCE). The authors related such behavior to the presence of defects and surface anisotropy in the films, which broke the condition for uniform rotation of the magnetization vector.

Morelli et al. (1996) investigated the magnetic entropy change \( \Delta S_M \) induced by the magnetic field in doped lanthanum manganite the 2.4 \( \mu \)m thick polycrystalline films of La\(_{0.67}\)A\(_{0.33}\)MnO\(_3\) (A = Ca, Ba, or Sr) display FM–PM transition at 250, 300, and 350 K, respectively. The films were fabricated by a metalorganic deposition technique. The \( \Delta S_M(T) \) dependences were calculated on the basis of magnetization data by using eq. (2.71). Near the Curie temperatures, wide maxima of \( \Delta S_M \) were observed with the following values (for \( H = 50 \text{kOe} \) applied parallel to the film plane): \( 2 \times 10^4 \text{ erg/g K} \) for A = Ca, \( 1.4 \times 10^4 \text{ erg/g K} \) for Ba, and \( 1.5 \times 10^4 \text{ erg/g K} \) for Sr.

5. Magnetocaloric effect in oxides

5.1. Garnets

The MCE in polycrystalline rare earth garnets R\(_3\)Fe\(_5\)O\(_{12}\) (R = Gd, Tb, Dy, Ho, Er, Tm, Yb, and Y) was studied by Belov et al. (1968, 1969, 1970, 1972), Belov and Nikitin (1970a, 1970b), Talalaeva et al. (1969) and Clark and Callen (1969).

Figure 5.1 shows the temperature dependences of MCE in R\(_3\)Fe\(_5\)O\(_{12}\) polycrystals (R = Y, Gd, Tb, Dy, Ho, Er, Yb, Tm) induced by the magnetic field change of 16 kOe in the
temperature range from 78 to 600 K (Belov et al. 1969). One can see that for \( R = Y \) the MCE is positive in the whole temperature range and has a maximum near the Curie temperature. For \( R = Gd \) the \( \Delta T(T) \) curve becomes more complicated. It also has a positive maximum near the Curie temperature, but then near 462 K, the MCE becomes negative. At \( T = 285 \) K the MCE suddenly changes its sign and in low temperature region another maximum appears. Analogous behavior was observed in other rare earth garnets. In the garnets with \( R = Tm \) and \( Yb \) the compensation points lie in the region of liquid helium temperatures. Clark and Callen (1969) measured the MCE in these compounds and found that the MCE induced by 110 kOe is negative near 4.2 K.

Such behavior is related with the ferrimagnetic structure of the rare earth iron garnets. According to the Néel model (Néel 1954) these materials have a magnetic structure consisting of three magnetic sublattices. The \( R^{3+} \) ions occupy dodecahedral sites (c-sublattice) and the \( Fe^{3+} \) ions occupy octahedral (a-sublattice) and tetragonal (d-sublattice) sites. The a- and d-sublattices are connected by strong antiferromagnetic exchange interactions. The weaker antiferromagnetic interaction takes place between d- and c-sublattices and the c-c and a-c interactions are weak and positive (Anderson 1964). Such exchange field distribution leads to a strong paraprocess in the c-sublattice in the whole temperature range below \( T_C \), which displays itself in a strong temperature and field dependence of the c-sublattice magnetic moment. An intensive paraprocess in the a- and d-sublattices is pos-
sible only near $T_C$ and the total magnetic moments of the d- and a-sublattices have weak field and temperature dependence at low temperatures.

Belov and Nikitin (1965, 1970a), in the framework of MFA, estimated the values of effective fields acting in the RE magnetic sublattice ($H_{2\text{eff}}$) and in the iron a–d magnetic sublattices ($H_{1\text{eff}}$) in rare earth iron garnets. It was shown that $H_{2\text{eff}} \approx 3 \times 10^5$ Oe and $H_{1\text{eff}} \approx 1.7 \times 10^6$ Oe, i.e., $H_{1\text{eff}} \gg H_{2\text{eff}}$.

Due to the difference in temperature dependences of the c- and a-, d-sublattice magnetizations, the compensation temperature $T_{\text{comp}}$, characteristic for ferrimagnets, appears in the garnets with heavy rare earth metals. Above $T_{\text{comp}}$ the magnetic moment of the c-sublattice $\widetilde{M}_R$ is lower than the total magnetic moment of the a- and d-sublattices $\tilde{M}_{Fe}$ and below $T_{\text{comp}}$ the inverse situation takes place. The resultant magnetic moment of the rare earth iron garnet is $\tilde{M} = \widetilde{M}_R + \tilde{M}_{Fe}$ and it is oriented along the field direction. This leads to a change of the $\widetilde{M}_R$ and $\tilde{M}_{Fe}$ orientations relative to the field at $T = T_{\text{comp}}$. Such behavior was observed by neutron diffraction measurements (Bertaut et al. 1956; Herpin and Meriel 1957; Prince 1957).

Belov and Nikitin (1970) considered the MCE and heat capacity near the compensation point of rare earth iron garnets in the framework of MFA using thermodynamic formulae (2.16) and (2.95), which were presented in vector form:

$$dT = -\frac{T}{C_{H,p}} \left( \frac{\partial \tilde{M}}{\partial T} \right)_{H} d\tilde{H}, \quad (5.1)$$

$$\Delta C = C_H - C_M = -T \left( \frac{\partial \tilde{M}}{\partial T} \right)_H \left( \frac{\partial \tilde{H}}{\partial T} \right)_M. \quad (5.2)$$

The total MCE was determined as the sum:

$$\Delta T = \Delta T_{Fe} + \Delta T_{R}. \quad (5.3)$$

Since $|\partial M_R/\partial T| \gg |\partial M_{Fe}/\partial T|$ and $|\partial M_R/\partial H| \gg |\partial M_{Fe}/\partial H|$ below $T_C$, the main contribution to the MCE in the low temperature region far enough from $T_C$ is provided by the rare earth a-sublattice. On the basis of this the following equation for the MCE was obtained:

$$\Delta T = \frac{I_{20}}{C_{H,p}k_B} \frac{\partial B_f(x_2)}{\partial x_2} \tilde{H} \left( \frac{I_{20}}{2n\nu_2} \tilde{H} + 2\mu_B s_2 \tilde{H}_{2\text{eff}} \right), \quad (5.4)$$

where $I_{20}$ is the magnetization of the RE sublattice at $T = 0$ K, $\nu_2$ is the number of the RE atoms in the molecule, $s_2$ is the spin of the RE atom, $n$ is the number of molecules in the unit volume, $B_f$ is the Brillouin function. $\tilde{H}_{2\text{eff}}$ is the molecular field acting on the RE sublattice due to the iron a–d sublattice:

$$H_{2\text{eff}} = \frac{z_{21}I_{21}}{\mu_B} \frac{I_1}{I_{10}}, \quad (5.5)$$
where \( z_{21} \) is the number of the nearest neighbors of the a–d sublattice to an atom of the RE sublattice; \( I_{21} \) is the exchange integral describing the interactions between the RE and Fe sublattices; \( I_1 \) is the magnetization of the a–d sublattices, \( I_{10} \) equals \( I_1 \) at \( T = 0 \) K;

\[
x_2 = \frac{I_{20}}{n\nu_{2}k_{B}T} H + \frac{2\mu_{B}S_{2}}{k_{B}T} H_{2\text{eff}}.
\]  

(5.6)

If the directions of \( \vec{H} \) and \( \vec{H}_{2\text{eff}} \) coincides, then \( \Delta T > 0 \). In this case the external magnetic field increases the magnetic order in the c-sublattice, which leads to a decrease of the magnetic entropy and to sample heating. If \( \vec{H} \) and \( \vec{H}_{2\text{eff}} \) are aligned in opposite directions, then \( \Delta T < 0 \). The external magnetic field \( H \) in this case acts against \( H_{2\text{eff}} \) and decreases the magnetic order in the c-sublattice. Such a process is accompanied by a magnetic entropy increase and a corresponding sample cooling. The paraprocesses of these two types were called ferromagnetic and antiferromagnetic ones, respectively (Belov 1968, Belov et al. 1968, 1969, 1972).

The ferro- and antiferromagnetic paraprocesses can be realized in the same magnetic sublattice at various temperature ranges, but in the rare earth iron garnets the MCE below \( T_C \) is determined by the paraprocess in the c-sublattice. Near \( T_C \) the ferromagnetic paraprocess in the iron a–d sublattice overcomes the antiferromagnetic one in c-sublattice and MCE becomes positive at some temperature, reaching a maximum near \( T_C \).

The sign change of \( \Delta T \) at \( T_{\text{comp}} \) is related with the change of the \( M_{\text{Fe}} \) orientation (and, consequently, the \( H_{2\text{eff}} \) orientation) relative to the magnetic field direction. The jump of \( \Delta T \) observed at \( T_{\text{comp}} \) should be inversely proportional to \( T_{\text{comp}} \), as it follows from eq. (5.4). This was confirmed experimentally in rare earth iron garnets by Belov et al. (1969). As it was noted by Belov and Nikitin (1970a, 1970b), the existence of \( \Delta T \) jumps at \( T_{\text{comp}} \) points to the first-order character of this magnetic phase transition.

If the magnetic c-sublattice in the garnet is absent, as is in the case for \( R = Y \), one can observe a \( \Delta T(T) \) curve with one maximum near the Curie point, caused by the paraprocess in the a–d sublattice (although a- and d-sublattices are connected by negative exchange interaction, the ferromagnetic paraprocess in the d-sublattice prevails in the whole temperature range), see fig. 5.1.

Below \( T_{\text{comp}} \) at \( T \approx 90 \) K the MCE in \( \text{Gd}_3\text{Fe}_5\text{O}_{12} \) displays an additional maximum which is higher than one near \( T_C \). Also in the garnets with Ho, Dy and Tb an increase of the MCE below \( T_{\text{comp}} \) was observed (see fig. 5.1). Such behavior was related with a sharp change of the long range magnetic order, which took place in the RE sublattice in this temperature range (Belov 1961b; Belov and Nikitin 1970b). The low temperature of this ordering is due to the weakness of the effective field acting on the RE sublattice due to the a–d iron sublattice.

The replacement of Fe in the garnets by nonmagnetic ions can lead to a further decrease of the effective field \( H_{2\text{eff}} \) and, consequently, to an increase of the RE sublattice paraprocess and the MCE in low temperature range. Such MCE increase was observed experimentally in \( \text{Gd}_3\text{Ga}_x\text{Fe}_{5-x}\text{O}_{12} \) (\( 0 \leq x \leq 1.5 \)) by Belov et al. (1972) (see fig. 5.2). The gadolinium gallium iron garnets (GGG) with \( x > 1.5 \) have superparamagnetic properties and will be considered in section 8.
The magnetothermal properties of gadolinium gallium garnet Gd$_3$Ga$_5$O$_{12}$ (GGG), dysprosium gallium garnet Dy$_3$Ga$_5$O$_{12}$ (DGG) and dysprosium aluminum garnet Dy$_3$Al$_5$O$_{12}$ (DAG) were studied by Fisher et al. (1973), Filippi et al. (1977), Daudin et al. (1982), Hashimoto (1986), Li et al. (1986), Kimura et al. (1988), Kuz'min and Tishin (1991, 1993a, 1993b), Schiffer et al. (1994).

GGG and DGG have antiferromagnetic ordering below $T_N = 0.8$ K and 0.373 K, respectively. Above $T_N$ they display simple paramagnetic behavior (Filippi et al. 1977; Yazawa et al. 1986). Figure 5.3 shows the temperature dependences of the magnetic entropy change for various $\Delta H$ for GGG and DAG (Hashimoto 1986; Li et al. 1986).

Below 20 K the population of all but the ground Kramers doublets of the Dy ions in DGG and DAG can be neglected, since the energy of the exited state is larger than the thermal agitation energy (Kuz'min and Tishin 1991). Therefore the value $J = 1/2$ can be used for the total angular momentum quantum number of these ions. For Gd$^{3+}$ ion the crystal field splitting of the ground state with $J = 7/2$ ($g$-factor equals 2) is negligible for $T > 4.2$ K and this $J$ value is thought to be the largest among the rare earth ions in the low temperature range. Figure 5.3 illustrates the $\Delta S_M$ increase for GGG in comparison with DAG in low temperature range caused by this effect.

Hashimoto (1986) by means of MFA studied the influence of the $g$-factor and $J$ quantum number values on the temperature dependence of $\Delta S_M$. The calculations were made for antiferromagnetic systems ($T_N = 1$ K) with $g_J = 2$ ($J$ was being varied) and $J = 1/2$ ($g_J$ was being varied) and for $\Delta H = 60$ kOe. It was found that $\Delta S_M$ increased with increasing $J$ and $g_J$. For $J = 7/2$ and $g_J = 2$ the $\Delta S_M$ value was smaller than that for $J = 1/2$ and $g_J \geq 10$ at temperatures above 20 K.

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**Fig. 5.2.** Temperature dependences of the MCE induced by 16 kOe in Gd$_3$Ga$_x$Fe$_{5-x}$O$_{12}$ ($0 \leq x \leq 1.5$) (Belov et al. 1972).
As it was shown by Numazawa et al. (1983), the thermal conductivity of GGG is \( \approx 1 \) W/cm K at \( T = 13 \) K and \( \approx 0.3 \) W/cm K at 4 K for DGG. The thermal conductivity of DAG is about twice of that in GGG (Hashimoto 1986).

The heat capacity of DGG and GGG was measured by Fisher et al. (1973), Filippi et al. (1977) and Schiffer et al. (1994). DGG displays a sharp \( \lambda \)-type heat capacity anomaly (with the height of \( \approx 3R \)) at \( T_N = 0.35 \) K. GGG shows a broad maximum with a value of about 2.4 R near \( T_N = 0.8 \) K. In an external magnetic field of 9 kOe the heat capacity maximum in GGG becomes sharp and shifts to 0.4 K. The heat capacity of \((\text{Dy}_{0.5}\text{Gd}_{0.5})_3\text{Ga}_5\text{O}_{12}\) was studied by Numazawa et al. (1996) in the temperature range from 0.65 to 4 K. At 0.65 K its heat capacity was about three times larger than that of GGG. The peak in \( C(T) \) was expected to be below 0.65 K.

The field dependences of the MCE near the compensation point \( T_{\text{comp}} \) in \( \text{R}_3\text{Fe}_5\text{O}_{12} \) (\( \text{R} = \text{Gd}, \text{Dy} \) and \( \text{Ho} \)) were studied by Belov et al. (1970). Tsiablikov (1956), Pahomov and Gusev (1964) and Clark and Callen (1968) have shown, that in ferrimagnets in some field and temperature intervals \((H_{c1} < H < H_{c2}, T_{c1} < T < T_{c2})\) a noncollinear magnetic structure can appear as a result of competition between the external magnetic field and the negative intersublattice exchange interaction. \( H_{c1} \) and \( H_{c2} \) can achieve essential values, but near \( T_{\text{comp}} \) they should abruptly decrease (Clark and Callen 1968).

The noncollinear magnetic structure is characterized by a temperature independence of the total magnetic moment \((\partial M/\partial T = 0)\) which, according to the eq. (2.16), gives \( \partial T/\partial H = 0 \). Consequently, the \( \Delta T(H) \) dependence should have the following form in the noncollinear phase: an increase of \( \Delta T \) with \( H \) for \( H < H_{c1} \) with subsequent saturation for \( H > H_{c1} \). This saturation behavior of \( \Delta T(H) \) was observed near \( T_{\text{comp}} \) in \( \text{R}_3\text{Fe}_5\text{O}_{12} \) (\( \text{R} = \text{Gd}, \text{Dy}, \text{Ho} \)) by Belov et al. (1970). Some field dependence of \( \Delta T \) in the noncollinear phase revealed for \( \text{R} = \text{Dy} \) and \( \text{Ho} \) was related by the authors with the rare earth ion anisotropy.
5.2. Perovskites

Rare earth orthoaluminates (REOA) RAIO₃ have an orthorhombically distorted perovskite structure (Geller and Bala 1956). REOA with R = Gd, Dy, Er display antiferromagnetic order below $T_N = 3.875$ K (Gd), 3.52 K (Dy) and 0.6 K (Er) and paramagnetism above $T_N$ (Schuchert et al. 1969; Blazey et al. 1971; Sivardiere and Quezel-Ambrunaz 1971; Kimura et al. 1995). DyAlO₃ and ErAlO₃ are characterized by a substantial magnetic anisotropy (for DyAlO₃ $\mu_{\text{eff}} = 6.88 \mu_B$ along the $b$-axis and 0.8 $\mu_B$ along the $c$-axis (Kolmakova et al. 1990)) and GdAlO₃ is almost magnetically isotropic. The magnetic entropy change $\Delta S_M$ induced by a field in GdAlO₃ and DyAlO₃ was calculated by Kuz'min and Tishin (1991, 1993a, 1993b) in the framework of MFA ($J$ was taken to be $7/2$ and $1/2$, for Gd and Dy perovskites, respectively) (see fig. 5.4).

Kimura et al. (1995, 1997) determined $\Delta S_M$ for RAIO₃ (R = Dy, Ho, Er) on the basis of magnetization measurements along various crystal axes and eq. (2.71). It was established that in ErAlO₃ and DyAlO₃ magnetization decreased with temperature increasing for all crystal axes. The same behavior was observed in HoAlO₃ along $a$- and $b$-axes, but along $c$-axis its magnetization remained almost constant. The easy magnetization axis in DyAlO₃ and ErAlO₃ are $b$- and $c$-axis, respectively (see Kuz'min and Tishin 1991).

The experimental $\Delta S_M$ results are shown in fig. 5.5(a). As one can see a substantial dependence of $\Delta S_M$ character on the direction of a measurement is observed. The experimental results for DyAlO₃ and ErAlO₃ along the easy axes are in good agreement with
Fig. 5.5. (a) Temperature dependences of the magnetic entropy change $\Delta S_M$ induced by a various changes of a magnetic field, applied along $a$- (solid circles ($\Delta H = 30$ kOe), solid triangles (40 kOe), solid squares (50 kOe)), $b$- (open circles (30 kOe), open triangles (40 kOe), open squares (50 kOe)) and $c$-axis (open diamonds (30 kOe), solid diamonds (40 kOe), inverted open triangles (50 kOe)) in DyAlO$_3$ (1); HoAlO$_3$ (2); ErAlO$_3$ (3) single crystals, respectively. The $\Delta S_M$ is calculated on the basis of the experimental magnetization data. (b) Comparison of $\Delta S_M$ temperature dependences in DyAlO$_3$ (solid triangles) measured along $b$-axis and in ErAlO$_3$ (solid circles) along $c$-axis with that in Gd$_3$Ga$_5$O$_{12}$ (open diamonds) and Dy$_3$Al$_5$O$_{12}$ (open triangles) measured along $[1 1 1]$ direction with a magnetic field change of 50 kOe (Kimura et al. 1997).

the calculations of Kuz'min and Tishin (1991). Kimura et al. (1995) made a comparison of $\Delta S_M$ induced by a field of 50 kOe for ErAlO$_3$ measured along $c$-axis, DyAlO$_3$ measured along $b$-axis and Dy$_3$Al$_5$O$_{12}$ and Gd$_3$Ga$_5$O$_{12}$ measured along $[1 1 1]$ direction – see fig. 5.5(b). It is evident that $\Delta S_M$ for ErAlO$_3$ and DyAlO$_3$ is superior to that of Dy$_3$Al$_5$O$_{12}$ and Gd$_3$Ga$_5$O$_{12}$. This is in agreement with the conclusion that DyAlO$_3$ and ErAlO$_3$ are
promising materials for magnetic refrigeration below 20 K, made by Kuz'min and Tishin (1991) on the basis of theoretical calculations.

Perovskite-type manganese oxides $R_{1-x}B_xMnO_3$ (R is a rare earth metal and B is a divalent alkali metal: Ca, Ba, Sr) are characterized by "colossal" magnetoresistance near the magnetic ordering temperature (Von Helmolt et al. 1993; Jin et al. 1994). In $La_{1-x}Ca_xMnO_3$ the colossal magnetoresistance takes place for $0.2 < x < 0.5$, where a transition from the paramagnetic insulating state to the ferromagnetic metallic state is observed. Samples with $0.5 < x < 1$ display the antiferromagnetic insulating state in the low temperature range. The magnetic phase diagram of $La_{1-x}Ca_xMnO_3$ system was constructed on the basis of the temperature dependences of the heat capacity by Ramirez et al. (1996). For $x > 0.5$, above $T_N$, an additional "charge ordering" transition occurs, which is accompanied by a maximum in the $C(T)$ curves.

Manganese perovskites are characterized by a considerable coupling between the magnetic and the lattice subsystems. This leads to an abrupt change of the magnetization, a discontinuous variation in the volume and softening of Young's modulus at the Curie temperature.

The sharp magnetization change should give a considerable magnetic entropy variation at the Curie point. The temperature dependences $\Delta S_M(T)$ in the ($La_{1-x}Ca_x$) manganese oxide polycrystals were investigated by Zhang et al. (1996) and Guo et al. (1997a, 1997b). $\Delta S_M$ was determined on the basis of magnetization measurements. The results for $T = T_C$ are presented in table 5.1.

Zhang et al. (1996) studied $\Delta S_M$ in $La_{0.67}Ca_{0.33}MnO_3$. Substitution of Y reduces the saturation magnetization and consequently, $\Delta S_M$ (see table 5.1). The reduction was attributed by the authors to a decrease of the ferromagnetic coupling due to the contraction of the crystal lattice under substitution.

Guo et al. (1997a) determined $\Delta S_M$ in $La_{1-x}Ca_xMnO_3$ ($x = 0.20; 0.33; 0.45$). The $\Delta S_M(T)$ curves for $x = 0.20$ and 0.33 show a relatively narrow peak at $T_C$ (see fig. 5.6). For $x = 0.45$ the maximum in the $\Delta S_M(T)$ curve is broader and smaller, which is consistent with a less sharp change of the magnetization at $T_C$ in this sample compared with $x = 0.2$ and 0.33. $|\Delta S_M|$ at $T_C$ for $x = 0.2$ is larger than that of gadolinium ($\approx 4.2 J/kg K$). It should be noted, that Zhang et al. (1996) obtained for $x = 0.33$ a $|\Delta S_M|$ value which is more than two times smaller than that measured by Guo et al. (1997a).

Polycrystalline $La_{0.75}Ca_{0.25}MnO_3$ samples with different average grain sizes were investigated by Guo et al. (1997b). $T_C$ was found to be 177 K and 224 K for grain sizes of 120 and 300 nm, respectively. The lowering of $T_C$ was accompanied by a broadening of the magnetic phase transition in the $M(T)$ curve. This leads to the broadening of the $\Delta S_M(T)$ peak and its decrease in the sample with 120 nm grain size. The values of $\Delta S_M$ at the Curie point are presented in table 5.1.

Recent MCE investigations of $La_{0.65}Ca_{0.35}Ti_1-xMn_xO_3$ and $La_{0.5+x+y}Li_{0.5-3y}Ti_{1-3x}Mn_{3+x}O_3$ conducted by Bohigas et al. (1998) suggest that the compounds are good candidates for working materials in enough wide temperature region.

The polycrystalline perovskite manganese oxide system $La_{1-x}Na_xMnO_3$ ($x = 0.075, 0.10, 0.165$, and 0.20) was studied by Zhong et al. (1998). The Curie temperature in this system varies from 193 K ($x = 0.075$) to 343 K ($x = 0.20$). $\Delta S_M(T)$ dependences were determined from magnetization measurements with the help of eq. (2.71) – $\Delta S_M$ maximum.
TABLE 5.1
Magnetic entropy change $\Delta S_M$ induced by the magnetic field change $\Delta H$ at the Curie point for manganese oxides.*

<table>
<thead>
<tr>
<th>Substance</th>
<th>$T_C$</th>
<th>$-\Delta S_M$, J/kg K</th>
<th>$\Delta H$, kOe</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$La_{0.67}Ca_{0.33}MnO_3$</td>
<td>260</td>
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</table>

* See also data listed in work by Bohigas et al. (1998)

References:
[1] Zhang et al. (1996)

was observed near $T_C$ and for $\Delta H = 10$ kOe was 1.32, 1.53, 2.11, and 1.96 J/kg K for $x = 0.075, 0.10, 0.165,$ and 0.20, respectively.

5.3. 3d oxide compounds

Nikolaev et al. (1966) observed a change of sign of the MCE in nickel ferrite-chromite NiFeCrO$_4$ at the magnetic compensation point ($T_{\text{comp}} = 333$ K). This effect can be explained on the basis of the antiferromagnetic and ferromagnetic paraprocess conception (see section 5.1). The MCE in manganese spinel ferrites-chromites MnFe$_{2-x}$Cr$_x$O$_4$ ($0 \leq x \leq 1.6$) was measured by Belov et al. (1974). The maximum MCE value in MnFe$_2$O$_4$ is $\Delta T \sim 0.48$ K for $H = 16$ kOe near $T_C \approx 570$ K. The MCE studies made it possible to find a compensation point for the composition with $x = 1.085$. It appears because of the temperature dependence of the local slant angles of the Fe$^{3+}$ and Cr$^{3+}$ magnetic moments in the octahedral B-sublattice. For large Cr concentrations the presence of the slant angles gives an additional contribution to the ferromagnetic paraprocess in the B-sublattice near $T_C$ and, consequently, to the total MCE.

The MCE in the spinel Li$_2$Fe$_5$Cr$_5$O$_{16}$ was measured by Belov et al. (1968). A sign change of the MCE was also observed at the compensation point (see fig. 5.7). In the low temperature region the MCE was not high and decreased with decreasing temperature (compare with low temperature MCE in Gd$_3$Fe$_5$O$_{12}$, figs 5.1 and 5.2). Such behavior was related with the low intensity of the paraprocess in the A- and B-sublattices due to the strong intersublattice exchange interactions.
Fig. 5.6. Temperature dependences of the magnetic entropy change $\Delta S_M$ induced by a magnetic field of 15 kOe in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$: (a) $x = 0.2$ and Gd; (b) $x = 0.33$ and 0.45 (Guo et al. 1997a).

Sucksmith et al. (1953) obtained the $I_s(T)$ curve of the mixed magnesium–zinc ferrite $\text{MgOZnO} \cdot 2\text{Fe}_2\text{O}_3$ from $\Delta T (I^2)$ measurements.

The MCE in hexagonal ferrites was investigated by Zhilyakov et al. (1993, 1994), Naiden and Zhilyakov (1997) and Belov et al. (1977). Zhilyakov et al. (1993) studied the MCE of polycrystalline $\text{BaFe}_{12-x}\text{Co}_x\text{Ti}_x\text{O}_{19}$ (CoTi–M structure $x = 0–3.0$) and $\text{BaCa}_{2-x}\text{Zn}_x\text{Fe}_{16}\text{O}_{27}$ (CoZn–W structure, $x = 0–2.0$) in the temperature range of 150–500 K (which is below $T_C$). In these ferrimagnets warming causes a set of spin-reorientation transitions from easy cone to easy plane (at the temperature $T_1$), from easy plane to easy cone ($T_2$) and from easy cone to easy axis ($T_3$). Measurements of the spontaneous MCE (at $H = 0$) revealed a peak $\Delta T$ value of about 0.1 K near 310 K where the spin reorientation transition from easy plane to easy cone takes place. In the presence
Fig. 5.7. Temperature dependence of the MCE in the spinel Li$_2$Fe$_5$Cr$_5$O$_{16}$ induced by a magnetic field of 16 kOe (Belov 1968).

Fig. 5.8. Temperature dependence of the MCE in CoZn-W with $x = 1.3$ in various magnetic fields: (1) $\Delta H = 2$ kOe; (2) 8 kOe; (3) 12 kOe (Zhilyakov et al. 1994).

of a magnetic field in CoTi–M ($x = 1.2$) and CoZn–W ($x = 1.0$) ferrites the maxima at the spin-reorientation transitions and sign changes of the MCE from negative to positive at $T \approx 300$ K and from positive to negative at $T \approx 420$ K were observed. The maximum absolute value of the negative MCE was about 0.2 K at $T \approx 150$ K in CoZn–W ferrite and the value for the positive MCE was about 0.1 K at $T \approx 340$ K in CoTi–M ($x = 1.2$) for $\Delta H$ of 7 kOe. The MCE temperature behavior was related by the authors with a competition between the anisotropy constants determining the magnetocrystalline anisotropy along the hexagonal axis.

Polycrystalline and basal plane textured samples of CoZn–W hexaferrites ($0 \leq x \leq 2.0$) were measured by Zhilyakov et al. (1994). For the samples with $x = 1.1$–1.5 the first-
order spin-reorientation transitions are observed in the presence of a magnetic field in the temperature interval from 77 to 250 K. Figure 5.8 shows the MCE at such a transition \((T_2 = 250 \text{ K})\) in various magnetic fields. The value of the MCE is comparable with that observed in rare earth single crystals (see section 7). The estimations made by the authors showed that the main contribution to the MCE at \(T = T_2\) is related with the field induced spin-reorientation transitions.

Naiden and Zhilyakov (1997) calculated the MCE in a CoZn-W \((x = 1.38)\) hexaferrite single crystal along a hexagonal axis and in the basal plane on the basis of the equation similar to eq. (4.7) and experimental data on the temperature dependences of the magnetization, magnetocrystalline anisotropy constants and heat capacity. Peaks of negative (approximately \(-0.65 \text{ K}\)) and positive \((\sim 1.5 \text{ K})\) MCE were observed in \(H = 8 \text{ kOe}\) applied along the \(c\)-axis and in the basal plane at a temperature of about 210 K and 230 K, respectively \((T_2\) for this compound is equal to 220 K).

A \(\text{BaCo}_{1.65}\text{Fe}^{2+}_{0.35}\text{Fe}^{3+}_{16}\text{O}_{27}\) single crystal was investigated by Belov et al. (1977). The anomalies corresponding to the second-order phase transition, at which the spins were turned from the basal plane and formed a cone with increasing temperature, were observed near 390–400 K in the temperature dependences of the MCE, measured in a field of 10 kOe aligned in the basal plane and the along \(c\)-axis. In the case of the basal plane measurements there was a maximum with a value of about 0.05 K, and in the case of the \(c\)-axis measurements there was a sign change of the MCE in the \(\Delta T(T)\) curves. Near the Curie temperature \((\sim 750 \text{ K})\) a value of \(\Delta T = 0.16 \text{ K}\) was observed for the both field directions. \(\Delta T\) oscillations with sign changes were found when changing of the magnetic field orientation. The character of the oscillations was dependent on the measurement temperature, which was related with different values of the cone angle.

Druzhinin et al. (1979) calculated the temperature dependences \(\Delta T(T)\) for various values of the angle formed by the field and the threefold crystal axis in corundum \((\text{Al}_2\text{O}_3)\) with 0.13% \(\text{V}^{3+}\). The calculations were made with allowance for uniaxial magnetic anisotropy and uniaxial \(g\)-tensor anisotropy on the basis of a spin Hamiltonian with the parameters known from the experiment. The sign and value of the MCE were shown to depend on the angle between the field and the threefold axis. Oscillations of \(\Delta T\) in the angle dependence were observed in the temperature interval from 0 to 8 K.

Litvinenko et al. (1973) studied the MCE in an antiferromagnetic \((T_N = 32 \text{ K})\) siderite \(\text{FeCO}_3\) single crystal in pulsed fields up to 300 kOe. The sample displays essential field hysteresis at the metamagnetic transition from the antiferromagnetic to ferromagnetic state. The value of the MCE at \(T = 4.2 \text{ K}\) in a field of 300 kOe was 24 K.

### 5.4. Other oxides

\(\text{RXO}_4\) (R = rare earth, \(X = \text{V}, \text{As}, \text{P}\)) compounds display at low temperatures a crystallographic phase transition caused by the cooperative Jahn–Teller effect, which gives additional contribution to the entropy change. A magnetic field can also influence this transition. DyVO\(_4\) exhibits the crystallographic transition at 14.3 K and an antiferromagnetic one at 3 K.

Figure 5.9 shows temperature dependences of the total entropy in DyVO\(_4\) in various fields determined from the heat capacity measurements. The shoulders near 3 K and 15 K in the zero magnetic field entropy curve are related with antiferromagnetic and structural phase transition, respectively.
6. Magnetocaloric effect in intermetallic compounds

6.1. Rare earth–nonmagnetic element

The heat capacity of RAl₂ (R = Gd, Dy, Er, Ho) and (Dy₁₋ₓErₓ)Al₂ (x = 0–1) alloys was measured by Gschneidner et al. (1994a, 1994b, 1996a, 1996b), Ranke et al. (1998a) and by Hashimoto (1991), Hashimoto et al. (1986). The RAl₂ compounds have the cubic Laves phase (Cu₂Mg-type) structure.

The saturation high temperature values of the magnetic entropy $S_M$ (see section 2.3) were calculated by Gschneidner et al. (1994a, 1994b, 1996a, 1996b) on the basis of the magnetic heat capacity ($C_M$) data by eq. (2.76). The prorated zero-field heat capacities of LaAl₂ and LuAl₂ were used to evaluate the lattice contributions needed for the $C_M$ calculations of (Dy₁₋ₓErₓ)Al₂ system. The magnetic entropy change $\Delta S_M$, induced by field changes was obtained from the heat capacity measured at various magnetic fields by the method described in section 3.3.

The experimental data on $S_M$, $\Delta S_M$ and $\Delta T$ are presented in table 6.1. The majority of the results on rare earth–nonmagnetic element alloys was already summarized earlier in the report of Gschneidner et al. (1996a, 1996b). The amount of magnetic entropy $S_M$ utilized in the magnetic ordering process (column 6 of table 6.1) was determined on the basis of the values of the theoretically available maximum entropy, calculated by means of eq. (2.70) using $J$ for the corresponding RE element (see table 6.2). The values of $\Delta S_M$ at $T = T_C$ are presented in column 8 of table 6.1 and their amounts relative to the theoretically available entropies are shown in column 9 of table 6.1. The values of $\Delta T$ are taken at the temperature $T_{\text{max}}$ corresponding to the maximum of the temperature dependence of the MCE. The Curie temperatures were determined by Gschneidner et al. (1994a, 1994b, 1996a, 1996b) from the magnetic ac susceptibility measurements.

The heat capacity measurements of (Dy₁₋ₓErₓ)Al₂ alloys made by Gschneidner et al. (1994a, 1994b, 1996a, 1996b) for $x$ from 0.6 to 1.0 revealed a sharp peak below 14 K. Its height decreased with decreasing $x$. For $x$ from 0 to 0.75 the heat capacity showed a broad $\lambda$-type anomaly at the Curie temperature. For $x = 0.6, 0.75$ and 0.9.

![Fig. 5.9. Temperature dependences of the total entropy DyVO₄ in various magnetic fields (Daudin et al. 1982).](image-url)
The Curie temperature ($T_C$), temperature of the maximum in the $\Delta T(T)$ curves ($T_{\text{max}}$), magnetic entropy $S_M$, magnetic entropy change $\Delta S_M$ induced by a magnetic field change $\Delta H$ at $T = T_C$, value of magnetocaloric effect $\Delta T$ induced by $\Delta H$ at $T = T_{\text{max}}$ of polycrystalline RE–nonmagnetic metal alloys. The values of $S_M$ and $\Delta S_M$ are in the units of J/mol K per RE atom ($J/(\text{mol R K})$). All measurements were made on polycrystals.

<table>
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<th>Compound</th>
<th>$T_C$, K</th>
<th>$T_{\text{max}}$, K</th>
<th>$\Delta T$, K</th>
<th>$\Delta H$, kOe</th>
<th>$S_M$, J/(mol R K)</th>
<th>% of theor. value</th>
<th>$-\Delta S_M$ at $T = T_C$</th>
<th>exper. value, J/(mol R K)</th>
<th>% of theor. value</th>
<th>$\Delta H$, kOe</th>
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<td>$\Delta H$, kOe</td>
<td>$S_M$, J/(mol R K)</td>
<td>% of theor. value</td>
<td>$-\Delta S_M$ at $T = T_C$</td>
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<td>% of theor. value</td>
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References:

(a) Gschneidner et al. (1996b)
(b) Gschneidner et al. (1996a)
(c) Hashimoto et al. (1986)
(d) Johanson et al. (1988)
(e) Korte et al. (1998a)
(f) Nikitin et al. (1989a)
(g) Tanoue et al. (1992)
(h) Azhar et al. (1985)
(i) Buschow et al. (1975)
(j) Sill and Esau (1984)
(k) Pecharsky et al. (1996)
(l) Tokai et al. (1992a)
(m) Sahashi et al. (1987).
TABLE 6.2
Total angular momentum and maximum value of the magnetic entropy $S_M$ in RE metals.

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<th>Element</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Pm</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
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Fig. 6.1. Temperature dependences of the MCE induced by a magnetic field change from 0 to 75 kOe for (Dy$_{1-x}$Er$_x$)Al$_2$ alloys (Gschneidner et al. 1996b).

both anomalies were observed. The low temperature peak was related by the authors with Schottky anomaly due to the splitting of the ground states of the RE ions with $L \neq 0$ by the crystalline electric field. Earlier Schottky anomaly at about 23 K was found by Inoue et al. (1977) in the heat capacity of ErAl$_2$.

The temperature dependences of the MCE in the (Dy$_{1-x}$Er$_x$)Al$_2$ system are shown in fig. 6.1. The curves have caret-like character with broad maxima, which can be due to the possible spin-reorientation transitions. The maximum of $\Delta T$ was found in ErAl$_2$ and the lowest value was observed for DyAl$_2$. The low-temperature anomalies in the $\Delta T(T)$ curves were related by the authors with crystalline field effects. The magnetization measurements showed that the hysteresis in the (Dy$_{0.5}$Er$_{0.5}$)Al$_2$ alloy was about 340 Oe at 2 K and became zero at 17 K (Gschneidner et al. 1994b).

Hashimoto et al. (1986, 1991) measured the heat capacity and the magnetization of the RAl$_2$ compounds with R = Er, Ho and Dy and of (Gd$_{0.1}$Dy$_{0.9}$)Al$_2$ and (Dy$_{0.5}$Ho$_{0.5}$)Al$_2$. The $\Delta S_M(T)$ curves, determined from the magnetization data are shown in fig. 6.2 and
\[ \Delta S_M \text{ at } T = T_C \] are presented in table 6.1. One can see, that the \( \Delta S_M(T) \) values for ErAl\(_2\) and DyAl\(_2\) obtained by Hashimoto et al. (1986, 1991) are higher than those of Gschneidner et al. (1996b).

Zimm et al. (1992) studied the heat capacity and measured directly the MCE in (Gd\(_{0.14}\)Er\(_{0.86}\))Al\(_2\) alloy (see table 6.1). The \( \Delta T(T) \) curves of this material for various magnetic fields have broad maxima at \( T_{\text{max}} \approx 25 \text{ K} \), although the magnetic susceptibility measurements give \( T_C \approx 40 \text{ K} \). The authors related the broad \( \Delta T \) maximum with random distribution of Er and Gd atoms on the rare earth sites, which leads to the variation of the local magnetic environments.

Johanson et al. (1988) measured the heat capacity of the Gd\(_{0.06}\)Er\(_{0.94}\)Al\(_2\) alloy. The Curie temperature defined from the heat capacity anomaly was 13 K, and the MCE obtained from the temperature dependences of the heat capacity measured at various magnetic fields, was 13 K for \( T = 30 \text{ K} \) for a field change of 80 kOe.

The MCE in Gd\(_3\)Al\(_2\), which orders ferromagnetically below \( T_C \) and antiferromagnetically below 51 K (Gschneidner et al. 1996a), was measured by a direct method by Nikitin et al. (1989), see table 6.1. The Curie temperature was defined by Nikitin et al. (1989) from magnetization data with the help of Arrott plots.

The ErAgGa compound has the CeCu\(_2\)-type structure and, as it was shown by Sill and Esau (1984) to order ferromagnetically at about 3 K. The heat capacity measurements reveal two overlapping maxima at about 3 K and about 5 K. Ac susceptibility measurements showed a considerable frequency dependence below 8 K, which was explained by Pecharsky et al. (1996) by the existence of a spin-glass state. The additional maximum in the temperature dependences \( C(T) \) measured in the zero field was related with the Schottky anomaly caused by the crystalline electric field splitting of low-lying energy levels of the Er ions.

![Figure 6.2](image-url)

**Fig. 6.2.** Temperature dependences of \( \Delta S_M \) induced by a magnetic field change of 50 kOe in RA\(_2\) alloys: (A) ErAl\(_2\); (B) HoAl\(_2\); (C) (Ho\(_{0.5}\)Dy\(_{0.5}\))Al\(_2\); (D) DyAl\(_2\); (E) (Dy\(_{0.9}\)Gd\(_{0.1}\))Al\(_2\) (Hashimoto 1991).
The GdPd compound has the orthorhombic CrB-type structure and orders ferromagnetically below $T_C = 38$ K. The $\Delta T(T)$ curves measured directly by Zimm et al. (1992) for various $\Delta H$ have sharp peaks near $T_C$. The $\Delta T$ values are presented in table 6.1.

Tanoue et al. (1992) investigated the heat capacity, magnetic susceptibility and magnetization of the Gd$_3$Pd$_4$ compound that has the rhombohedral Pu$_3$Pd$_4$-type structure. It was found that Gd$_3$Pd$_4$ orders antiferromagnetically at 18 K. At about 6 K it displays another transition of ferromagnetic nature. In the presence of a magnetic field up to 98.5 kOe an additional heat capacity peak at about 13 K developed, which was attributed to a spin-reorientation transition. The entropy associated with the anomaly is about 2% of the total magnetic entropy $S_M$. The magnetic entropy $S_M$, calculated from heat capacity measurements by eq. (2.76) (for the temperature range from 0 to 40 K), was equal to 16.41 J/(mol Gd K), which is in good agreement with theoretical data on Gd (see table 6.2). The temperature dependences of the magnetic entropy change $-\Delta S_M(T)$ have maxima at about 20 K with the values of $\approx 0.17$ J/(mol Gd K) for $\Delta H = 53.2$ kOe and $\approx 1.7$ J/(mol Gd K) for $\Delta H = 98.5$ kOe ($-\Delta S_M$ values at $T = T_C$ are given in table 6.1).

The intermetallic compound GdRh has the cubic CsCl structure and orders ferromagnetically below the Curie temperature. Its heat capacity was studied by Azhar et al. (1985) and Buschow et al. (1975). Curie temperature values of 19.93 K and 20 K were defined from the temperature dependences of the heat capacity by Azhar et al. (1985) and Buschow et al. (1975), respectively. From magnetization measurements gave $T_C = 24$ K was found (Buschow et al. 1975). The magnetic entropy $S_M$, determined by eq. (2.76) (for $T \to \infty$) from the heat capacity data, was obtained to be 17.4 J/mol K, very close to the theoretical value for Gd (see table 6.2).

The heat capacity of the carbide alloys Er$_3$AlC$_x$ ($x = 0.1; 0.25; 0.5$, and 1) was investigated by Pecharsky et al. (1996) and Gschneidner et al. (1996a, 1996b). Er$_3$AlC has an anti-perovskite-type crystal structure and, according to the measurements of Tokai et al. (1992a), orders magnetically at 2.8 K, showing $\lambda$-type heat capacity anomaly. An analogous anomaly was observed by Pecharsky et al. (1996) at 3.1 K. Ac susceptibility measurements of Pecharsky et al. (1996) revealed in the Er$_3$AlC alloy a small negative paramagnetic Curie temperature ($-1.6$ K), which was taken as evidence of antiferromagnetic ordering. As proposed by the latter authors, this antiferromagnetic state transforms to a ferromagnetic one by a magnetic field of about 24.6 kOe.

For the other carbide phases two heat capacity maxima were revealed: one at low temperature and another one at approximately 8 K. X-ray diffraction studies made by Pecharsky et al. (1996) on Er$_3$AlC$_x$ ($x = 0.1; 0.25; 0.5$) showed that these compounds contain two phases: Er$_3$AlC and Er$_2$Al. The low-temperature heat capacity maximum in Er$_3$AlC$_x$ was attributed by the authors to the antiferromagnetic ordering of Er$_2$Al ($\approx 6$ K).

The MCE of ErAlC$_x$ ($x = 0.1; 0.25; 0.5$), determined on the basis of heat capacity data, displays a wide maximum due to the presence of two phases with slightly different magnetic ordering temperatures. From table 6.1 one can see a gradual decrease of the MCE in Er$_3$AlC$_x$ with increasing $x$. This was related by the authors with a reduction of Er$_3$AlC phase content and an increase of the amount of the antiferromagnetic Er$_2$Al phase.

Sahashi et al. (1987) studied the heat capacity of Al-rich RA$_2$ (R = Dy, Ho, Er and Ho$_{0.5}$Dy$_{0.5}$) high density sintered compounds. To prepare the samples the powder metallurgical route was used. From the ingots of arc-melted RA$_2$ (R = Dy, Ho, Er and
H0.5Er0.5) 3 µm sized powder was ball milled in ethanol. The milled powder was pressed under \( 10^3 \) kg/cm\(^2 \) and then sintered in an argon atmosphere for 1.5 hours at 1105°C. X-ray analyzes showed, that the Laves phase RA12 in the samples is surrounded by the RA13 phase with cubic Cu3Au structure. The Curie temperatures of the ErAl2.20, HoAl2.24, (Ho0.5Dy0.5)Al2.25 and DyAl2.22 alloys prepared in this way were obtained from \( C(T) \) curves and are somewhat lower than in the corresponding stoichiometric compounds, see table 6.1. The \( \Delta S_M(T) \) curves exhibit maxima near the Curie temperatures with values given in table 6.1. The \( \Delta S_M \) maxima in the sintered compounds were broader than in the corresponding RA12 compounds, which have relatively sharp peaks.

6.2. Rare earth–nickel

In this section magnetothermal properties of R3Ni, RNi2, RNi, RNi5 and RNiAl (R = rare earth element) compounds will be considered. According to magnetic investigations (Kirchmayr and Poldy 1978; Taylor and Darby 1972) Ni in these compounds has no magnetic moment.

The heat capacity of GdNi, HoNi and ErNi was measured by Sato et al. (1990). GdNi is a simple ferromagnet, while in HoNi and ErNi a noncollinear magnetic structure due to the crystalline field effects is observed. Heat capacity anomalies were revealed at the Curie temperature \( T_C \): 70 K for GdNi and 10 K for ErNi. The heat capacity of HoNi displayed an anomaly at the temperature of the spin-reorientation transition equal to 13 K \( (T_C = 37 K) \) according to the susceptibility measurements of Sato et al. (1982). The magnetic ordering entropy, determined by Sato et al. (1990) from the heat capacity data and eq. (2.76) in the temperature interval from 0 to 15 K, is equal to 15 J/mol K. This is inconsistent with the value calculated by eq. (2.70) for the Er\(^{3+} \) ionic state (see table 6.2). The authors attributed this difference to the crystalline field splitting of the Er ion ground state. The magnetic entropy due to the crystalline field effect estimated by Sato et al. (1990) on the basis of point charge model, was calculated to be 11 J/mol K at 15 K. Zimm et al. (1992) measured the temperature dependences of the MCE in GdNi directly. A relatively sharp peak was observed near \( T_C \) (the values of \( \Delta T \) in various magnetic fields are given in table 6.3).

The heat capacity of the compounds RNi2 (R = Tb, Dy, Ho, Er), (Dy0.26Er0.74)Ni2, (Gd0.1Dy0.9)Ni and (Er1-xDyx)Ni2 was studied by Gschneidner et al. (1996a), Tomokiyo et al. (1986), Hashimoto et al. (1992), Ranke et al. (1998a) and Yayama et al. (1987). The heat capacity measurements allowed Gschneidner et al. (1996a) to determine the temperature dependences of \( S_M \) and \( \Delta S_M \). As one can see from tables 6.2 and 6.3, in the Ni-based compounds approximately 60% of the theoretically available magnetic entropy is utilized in the magnetic ordering process, while in the Al-based compounds (RA12) this value is about 90%. The authors attributed this to crystalline field effects above \( T_C \). The results of Tomokiyo et al. (1986) are shown in fig. 6.3. The \( \Delta S_M \) for DyNi2 and ErNi2 was evaluated from the heat capacity data, and that of HoNi2 was obtained from the magnetization data by eq. (2.71). As follows from table 6.3 the results of Tomokiyo et al. (1986) for \( \Delta S_M(T_C) \) at \( \Delta H = 50 \) kOe are about two times higher than those of Gschneidner et al. (1996a) at \( \Delta H = 75 \) kOe.

Foldeaki et al. (1997) obtained \( \Delta S_M(T) \) curves from magnetization measurements for GdNi2 and DyNi2. The maximum \(- \Delta S_M \) values at \( T = T_C \) were obtained to be \( \approx 28 \) J/kg K for DyNi2 and \( \approx 14 \) J/kg K for GdNi2 at \( \Delta H = 70 \) kOe. As one can see,
The Curie temperature ($T_C$), temperature at which the maximum in the $\Delta H(T)$ curves ($T_{\text{max}}$), magnetic entropy $S_M$, magnetic entropy change $\Delta S_M$ induced by a magnetic field change $\Delta H$ at $T = T_C$, value of magnetocaloric effect $\Delta T$ induced by $\Delta H$ at $T = T_{\text{max}}$ of polycrystalline rare earth intermetallic alloys and compounds with Ni. The values of $S_M$ and $\Delta S_M$ are in the units of J/mol K per RE atom (J/(mol K)). All measurements were made on polycrystals.

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*Notes:* 
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\(\text{c}) - \text{from Ref. 23.} 
\(\text{d}) - \text{from Ref. 24.} 
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References:
(a) Zimm et al. (1992)
(b) Sato et al. (1990)
(c) Gschneidner et al. (1996a)
(d) Gschneidner et al. (1994b)
(e) Tomokiyo et al. (1986)
(f) Gschneidner et al. (1995), Korte et al. (1998a)
$\Delta S_M$ in DyNi$_2$ is two times larger than in GdNi$_2$. The low-field (100 Oe) temperature dependence of the magnetic susceptibility of the DyNi$_2$ displays irreversible character. There is a substantial hysteresis for the field-cooled and zero-field cooled curves. The Arrott plots of DyNi$_2$ compound, constructed in the temperature range from 5 to 50 K, did not display linear sections at any temperatures. The authors related this behavior to the complex nature of a magnetic transition at $T = T_C$ and a noncollinear magnetic structure below $T_C$ due to the presence of crystalline field effects. The irreversible behavior described above was not observed for GdNi$_2$.

The temperature dependences of the MCE for GdNi$_2$ were obtained with the help of a direct method by Zimm et al. (1992) and for TbNi$_2$ from magnetization data by Gschneidner et al. (1995). MCE peaks were observed near $T_C$ and the maximum $\Delta T$ values are presented in table 6.3.

Tishin (1990g) on the basis of MFA calculated the field dependences of magnetic entropy change $-\Delta S_M(H)$ (the magnetic field varied from 0 to $H$) at $T = T_C$ for GdNi, GdNi$_2$ and GdNi$_5$ (as in GdNi and GdNi$_2$, nickel in GdNi$_5$ is nonmagnetic). The nonlinear character of $-\Delta S_M(H)$ curves was observed for $H$ below 50 kOe (the maximum magnetic field value was 100 kOe). At $H = 100$ kOe the value of $-\Delta S_M(H)$ was found to be about 2.7 J/mol K for GdNi, 1.7 J/mol K for GdNi$_2$ and 1.3 J/mol K for GdNi$_5$.

Based on theoretical investigations using Hamiltonian which includes both the crystalline electric field as well as exchange interaction, Ranke et al. (1998b) predicted an anomalous increase of $S_M$ in paramagnetic PrNi$_5$. Their heat capacity measurements confirmed this result.

The heat capacity of Er$_3$Ni, ErNi, Er$_{1-x}$Dy$_x$Ni$_2$, Er(Ni$_{1-x}$Co$_x$)$_2$ and Er$_{0.9}$Yb$_{0.1}$Ni was investigated by Yayama et al. (1987), Li et al. (1988), Sahashi et al. (1990), Sato et al. (1990), Hashimoto et al. (1992), and Tokai et al. (1992a, 1992b). It was found that these compounds have substantial heat capacity values in the low temperature region. Er$_3$Ni has a broad heat capacity maximum near the ordering temperature at about 8 K, and above 15 K its heat capacity is comparable with that of Pb. The dilution of ErNi by Yb
led to a decrease of the magnetic transition temperature to about 4 K with preservation of
the sharpness of the heat capacity peak. Gschneidner et al. (1995) measured the heat ca-
pacity of R3Ni (R = Pr, Nd and Er) and Er6Ni2X (X = Sn, Pb and Sn0.75Ga0.25) alloys in
a temperature interval from 1.5 to 40 K. The R3Ni compounds order antiferromagnetically
below the ordering temperatures determined from \( C(T) \) curves and listed in table 6.3. The
total heat capacity peak at the ordering temperature is of the \( \lambda \)-type. It is narrow in Nd3Ni
(with the maximum value of \( \approx 0.7 \, \text{J/K cm}^3 \)) and broader in Pr3Ni (\( \approx 1.9 \, \text{J/K cm}^3 \)) and
Er3Ni (\( \approx 0.42 \, \text{J/K cm}^3 \)). The broad heat capacity maximum in the Er3Ni compound was
explained by a substantial contribution to the total heat capacity from the Schottky anomaly
above \( T_N \). The magnetic entropy determined by Gschneidner et al. (1995) from the heat ca-
pacity data are listed in table 6.3 (in J/mol K). They are in good agreement with the \( S_M \)
value expected a ground state doublet of the Er ions (\( J = 1/2 \)): \( 3R \ln 2 = 17.3 \, \text{J/mol K} \).
This confirms the presence of strong crystalline electric field effects in the R3Ni (R = Pr,
Nd, Er) compounds. The Er6Ni2X alloys (X = Sn, Pb, and Sn0.75Ga0.25) ordered ferromag-
netically below about 18 K and had heat capacities essentially higher than that of Pb in this
temperature range.

Korte et al. (1998a, 1998b) undertook a study of the magnetic properties, heat capacity
and MCE in (Gd1-xErx)NiAl pseudo-ternary alloys (\( x = 0; 0.30; 0.46; 0.50; 0.55;
0.60; 0.80; 1.00 \)). All these alloys have the ZrNiAl-type crystalline structure. By means
of specific heat and magnetic susceptibility measurements it was shown that ErNiAl or-
ders antiferromagnetically below 6 K. The temperature dependences of the heat capacity
of other alloys displayed a series of peaks (for example (Gd0.54Er0.46)NiAl at \( T = 23, 28 \)
and 58 K). The authors attributed the low-temperature heat capacity anomalies to antifer-
romagnetic transitions and the upper anomalies to ferromagnetic ordering. Magnetic sus-
cceptibility measurements confirmed these suppositions. The lowest \( (T_1) \) and highest \( (T_2) \)
ordering temperatures obtained from the heat capacity measurements (for (Gd0.2Er0.8)NiAl
from ac susceptibility data) are presented in table 6.3. The \( \Delta S_M(T) \) curves (measured for
\( \Delta H = 50 \, \text{kOe} \)) of ErNiAl and (Gd0.2Er0.8)NiAl have peaks near the antiferromagnetic
ordering temperatures. In Gd-rich alloys a broad maximum due to the remaining con-tri-
bution from the low-temperature antiferromagnetic ordering process was observed. The
\( \Delta T(T) \) curves show an analogous behavior, see fig. 6.4. (Gd0.54Er0.46)NiAl has a wide
temperature range with almost flat \( \Delta S_M(T) \) behavior. This was related by the authors with
the existence of multiple ordering processes with entropy changes comparable in magni-
tude for both the AFM and the FM transitions. Similar \( \Delta T(T) \) and \( \Delta S_M(T) \) curves were
observed for \( x = 0.3 \) and 0. Comparison of the maximum values of \( \Delta S_M \) and \( \Delta T \) for the
(Gd0.54Er0.46)NiAl, (Dy0.25Er0.75)Al2 and (Dy0.40Er0.60)Al2 alloys showed that although
the value of \( \Delta S_M \) in these three materials is comparable, the \( \Delta T(T_{\text{max}}) \) value is larger in
the \((\text{R}_{1-x}\text{R}_{x})\text{Al}_{2}\) compounds. This is connected with the large lattice heat capacity of the
RNiAl compounds.

Table 6.3 contains also \( S_M, \Delta S_M \) and MCE data obtained by Gschneidner et al. (1994a,
1994b, 1996a) from the heat capacity measurements.

### 6.3. Rare earth–iron

The MCE in the intermetallic compounds RFe2 (R = Tb, Er, Y) and RFe3 (R = Ho, Y) and
Tb2Y1-xFe2 (\( x = 0; 0.2; 0.33; 0.45; 0.8; 1.0 \)) alloys was measured directly by Nikitin
et al. (1973, 1975) in the temperature interval from 80 to 700 K. Since YFe$_2$ and YFe$_3$ have only one magnetic sublattice, they display $\Delta T(T)$ curves characteristic of a simple ferromagnet with one maximum near the Curie temperature $T_C$. ErFe$_2$ and HoFe$_3$ are ferrimagnets with two magnetic sublattices and compensation temperatures $T_{comp}$ at 490 K and 389 K, respectively. Their $\Delta T(T)$ curves show a behavior analogous to that in gadolinium iron garnet: when increasing the temperature the MCE suddenly changes its sign from positive to negative near $T_{comp}$ (see section 5.1 and fig. 5.1). The estimations made from MCE and Curie point data on the basis of MFA (Nikitin and Bisliev 1974) showed that the effective field $H_{2eff}$ acting in the RE magnetic sublattice is about $1.6 \times 10^6$ Oe in ErFe$_2$ and about $10^6$ Oe in HoFe$_3$ (Nikitin et al. 1973). This is considerably higher than $H_{2eff}$ in rare earth iron garnets ($\sim 3 \times 10^5$ Oe) and leads to a weak paraprocess in the RE magnetic sublattice and to an MCE temperature behavior analogous to that observed in the Li$_2$Fe$_5$Cr$_5$O$_{16}$ spinel below $T_{comp}$ (see fig. 5.7). In Tb$_x$Y$_{1-x}$Fe$_2$ alloys the compensation behavior of the MCE was observed for $x = 0.33$ and 0.45. For the other compounds only one maximum at $T = T_C$ was observed in the $\Delta T(T)$ curves. The values of MCE at $T = T_C$ for the RFe$_2$ and RFe$_3$ compounds and Tb$_x$Y$_{1-x}$Fe$_2$ alloys investigated by Nikitin et al. (1973, 1975) are presented in table 6.4. Minimum $\Delta T(T_C)$ value among Tb$_x$Y$_{1-x}$Fe$_2$ alloys is observed for $x = 0.5$ (see table 6.4). For this composition $T_{comp}$ coincides with $T_C$.

Jin et al. (1991) measured the MCE in as-cast R$_x$Ce$_{2-x}$Fe$_{17}$ ($R = Y$ or Pr and $x = 0$–2) alloys by a direct method at room temperature. Some of their results are listed in table 6.4 along with the Curie temperatures obtained by interpolation between the values for corresponding R$_2$Fe$_{17}$ compounds. Annealing of the samples at 800–1000°C for several hours

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**Fig. 6.4.** Temperature dependences of the MCE induced by $\Delta H = 50$ kOe for the (Gd$_{1-x}$Er$_x$)NiAl alloys (Korte et al. 1998a).
TABLE 6.4

The Curie temperature $T_C$, and magnetocaloric effect $\Delta T$ induced by $\Delta H$ at $T = T_C$ of some polycrystalline rare earth–iron intermetallic alloys and compounds. All measurements were made on polycrystals.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_C$, K</th>
<th>$\Delta T$, K</th>
<th>$\Delta H$, kOe</th>
<th>$\Delta T$, K</th>
<th>$\Delta H$, kOe</th>
</tr>
</thead>
<tbody>
<tr>
<td>YFe$_3$</td>
<td>535$^a$</td>
<td>1.4$^b$</td>
<td>15.8$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HoFe$_3$</td>
<td>567$^c$</td>
<td>$\approx 0.55^b$</td>
<td>15.8$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>YFe$_2$</td>
<td>535$^d$</td>
<td>$\approx 1.25^d$</td>
<td>15.8$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tb$<em>{0.2}$Y$</em>{0.8}$Fe$_2$</td>
<td>$\approx 570^d$</td>
<td>$\approx 0.7^d$</td>
<td>15.8$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tb$<em>{0.33}$Y$</em>{0.67}$Fe$_2$</td>
<td>$\approx 596^d$</td>
<td>$\approx 0.4^d$</td>
<td>15.8$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tb$<em>{0.45}$Y$</em>{0.55}$Fe$_2$</td>
<td>$\approx 610^d$</td>
<td>$\approx 0.25^d$</td>
<td>15.8$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tb$<em>{0.33}$Y$</em>{0.67}$Fe$_2$</td>
<td>$\approx 670^d$</td>
<td>$\approx 0.5^d$</td>
<td>15.8$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TbFe$_2$</td>
<td>695$^d$</td>
<td>$\approx 0.75^d$</td>
<td>15.8$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ErFe$_2$</td>
<td>575$^b$</td>
<td>0.2$^b$</td>
<td>15.8$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y$<em>2$Fe$</em>{17}$</td>
<td>320$^e$</td>
<td></td>
<td></td>
<td>$\approx 1.4^f$</td>
<td>8$^f$</td>
</tr>
<tr>
<td>Y$<em>{1.5}$Ce$</em>{0.5}$Fe$_{17}$</td>
<td>308</td>
<td>$\approx 5^f$</td>
<td>8$^f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y$<em>{1.2}$Ce$</em>{0.8}$Fe$_{17}$</td>
<td>300</td>
<td>$\approx 6.9^f$</td>
<td>8$^f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y$<em>{0.8}$Ce$</em>{1.2}$Fe$_{17}$</td>
<td>290</td>
<td>$\approx 5^f$</td>
<td>8$^f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce$<em>2$Fe$</em>{17}$</td>
<td>$\approx 270^a$</td>
<td>$\approx 1.4^f$</td>
<td>8$^f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr$<em>{0.5}$Ce$</em>{1.5}$Fe$_{17}$</td>
<td></td>
<td>$\approx 3.5^*f$</td>
<td>8$^f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PrCe$_{17}$</td>
<td>274</td>
<td>$\approx 4.5^*f$</td>
<td>8$^f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr$<em>{1.2}$Ce$</em>{0.8}$Fe$_{17}$</td>
<td></td>
<td>$\approx 8^*f$</td>
<td>8$^f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr$<em>{1.3}$Ce$</em>{0.7}$Fe$_{17}$</td>
<td></td>
<td>$\approx 7^*f$</td>
<td>8$^f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr$<em>2$Fe$</em>{17}$</td>
<td>$\approx 278^a$</td>
<td>$\approx 13^*f$</td>
<td>8$^f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\approx 10^*f$</td>
<td>8$^f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\approx 21.5^*f$</td>
<td>8$^f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\approx 5^*f$</td>
<td>8$^f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\approx 8^*f$</td>
<td>8$^f$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Before annealing
** After annealing

References:
(a) Kirchmayr and Poldy (1978)
(b) Nikitin et al. (1973)
(c) Taylor and Darby (1972)
(d) Nikitin et al. (1975)
(e) Nikitin et al. (1991a)
(f) Jin et al. (1991)

Wada et al. (1993) investigated the heat capacity and magnetic entropy of Ce(Fe$_{1-x}$Co$_x$)$_2$ ($x = 0-0.3$) alloys. The Laves phase compound CeFe$_2$ is an example of a system which is intermediate between localized magnetism and itinerant ferromagnetism. The magnetic measurements showed that CeFe$_2$ is a ferromagnet with $T_C = 230$ K and the magnetic moment per iron atom is about 1.15 $\mu_B$, which is lower than for other RFe$_2$ compounds (Deportes et al. 1981). The paramagnetic iron moment in CeFe$_2$ was found to be 0.5 $\mu_B$. The authors explained this by the Pr–Fe phase diagram: the Pr$_2$Fe$_{17}$ phase is an incongruently melting compound and cannot be formed directly from the melt.
at 300 K (Lindlay et al. 1988). Such a small magnetic moment in CeFe$_2$ was attributed to substantial hybridization of the iron 3d band states with the 4f band states of Ce (Eriks-son et al. 1988). The substitution of small amount of Co ($0.04 < x < 0.3$) in CeFe$_2$ led to an antiferromagnetic phase at low temperatures, which upon heating turned into a ferromagnetic phase at the temperature $T_{\text{AFM--FM}}$. Electrical resistivity and lattice parameter measurements showed that the transition at $T_{\text{AFM--FM}}$ was of the first order. Magnetization measurements made on the alloys with $x = 0.1$ and $0.2$ at $T = 4.2$ K in fields up to 250 kOe revealed a metamagnetic transition (at ~80 kOe) with a considerable field hysteresis. The compounds with $x = 0$ and $x \geq 0.3$ showed usual ferromagnetic behavior.

Heat capacity measurements made on CeFe$_2$, Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$, Ce(Fe$_{0.8}$Co$_{0.2}$)$_2$ and Ce(Fe$_{0.7}$Co$_{0.3}$)$_2$ revealed anomalies at the Curie temperatures of 227 K, 180 K, 162 K, and 156 K, respectively. In the Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ alloy an additional sharp peak was observed in the $C(T)$ curve at $T_{\text{AFM--FM}} = 80$ K. A less pronounced heat capacity anomaly at $T_{\text{AFM--FM}} = 68$ K was also observed in the Ce(Fe$_{0.8}$Co$_{0.2}$)$_2$ alloy. Using eq. (2.76) and heat capacity data, Wada et al. (1993) calculated the temperature dependences of the magnetic entropy $S_M$ of the Ce(Fe$_{1-x}$Co$_x$)$_2$ system for $x = 0; 0.1; 0.2; 0.3$. The data on paramagnetic CeCo$_2$ were used to evaluate the lattice and electronic contributions to the heat capacity. For CeFe$_2$, $S_M$ started to increase at temperatures above 100 K and above $T_C$ it reached a saturation value of 2.5 J/mol K. Analogous results were observed for $x = 0.3$ (the saturation $S_M$ value was about 1 J/mol K). Equation (2.70), which is valid for magnetic systems with localized moments, gave the value $S_M = 11.5$ J/mol K for the two iron atoms ($J = 1/2$). This value is inconsistent with the value 2.5 J/mol K obtained for $S_M$ in the CeFe$_2$ compound, which points to the intermediate character of magnetism in CeFe$_2$.

More complicated behavior was displayed by the $S_M(T)$ curves for $x = 0.1$ and 0.2. At $T = T_{\text{AFM--FM}}$ a sharp entropy change $\Delta S_{\text{AFM--FM}}$ ($\Delta S_{\text{AFM--FM}} = 1.2$ and 0.8 J/mol K for $x = 0.1$ and 0.2, respectively) was observed with subsequent gradual rise to the saturation value of 2.3 J/mol K for $x = 0.1$ and to 1.5 J/mol K for $x = 0.2$ above $T_C$. The authors regarded the entropy change $\Delta S_{\text{AFM--FM}}$ at $T_{\text{AFM--FM}}$ as the magnetic entropy change. $\Delta S_{\text{AFM--FM}}$ was considered to consist of the following three contributions: the entropy change due to a difference in the degree of magnetic order in antiferromagnetic and ferromagnetic states, the lattice entropy change and the electronic entropy change. It was shown that the first two contributions in the considered alloys were close to zero. The main contribution to $\Delta S_{\text{AFM--FM}}$ is due to the electronic entropy change which arises from the difference between the values of the electronic heat capacity coefficient $a_e$ for ferromagnetic and antiferromagnetic states (50 and 36.6 mJ/K$^2$ mol, respectively for $x = 0.1$) (see eq. (2.62)).

6.4. Rare earth–cobalt

The magnetic properties of the cubic Laves phase intermetallic compounds RCo$_2$ (R = rare earth) are well described by the s–d model in which the coexistence of localized spins and itinerant 3d electrons is assumed (Bloch and Lemaire 1970). According to this model the rare earth ions have localized magnetic moments and the 3d magnetic moment of Co is induced by the molecular field produced by the rare earth magnetic sublattice. DyCo$_2$, HoCo$_2$ and ErCo$_2$ exhibit the first-order transitions from paramagnetism to ferrimagnetism at the Curie points of 135, 77, and 33 K, respectively (Bloch et al. 1971; Voiron and...
Bloch et al. (1971; Kamarad et al. 1995). Bloch et al. (1975) explained the first- and second-order transitions in the RCo$_2$ compounds with the help of an s–d model and an expansion of the magnetic free energy as a power series of the d-electron magnetization. Dilution of the rare earth element in HoCo$_2$ compounds by Y led to a change from the first-order transition to the second-order type (Pillmayr et al. 1987).

Foldeaki et al. (1997) measured the magnetization of RCo$_2$ (R = Dy, Ho, Er) compounds and on the basis of these data calculated the magnetic entropy change $\Delta S_M$ induced by a field change of 70 kOe. Maxima were observed near the Curie point and the maximum values of $-\Delta S_M$ were about 14.5 J/kg K (at $T \approx 140$ K) for DyCo$_2$, about 22 J/kg K (at $T \approx 85$ K) for HoCo$_2$ and about 28 J/kg K (at $T \approx 42$ K) for ErCo$_2$. It should be noted that two ErCo$_2$ samples were studied: “good” and “wrong”. The first, according to X-ray diffraction analysis, was a homogeneous one. The second had some distortions in crystalline structure and contained an oxide. The wrong ErCo$_2$ sample displayed $\Delta S_M$ values 30% smaller than the good one. The Arrott plots of the wrong ErCo$_2$ showed behavior, analogous to that observed in Dy–Zr nanocomposites. According to the authors opinion this indicates a multiphase nanosized crystalline structure in the wrong ErCo$_2$.

The heat capacity of ErCo$_2$ as a function of temperature was measured by Imay et al. (1995). A sharp anomaly associated with the first-order magnetic phase transition was found at 32 K. The magnetic contribution to the heat capacity, obtained by subtraction of the LuCo$_2$ heat capacity from the ErCo$_2$ experimental data, still persisted above $T_C$. This was explained by an interaction of the RE magnetic ions with a crystalline electric field. The temperature dependence of the magnetic entropy $S_M(T)$ calculated on the basis of the heat capacity data, displayed a discontinuous increase (from 5 to 17 J/mol K) at the Curie point, and at high temperatures (above 150 K) it reached its saturation value which is close to the value of 23.1 J/mol K calculated by eq. (2.70) for Er ions ($J = 15/2$, see table 6.2). The latter fact indicates that the Co magnetic moments have small contribution to the total $S_M$. The magnetic entropy discontinuity at $T_C$ was explained by the authors by the change of the Er ion ground state degeneracy from a singlet in the magnetically ordered state to a quartet in the paramagnetic state.

Nikitin and Tishin (1991) measured directly the MCE in the HoCo$_2$ compound. The results are shown in fig. 6.5. The value of the MCE temperature profile is consistent with the sharp character of the first-order magnetic phase transition. The estimation of $\Delta S_M$ made by Nikitin and Tishin (1991) on the basis of heat capacity data of Voiron et al. (1974) gave the value of $-6.4$ J/mol K at $T = 82$ K and $\Delta H = 60$ kOe.

Pillmayr et al. (1987) and Hilscher et al. (1988) investigated the heat capacity of the (R$_x$Y$_{1-x}$)Co$_2$ (R = Ho, Dy) alloy systems. The magnetic ordering entropy $S_M$ determined from these measurements dropped for $x < 0.2$ and for $x \geq 0.2$ it attained the theoretical values calculated on the basis of eq. (2.70) for Ho and Dy (see table 6.2). The magnetic entropy associated with the magnetic moment of Co (for $s = 1/2$ it is equal to 5.76 J/mol K) was not observed above $T_C$ in both alloy systems. This was attributed to the itinerant character of the Co magnetic moment (Pillmayr et al. 1987). According to the authors opinion the magnetic entropy decrease observed for $x < 0.2$ may point to an instability of the RE magnetic moment in this concentration range (Pillmayr et al. 1987; Hilscher et al. 1988).

Saito et al. (1995) measured the heat capacity of the Er$_3$Co compound, which below $T_C = 13$ K exhibited a noncollinear magnetic structure. Above $T_C$ a large magnetic con-
tribution to the heat capacity was found. It was related with crystalline electric field effects (Schottky-type anomaly) and was interpreted in the framework of the point-charge model.

7. Magnetocaloric effect in rare earth metals and alloys

7.1. Rare earth metals

The heavy rare earth metals (REM) Gd–Lu (except Yb) and Y have hexagonal close-packed (hcp) crystalline structures. In the magnetically ordered state they display complex magnetic structures (except Gd) (Taylor and Darby 1972). In Tb, Dy and Ho a helicoidal antiferromagnetic (HAFM) structure occurs in a certain temperature interval from $T_C$ to $T_N$. In the HAFM state, the magnetic moments within one and the same basal plane order ferromagnetically and are turned by some angle with respect to those in the neighboring basal plane. The axis of such antiferromagnetic spiral coincides with the six-fold crystallographic $c$-axis. The HAFM structure can be transformed by a field induced transition into the ferromagnetic state if the magnetic field exceeds some critical value $H_{Cr}$. In the
magnetic phase diagram $H_{cr}(T)$ one can identify the temperature $T_K$, which corresponds to the maximum value of $H_{cr}$ ($\frac{\partial H_{cr}}{\partial T} = 0$ here). Below $T_K$ the transition at $H = H_{cr}$ is of the first-order and above $T_K$ it has the second-order character. The first-order transition is accompanied by "jumps" and some field hysteresis in the $I(H)$ curves at $H = H_{cr}$. Below $T_C$ a ferromagnetic basal-plane phase was observed in Tb and Dy and in Ho a HAFM structure with a ferromagnetic component along the $c$-axis was found.

A more complicated magnetic structure was found in erbium. In the temperature range between $T_N = 85$ K and $T_{CY} = 53$ K a longitudinal spin wave along the $c$-axis occurs. Below $T_{CY}$ the structure changed to a cycloid in which the spin wave was superimposed on a basal plane spiral structure. Below $T_C = 18$ K the $c$-axis component ordered ferromagnetically and the basal planes retained the spiral ordering forming a ferromagnetic cone (conical phase) (Cable et al. 1965; Atoji 1974; Habenschuss et al. 1974).

Thulium, below $T_N = 56$ K, displays an antiferromagnetic longitudinal spin wave phase. Below 32 K it turns into a ferromagnetic type structure composed of four basal plane layers with magnetic moments aligned parallel to the $c$-axis, followed by three layers with moments aligned antiparallel (Brunet al. 1970).

Neodymium has two double-hcp crystalline structure with two crystallographically inequivalent (hexagonal and cubic) sites and a complicated antiferromagnetic structure. The magnetic moments on the hexagonal sites order at $T_N = 19.2$ K and on the cubic sites below 7.8 K (Johansson et al. 1970).

### 7.1.1. Gadolinium

Neutron diffraction studies made by Cable and Wollan (1968) showed that Gd exhibits ferromagnetic ordering from liquid helium temperatures to the Curie temperature $T_C = 293$ K. The easy magnetization axis is directed along the $c$-axis from $T_C$ down to the spin-reorientation temperature $T_{SR} \approx 230$ K below which the spontaneous magnetization vector departs from the $c$-axis and the easy cone arises.

The MCE, $\Delta S_M$ and heat capacity of single and polycrystalline gadolinium were studied by many authors (Brown 1976; Gschneidner and Pecharsky 1997a; Nikitin et al. 1978; Hashimoto et al. 1981; Maeda et al. 1983; Tishin 1990b, 1990c; Burkhanov et al. 1991; Dan'kov et al. 1992, 1996, 1998; Foldeaki et al. 1995). The temperature dependence of the MCE of Gd obtained by various methods displays a maximum near $T_C$ (see figs 3.5 and 7.1). An additional small MCE anomaly was found in a Gd single crystal for $H$ aligned along the $c$- and $a$-axis near $T_{SR}$ by Nikitin et al. (1978).

Nikitin et al. (1978) studied the dependence of the MCE in a Gd single crystal on the magnetic field orientation. For a hexagonal crystal the anisotropic part of the Gibbs free energy can be expressed as follows:

$$G_A = K_1 \sin^2 \Theta + K_2 \sin^4 \Theta + K_3 \sin^6 \Theta + K_6 \sin^6 \Theta \cos 6\phi,$$

where $\Theta$ is the angle between the spontaneous magnetization vector $\vec{I}_s$ and the $c$-axis, $\phi$ is the angle between the basal-plane component of $\vec{I}_s$ and the $a$-axis, $K_i$ are the anisotropy constants.

The last term in eq. (7.1) describes the basal-plane anisotropy which is usually small, and can be neglected. On the basis of eq. (7.1) and eq. (2.8a) the magnetic entropy change
\( \Delta S_\Theta \) arising during the variation of the \( \vec{I}_s \) direction from the initial value of \( \Theta_0 \) to the final value of \( \Theta_H \), which is the angle between the magnetic field and the c-axis, can be written down as:

\[
\Delta S_{A\Theta} = -\left( \frac{\partial K_1}{\partial T} \right)_{H,p} \sin^2 \Theta_H - \sin^2 \Theta_0 - \left( \frac{\partial K_2}{\partial T} \right)_{H,p} \sin^4 \Theta_H - \sin^4 \Theta_0
- \left( \frac{\partial K_3}{\partial T} \right)_{H,p} \sin^6 \Theta_H - \sin^6 \Theta_0.
\] (7.2)

The anisotropy constants \( K_i \) also depend on \( H \), which leads to a magnetic entropy change \( \Delta S_{A,H} \):

\[
\Delta S_{A,H} = -\left[ \left( \frac{\partial^2 K_1}{\partial H \partial T} \right)_p \sin^2 \Theta_H + \left( \frac{\partial^2 K_1}{\partial H \partial T} \right)_p \sin^4 \Theta_H \\
+ \left( \frac{\partial^2 K_3}{\partial H \partial T} \right)_p \sin^6 \Theta_H \right] \Delta H.
\] (7.3)

The total magnetic entropy change \( \Delta S_A = \Delta S_{A,\Theta} + \Delta S_{A,H} \) causes the anisotropic contribution to the MCE (Nikitin et al. 1978):

\[
\Delta T_A = \Delta T_{A,\Theta} + \Delta T_{A,H} = -\frac{T}{C_p} (\Delta S_{A,\Theta} + \Delta S_{A,H}),
\] (7.4)

where the first term \( \Delta T_{A,\Theta} \) is the contribution from the rotation of \( \vec{I}_s \) against a magnetic anisotropy force and the second term \( \Delta T_{A,H} \) is the contribution from the variation of the anisotropy constants in the applied field.

The total MCE was obtained as a sum of the MCE caused by a paraprocess (it was calculated by eq. (2.16)) and \( \Delta T_A \). The calculated \( \Delta T(T) \) curve was in good agreement with the experimental one.

The \( \Delta T_A \) values were determined from the experimental \( \Delta T(H) \) dependences measured at various \( T \) as the intercepts on the \( \Delta T \) axis by the extrapolation of the linear high field part of the \( \Delta T(H) \) curves. It was shown that near \( T_C \) the main contribution to \( \Delta T_A \) gave the second term in eq. (7.4). Below 230 K, the \( \Delta T_A \) value is determined by the first term. As it follows from eqs (7.2) and (7.3), in this case \( \Delta T_A = 0 \) for \( \Theta_H = \Theta_0 \). This allowed to determine the temperature dependence of the \( \Theta_0 \) (Nikitin et al. 1978), which was in good accordance with data obtained by other authors.

The magnetic entropy change \( \Delta S_M \) induced by the field change in Gd, was determined from the magnetization data with the help of eq. (2.71) and from magnetocaloric effect by eq. (2.80). Good agreement was found between the experimental data and MFA calculations (Maeda et al. 1983; Tishin 1990a, 1990b, 1990c). Figure 7.1(a) and (b) present various contributions to the entropy of Gd in zero magnetic field and in a field of 70 kOe, calculated by eqs (2.60)–(2.62) and (2.67) by Tishin (1990a). The MCE in Gd for \( \Delta H = 70 \) kOe determined by the method described in section 4.1 is shown in fig. 7.1(c) (curve 1). This figure also presents experimental values of the MCE in Gd (curve 2) obtained by Brown.
Fig. 7.1. Temperature dependences of calculated entropy and MCE for Gd. (a) $H = 0$; (b) $H = 70$ kOe: (1) total entropy; (2) lattice entropy; (3) magnetic entropy; (4) electronic entropy. (c) Experimental (curve 1) and calculated (curve 2) dependences of MCE in Gd for $\Delta H = 70$ kOe. (d) Temperature dependence of magnetic entropy $\Delta S_M$ in Gd for $\Delta H = 60$ kOe (curves 1, 2); $\Delta H = 10$ kOe (3, 4, 5); $\Delta H = 5$ kOe (6, 7) (calculated values – curves 1, 5, and 7; experimental values obtained from magnetization and MCE data – curves 2, 3, 6, and 4) (Tishin et al. 1990a).

(1976). It can be seen that the results of the calculations describe the experimental data quite well. The values of $g_J$, $J$, $T_C$, $T_N$ and $T_D$ used in the MFA calculations are presented in table 7.1. Figure 7.1(d) presents the theoretical and experimental $\Delta S_M$ curves for polycrystalline Gd. The values of $\Delta S_M$ determined by the results of magnetization and MCE measurements are quite close. The maximum $\Delta S_M$ and MCE values near the Curie temperature in Gd obtained by various authors are collected in table 7.2.

The heat capacity of polycrystalline Gd was measured from 15 to 335 K by Griffel et al. (1954), and on single-crystal samples near $T_C$ by Lanchester et al. (1980) and Glorieux et al. (1995). Dan’kov et al. (1998) measured the heat capacity and magnetic field dependences of polycrystalline and single-crystal gadolinium. As it was noted earlier by Gschneidner (1993), the magnetic properties of RE metals are critically dependent on their purity. In all samples a pronounced $\lambda$-type anomaly was observed near $T_C$ in
the temperature dependence of the zero-field heat capacity. The magnetic field effect on the \( \lambda \)-maximum was typical for ferromagnets: it was substantially broadened and shifted to higher temperatures with increasing magnetic field. A small zero-field heat capacity anomaly existed in the single-crystal sample at about 220–225 K (near \( T_{SR} \)), but was wiped out by the magnetic field above 20 kOe.

The significant reduction of the purity in the commercial Gd sample caused a sharp reduction of the maximum of the \( \lambda \)-type anomaly (~10% as compared to high purity samples) and its temperature (~5%). An excess heat capacity in the commercial sample appeared in the temperature range between 70 and 286 K and above 300 K. The authors related these features with straining of the crystal lattice and weakening of the exchange interactions due to the interstitial impurities (such as carbon) dissolved in Gd. The interstitial impurities had also a distinct effect on the MCE measured in pulsed fields: the MCE value in the commercially pure Gd was about two times lower than in the high-purity samples (the maximum of \( \Delta T \) was about 3.2 K at 288 K for \( \Delta H = 20 \) kOe in the commercial Gd).

7.1.2. Terbium

Terbium displays HAFM ordering in the temperature interval from \( T_N = 230 \) K to \( T_C = 220.6 \) K, which is characterized by weak critical fields: maximum \( H_{cr} = 190 \) Oe at \( T_K = 228.5 \) K (Bykhover et al. 1990). In fields above \( H_{cr} \) the HAFM structure in Tb and Dy is destroyed and a “fan” structure arises (in the given temperature interval), in which the magnetic moments in the basal planes form fan-type ordering around the field direction. Further increase of the field leads to complete ferromagnetic ordering at a field of about \( 2H_{cr} \) (Greenough and Hettiarachchi 1983; Drillat et al. 1984; Bagguley and Howe 1986).

When the HAFM structure is destroyed by a magnetic field, an MCE takes place because the entropies of the two phases (HAFM and fan or FM) are not equal. The MCE at the first-order transition at \( H = H_{cr} \) applied in the basal plane of Dy and Tb\(_x\)Y\(_{1-x}\) alloys was considered by Nikitin et al. (1977a, 1977b, 1979a), Nikitin and Andreenko (1981) and Nikitin et al. (1991b). It was shown that the transition is caused by changes in several interactions, namely the energy of exchange interaction between the basal planes the magnetoelastic energy, the Zeeman energy and the in-plane anisotropy energy. The first three contributions were shown to dominate.
TABLE 7.2
Ordering temperatures $T_N$ or $T_C$, temperature of the maximum in the $\Delta T(T)$ curves ($T_{\text{max}}^T$), temperature of the maximum in the $\Delta S_M(T)$ curves ($T_{\text{max}}^S$) and maximum values of $\Delta S_M$ (at $T = T_{\text{max}}^S$) and $\Delta T$ (at $T = T_{\text{max}}^T$) induced by a magnetic field change $\Delta H$ for the heavy rare earth metals.

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<th>Element</th>
<th>$T_C$, $T_N$, K</th>
<th>$T_{\text{max}}^T$, K</th>
<th>$\Delta T$, K</th>
<th>$\Delta H$, kOe</th>
<th>$T_{\text{max}}^S$, K</th>
<th>$-\Delta S_M$, J/mol K</th>
<th>$\Delta H$, kOe</th>
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<td></td>
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<td>3.1$^z$</td>
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</table>

* In J/kg K

** Measurements on single crystals (the direction of magnetic field is shown in parenthesis)

References:

(a) Nikitin et al. (1991d)
(b) Pecharsky and Gschneidner (1996)
(c) Gschneidner and Pecharsky (1997a)
(d) Benford and Brown (1981)
(e) Hashimoto et al. (1981)
(f) Brown (1976)
(g) Nikitin et al. (1978)
(h) Dankov et al. (1998)
(i) Tishin (1990b)
(j) Foldeaki et al. (1995)
(k) Dankov et al. (1992)
(l) Bykhovsky et al. (1990)
(m) Nikitin et al. (1989b)
(n) Tishin (1988)
(o) Druzhinin et al. (1977)
(p) Dankov et al. (1996)
(q) Nikitin and Tishin (1988)
(r) Hudgins and Pavlovic (1965)
(s) Nikitin et al. (1991a)
(t) Nikitin et al. (1991d)
(u) Tishin and Martinenko (1995)
(v) Green et al. (1988)
(w) Milton and Scott (1967)
(x) Zimm et al. (1988)
(y) Brun et al. (1970)
Nikitin et al. (1989) studied the MCE of Tb in fields up to 400 Oe applied along the easy magnetization direction (b-axis) in the temperature interval from $T_C$ to $T_N$ – see fig. 7.2. Between 220.5 and 223.4 K the MCE values are small and positive in weak fields and sharply increase above $H_{cr}$. For temperatures from 223.4 to 226 K the MCE is negative in fields $H < 350$ Oe. The negative MCE is characteristic of antiferromagnets, in which the external field reduces the magnetic order rather than enhances it, thus increasing the magnetic entropy (antiferromagnetic-type paraprocess). In the case of Tb the external field transforms the HAFM structure into the lower-symmetry fan structure. The magnetic phase diagram $H_{cr}(T)$ constructed on the basis of $\Delta T(H)$ curves (the magnetic field was changed from 0 to $H$) is in good accordance with that obtained from the magnetization measurements. $H_{cr}$ was defined as the field of the maximum increase of $\Delta T$.

Figure 7.3 shows the temperature dependences of the MCE in a single crystal of Tb induced by fields applied along the b-axis (Tishin 1988). The MCE maximum in Tb is
observed near \( T_N \) and is caused by a paraprocess, which is known to be the most strong near the temperature of the transition to a magnetically ordered state. Due to the complete destruction of the HAFM structure no MCE anomalies were observed near \( T_C \) for \( \Delta H \geq 10 \) kOe. The same results were obtained for measurements in the field applied along the \( \alpha \)-axis (hard axis in Tb) which is related with a small magnetic anisotropy of Tb in basal plane at high temperatures.

Calculations of the MCE in Tb, made by Tishin (1990a) on the basis of the MFA, have shown relatively satisfactory agreement with the experimental data near \( T_N \), see fig. 7.4: for \( \Delta H = 20 \) kOe the calculations leads to \( \Delta T = 6 \) K, while the experimental value is 5 K. The calculated MCE in strong magnetic fields is shown in the inset in fig. 7.4. As one can see, for \( \Delta H > 2000 \) kOe the maximum in the \( \Delta T(T) \) curve disappears and for \( T > T_N \) the MCE practically does not change. Note the disagreement of these results with the MCE value calculated earlier by Druzhinin et al. (1979) in the framework of MFA (the shape of the \( \Delta T(T) \) curves was quite similar): \( \Delta T = 120 \) K for Tb at \( T = T_N \) and \( \Delta H = 1500 \) kOe. According to Tishin (1990a), at \( T = T_N \) the MCE value of 120 K can be reached only in a field of 2250 kOe, while for \( \Delta H = 1500 \) kOe the MCE amounts to 98 K.

Druzhinin et al. (1977) determined the MCE in a Tb single crystal in fields up to 350 kOe from the experimental adiabatic dependences of the magnetization in the basal plane obtained by the pulse method. The MCE was calculated by integration of eq. (2.23):

\[
\Delta T = T - T_0 = T_0 \left\{ \exp \left[ \int_{I_0(T)}^{I_f} \frac{1}{C_I} \left( \frac{\partial H}{\partial T} \right)_I \, dI \right] - 1 \right\}, \tag{7.5}
\]
where \( I \) and \( T \) are the final values of temperature and magnetization and \( I_s(T_i) \) and \( T_i \) are the initial values of magnetization and temperature. A sharp MCE maximum with the value of 60 K was observed at \( T = 230 \) K.

The temperature dependences of the magnetic entropy change \( \Delta S_M \) in Tb was evaluated from magnetization measurements by eq. (2.71) (Dan'kov et al. 1996) and from heat capacity and MCE data (Nikitin et al. 1985a). In the latter case, the results of zero-field heat capacity measurements made by Jennings et al. (1957) and eq. (2.77) were used for the \( \Delta S_M(T) \) calculation (the field dependence of the heat capacity was not taken into account). Later, the \( \Delta S_M \) values for the heavy rare-earths have been calculated more exactly by Tishin (1994). In these calculations the field dependence of the heat capacity was taken into account. The result for Tb is shown in fig. 7.5. As one can see, \( \Delta S_M \) for \( \Delta H = 60.2 \) kOe has maximum near \( T_N \).

The heat capacity of Tb in the presence of a magnetic field was calculated by Nikitin and Tishin (1987) and Tishin (1988) on the basis of the zero-field measurements of Jennings et al. (1957). First, \( S(T, H) \) was calculated by eq. (2.76) and the MCE data, and then eq. (2.12) was used to calculate \( C(T, H) \). The results for \( H = 60.2 \) kOe is shown in the inset in fig. 7.3. The heat capacity maximum becomes broader and lower in the field and shifts to the higher temperature region.

### 7.1.3. Dysprosium

The HAFM structure arises in Dy between \( T_N \simeq 180 \) K and \( T_C \simeq 90 \) K. Dy is characterized by much higher critical fields than Tb: the maximum \( H_C \) value is about 11 kOe at \( T_K = 165 \) K (Bykhover et al. 1990).
Hudgins and Pavlovic (1965) performed detailed studies of the field and temperature dependences of the MCE in polycrystalline Dy in the fields up to 20 kOe and in the temperature interval from 77 to 320 K. The $\Delta T(H, T)$ curves were discussed in connection with the magnetic structure transformation. Later Tishin (1988) and Nikitin et al. (1985a) studied the MCE in polycrystalline Dy in fields up to 60 kOe.

Joint investigations of the MCE and magnetic properties of a Dy single crystal along the easy axis $a$ were made by Nikitin et al. (1979a) in magnetic fields up to 13 kOe. It was found that a field induced HAFM–FM transition at $H_{cr}$ causes a positive MCE ($\Delta T > 0$) within the temperature interval from 85 to 160 K. A change of sign of the MCE was found to take place at $T_K$, where $H_{cr}$ had its maximum and $\partial H_{cr}/\partial T = 0$. According to the Clausius–Clapeyron equation (2.82) $\Delta S_M$, and consequently $\Delta T$, at this temperature should be equal to zero. It was concluded that $T_K$ is a tricritical point in the magnetic phase diagram $H_{cr}(T)$ of Dy, where the first-order transition lines turn into the second-order transition line.

The MCE in Dy was also studied by Benford (1979) and Nikitin et al. (1991b). Figure 7.6 shows temperature dependences of the MCE in a Dy single crystal measured directly with the field applied along the $a$- and $b$-axis (Tishin 1988; Nikitin et al. 1991b). The MCE maximum observed for $H$ applied along the $a$-axis at $T = 177.5$ K is associated with the HAFM–PM phase transition. The sharp increase of the MCE near $T \approx 90$ K corresponds to the FM–HAFM transition. In the region from 165 to 178 K the MCE is negative for $\Delta H = 10$ kOe. A substantial change of the $\Delta T(T)$ behavior is observed when the field is increased. The broad plateaus in the temperature interval from 90 to 135 K and $H < 20$ kOe are due to the destruction of the HAFM structure by fields $H > H_{cr}$. In stronger fields the plateaus gradually disappear and an additional MCE maximum appears around 155–165 K, the temperature of the maximum increasing as the field is increased. The minimum in high fields corresponds to the tricritical point $T_K = 165$ K. The general character of the MCE behavior in fields applied along the $b$-axis is similar to that measured along the $a$-axis. The differences in the low-temperature region was related by Nikitin et al. (1991b) with a contribution from the change of magnetic basal-plane anisotropy energy.
Figure 7.7 shows the MCE in a Dy crystal obtained in various fields applied along the $a$-axis (Tishin 1988; Nikitin et al. 1991b). In the temperature interval from 85 to 165 K jumps in the $\Delta T(H)$ curves are observed. In the region from 165 to 178 K these jumps disappear and the MCE becomes negative in weak fields. Magnetization measurements showed that within the interval from 135 to 165 K the first-order transitions from HAFM to fan occurred (Nikitin et al. 1991b).
The second-order field induced transition HAFM–fan was observed from 165 K to $T_N$. In this case the field continuously deforms the HAFM structure until a fan structure is formed. This process is accompanied at an early stage by growth of the magnetic entropy due to lowering of the antiferromagnetic order. The maximum negative MCE (at $H \approx 10$ kOe) marks the point of maximum disorder in the magnetic structure.

Data on the magnetic entropy of Dy have been presented by Nikitin et al. (1985a, 1991b, 1991c), Nikitin and Tishin (1988) and Foldeaki et al. (1995). Figure 7.5 presents $\Delta S_M(T)$ curve for Dy for $\Delta H = 60.2$ kOe calculated on the basis of heat capacity and MCE data. The maximum of $\Delta S_M$ is observed near $T_N$. The $\Delta S_M(T)$ curve calculated for a Dy single crystal from MCE measurements leads to positive values in the temperature interval from 165 to 178 K. The temperature dependence of the magnetic entropy $S_M(0, T)$ of a high-purity Dy single crystal was determined by Nikitin et al. (1991c) by eq. (2.76) on the basis of heat capacity measurements. The saturation high-temperature $S_M$ value obtained in this way equals 23 J/mol K, which is in good agreement with the theoretical value from table 6.2. Foldeaki et al. (1995) determined the temperature and field dependences of $\Delta S_M$ in polycrystalline Dy from the magnetization measurements by eq. (2.71). A positive magnetic entropy change was observed on the $\Delta S_M(H)$ curve at $T = 174$ K at low fields (below 1.5 kOe). The MCE and $\Delta S_M$ values obtained experimentally in Dy by various methods are presented in table 7.2.

The heat capacity of Dy was measured by Griffel et al. (1956), Lounasmaa and Sundstrom (1966), Ramji Rao and Narayana Mytry (1978) and Nikitin et al. (1991c). Maxima on the $C(T)$ curve were observed near $T_N$ and $T_C$. The value of the maximum near the
Fig. 7.8. Temperature dependences of the heat capacity Dy in various magnetic fields: (1) $H = 0$; (2) $H = 20\, \text{kOe}$; (3) $60\, \text{kOe}$ (Nikitin and Tishin 1987).

HAFM–PM transition was shown to be in good agreement with the one calculated in the framework of MFA (Nikitin et al. 1991c).

Nikitin and Tishin (1987) using eq. (2.96) and MCE data calculated the heat capacity of Dy in magnetic fields up to 60 kOe from the zero-field heat capacity measurements of Griffel et al. (1956). The results are presented in fig. 7.8. The appearance of an additional maximum in the $C(T)$ curve for $H = 20\, \text{kOe}$ near $T = 160\, \text{K}$ was related by the authors with the occurrence of the fan structure. With increasing magnetic field the maximum disappears, which correlates with the transformation of the fan structure into the ferromagnetic one at high fields.

7.1.4. Holmium

The temperature dependences of the MCE of polycrystalline Ho measured directly for various $\Delta H$ are shown in fig. 7.9 (Nikitin et al. 1985a). MCE maxima are observed at $T_C = 20\, \text{K}$ ($\Delta T = 4.6\, \text{K}$ for $\Delta H = 60.2\, \text{kOe}$) and at $T_N = 132\, \text{K}$ ($\Delta T = 4.5\, \text{K}$ for $\Delta H = 60.2\, \text{kOe}$). The MCE is large in the temperature interval from 20 to 132 K with $\Delta T = 3.2$–$4.6\, \text{K}$ for $\Delta H = 60.2\, \text{kOe}$. Small MCE maxima are observed in the region of 70–90 K for $\Delta H = 30.1$–$60.2\, \text{kOe}$. They are due to a complex temperature dependence of the critical field $H_{cr}$, which destroys the HAFM structure. Green et al. (1988) found a MCE maximum in Ho near 136 K with the value of 6.1 K for $\Delta H = 70\, \text{kOe}$.

The heat capacity of Ho was measured by Jayasuria et al. (1985), Lounasmaa and Sundstrom (1966). Nikitin and Tishin (1987) on the basis of zero-field heat capacity and MCE data calculated $C(H, T)$ curves of Ho by eq. (2.96). It was shown that a broad maximum appears in the $C(H, T)$ curve in the temperature range from 90 to 130 K for $H = 20\, \text{kOe}$ which is higher than $H_{cr}$. As the field is increased up to 60 kOe, this maximum disappears and only a plateau remains in the $C(H, T)$ curve. The maximum was related by the authors with the tricritical point in the magnetic phase diagram $H_{cr}(T)$. 
The $\Delta S_M(T)$ curve for Ho, obtained from the MCE and heat capacity measurements, is shown in fig. 7.5. The sharp $\Delta S_M$ maximum occurs near $T_N$.

7.1.5. Erbium

The directly measured temperature dependence of the MCE of polycrystalline Er shows a maximum near the AFM–PM transition point $T_N$ (Nikitin et al. 1985a) (see fig. 7.10). At $\Delta H = 60.2$ kOe the maximum MCE value was 3.2 K. An extra maximum, which was attributed to the destruction of the AFM structure by a magnetic field, was observed at $T = 35$ K. The maximum value $\Delta T = 3.8$ K exceeds that near $T_N$ obtained for the same $\Delta H$ value. As well as Ho, Er shows a substantial MCE (about 3 K for $\Delta H = 60.2$ Oe) over a wide temperature interval from 30 to 85 K. Analogous $\Delta T(T)$ curves were obtained by Zimm et al. (1988) for polycrystalline Er. It was established that for $\Delta H = 75$ kOe the high-temperature (near $T_N$) and low-temperature MCE maxima...
The ASM(T) curve of Er for AH = 60.2 kOe is presented in fig. 7.5. The ASM maximum near TN has a value of 1.2 J/mol K, while the low temperature maximum is much higher with ASM = 2.5 J/mol K.

The heat capacity of Er was studied by Skochdopole et al. (1955), Schmitzer et al. (1987), Dreyfus et al. (1961), Hill et al. (1984) and Krusius et al. (1974). The temperature dependence of the zero-field heat capacity of Er measured by Zimm et al. (1988) displayed a large step at 84 K corresponding to the AFM ordering along the c-axis. The broad shoulder from 30 to 80 K corresponds to the ordering in the basal plane and the sharp peak near 20 K is related with the first-order transition to a conical magnetic structure. A magnetic field of 10 kOe wiped out the peak at 20 K but had only a small effect on the high-temperature anomaly.

Heat capacity measurements in the absence of a magnetic field were made by Pecharsky et al. (1993) on high-purity polycrystalline Er in the temperature interval 1.5–80 K. Besides the peaks at 19 K (conical phase transition) and 51.4 K (AFM ordering in the basal plane), additional anomalies at 25.1, 27.5, 42, and 48.9 K were revealed. They were related by the authors with the spin-slip transitions between different commensurate AFM structures (Gibbs et al. 1986; Bohr 1991).

7.1.6. Thulium

The ΔT(T) curves of Tm measured by a direct method are shown in fig. 7.11 (Nikitin et al. 1985a). A MCE maximum with the value of 1.5 K for ΔH = 60.2 kOe is observed near TN at 58 K. At lower temperatures the MCE becomes negative which may be due to the deformation of the AFM structure by the magnetic field and which is accompanied by a

---

Fig. 7.11. Temperature dependences of the MCE of polycrystalline Tm for different values of ΔH: (1) 60.2 kOe; (2) 50.2 kOe; (3) 40.3 kOe; (4) 30.1 kOe; (5) 20.1 kOe (Nikitin et al. 1985a; Tishin 1988).
magnetic entropy increase. Analogous $\Delta T(T)$ curves were obtained by Zimm et al. (1989), although the maximum $\Delta T$ values in corresponding magnetic fields were somewhat higher.

The temperature dependence of the zero-field heat capacity of Tm showed a large step near $T_N$ (Zimm et al. 1989). The application of 10 kOe did not have any noticeable influence on the $C(T)$ curve except rounding of the step at $T_N$.

### 7.1.7. Neodymium

The heat capacity and MCE of polycrystalline Nd were studied by Zimm et al. (1990) in the temperature range from 5 to 35 K and in fields up to 70 kOe. In the temperature dependences of the MCE measured by a direct method two maxima were found. The one near 20 K corresponds to magnetic ordering at the hexagonal sites, and the other, near 8 K, corresponds to ordering at the cubic sites. It should be noted that the latter maximum was much higher ($\Delta T \approx 2.5$ K at 10 K for $\Delta H = 70$ kOe) than the former ($\Delta T \approx 1.5$ K at 21 K for $\Delta H = 70$ kOe). The authors related this difference with a large magnetocrystalline anisotropy because of which only the basal plane component (the magnetic moments in the hexagonal sites order in the basal plane) of the external magnetic field in a crystallite can contribute to the magnetic ordering near $T_N$.

The relatively weak MCE in Nd (as compared with the heavy RE metals) was explained by the antiferromagnetic structure and crystalline field effects. The latter factor reduces the maximum available magnetic entropy from $R \ln 10$ ($J = 9/2$) in the absence of crystal field splitting to $R \ln 2$ ($J = 1/2$).

The heat capacity of Nd was measured by Lounasmaa and Sundstrom (1967) and Zimm et al. (1990). Two anomalies were observed at the corresponding magnetic phase transitions.

### 7.1.8. Theoretically available MCE in the heavy rare-earth metals

One of the fast developing areas of prospective applications of rare-earth metals is the design of new effective magnetic solid state refrigerators. The particular interest in magnetic refrigerators is associated with the possibility of their wide commercialization. Active prototypes of the latter are known by their high efficiency and notable life-in-service time. Hence, the practical use of the MCE has potentially a great future (see, for instance, Gschneidner and Pecharsky 1997a).

Nonetheless, the selection of magnetic materials that are good candidates for cooling media (magnetic refrigerant) is not straightforward, since a theory which could permit an accurate prediction of the magnetocaloric effect does not exist yet. Furthermore, modern experimental investigations in high magnetic fields up to 5 MOe and more are no longer something exotic. Since the MCE value in such fields can be extremely high, the possibility of its influence on the obtained experimental results needs to be accounted for.

Tishin’s papers (1990a) and (1998c) describe the results of a computer simulation analysis of the magnetocaloric effect (MCE) in rare earth metals and rare earth based materials. The analysis of Tishin (1990a) was developed for calculating peak values of the MCE in rare earth magnets using a mean-field approximation. The study by Tishin (1998c) concentrates on the variation of the key thermodynamic parameters such as magnetic field, temperature, the Curie and Debye temperatures of the magnetic materials in wide range of values. Results of theoretical studies of the MCE in large magnetic fields were described.
The possible mechanisms of magnetic entropy change in a paraprocess region were discussed. Tishin's (1998c) study shows that there is a strong influence of the Debye temperature of the magnetic materials on the MCE value in a wide temperature region (from 4.2 K to 200–230 K).

Based on the molecular field theory, Tishin (1990a and 1998b) performed numerical simulations of the MCE value, $\Delta T$, and the entropy, $S$, of heavy lanthanides. The used numerical approach was described in details by Tishin (1990a) and has been described also in section 3.3, the REM parameters used being listed in table 7.3. The magnetic fields considered were assumed to significantly exceed the critical magnetic fields necessary to destroy the antiferromagnetic state in the rare earth metals, and therefore, all calculations were performed for magnetic phase transition from the ferromagnetic to the paramagnetic state.

All results of the numerical simulation should agree quite well with the experimental data for the heavy lanthanides only for large magnetic fields, i.e., for fields in which the contribution of the AFM–FM phase transition to the magnetic entropy is rather small. During the simulation, the assumed values of the magnetic field ranged from 0 to 40 MOe and the initial temperature ranged from 10 K to 1000 K. It was found that the maximum value of magnetic field in our galaxy can reach about $10^{15}$ Oe (Kouveliotou et al. 1998). The energy spectrum can become extremely distorted in such high magnetic fields. Therefore, this naturally may affect the real field dependence of the magnetic entropy, $S_M$, and $\Delta T$. Phenomena like crossover are considered by the author to yield staircase-like $\Delta T(H)$ and $S_M(H)$ curves. But Tishin (1998c) proposed that its contribution to the total value of the
Fig. 7.12. Temperature dependences of the MCE in the heavy rare earth metals Gd, Tb, Dy, Ho, Er, and Tm for $\Delta H = 6$ MOe (Tishin 1990a).

overall MCE and the entropy should be relatively small. It should be noted that the results described can be applied to the real magnetic materials only outside the critical region. The calculations reveal the fact that if the temperature is high (near 1000 K), saturation of the MCE and magnetic entropy is absent even in the highest magnetic fields (up to 40 MOe), while near the temperature of the phase transition to the paramagnetic state the value of the magnetic entropy saturates in a field of about 10 MOe. In high fields ($H > 10$ MOe), the magnetic entropy practically equals zero up to the point $T \approx T_C$, i.e., there is no magnetic contribution to the entropy. This result leads to the following conclusion: in fields higher than 1 MOe the magnetic moments of the rare earth ions must be nearly completely aligned in a wide range of temperatures, up to the Curie temperature.

Tishin’s calculations point to the fact that the general behavior of the MCE as a function of temperature is transformed significantly under the influence of a magnetic field. Anomalies in the MCE curves for $T > T_C$ are observed in magnetic fields up to 40 MOe, but the MCE increases with temperature, when $H > 5$ MOe and $T > T_C$. When $H > 5$ MOe, the MCE increases up to $T = T_C$ and then decreases smoothly when $T > T_C$. The temperature and field dependencies of the MCE in REM behave similarly. Figure 7.12 presents the temperature dependence of the maximum MCE for heavy lanthanides (in the saturation field). Gadolinium has the minimum MCE at all considered temperatures. Tishin’s (1998c) analysis leads to the conclusion that at low temperatures the maximum MCE value (of heavy lanthanides) is determined by the Debye temperature, $T_D$, (i.e., by the small value of the lattice heat capacity). When the temperature exceeds 230 K the maximum MCE in all REM follows the total angular moments, $J$, and/or the effective magnetic moment, $\mu_{\text{eff}}$. The calculations show, that Tb has the largest MCE in fields up to 2 MOe, while Er has the lowest. In higher fields Ho has the maximum value of MCE, and Gd the minimum. Furthermore, in high fields (although not in the saturation fields) the MCE is defined not only by the magnetic entropy, but also by a number of other parameters associated with the magnetic and crystal structures of the lanthanides.

The field dependences of the magnetic entropy in the vicinity of the phase transition to the paramagnetic state are found to be arranged in order of increasing Curie temperatures.
of the lanthanides, except Gd. The calculations reveal that the MCE in REM continues to increase even when the magnetic entropy becomes almost equal to zero.

Calculations of the MCE value in the heavy RE metals as a function of the magnetic field at \( T = T_{\text{ord}} \) (here \( T_{\text{ord}} = T_C \) for Gd and \( T_N \) for the others RE metals) give satisfactory agreement with the experimental data for \( \Delta H = 60 \text{ kOe} \) only for Gd, Tb and Dy (Tishin 1990a). This result is quite clear, since in Ho, Er and Tm the HAFM structure persists in much higher fields than in Tb and Dy. It follows from the experimental data that the behavior of the \( \Delta T(T) \) curves is strongly influenced by these structures in fields up to 60 kOe (see above). One can suppose that in fields much higher than \( H_{\text{cr}} \) the MFA should describe the MCE sufficiently well.

The MFA calculations of \( \Delta S_M(T, H) \) in heavy RE metals at \( T = T_{\text{ord}} \) shown that a considerable rise in \( \Delta S_M \) is observed only in fields below 2 MOe, whereas in fields of about 6 MOe the values of \( \Delta S_M \) differ only slightly from their maximum values \( \Delta S_M^{\text{max}} \), calculated by eq. (2.70). Table 7.3 presents \( \Delta S_M^{\text{max}} \), the values of \( \Delta S_M \) calculated for \( \Delta H = 6 \text{ MOe} \) and 10 MOe, and maximum experimental \( \Delta S_M \) values for \( \Delta H = 60 \text{ kOe} \) near \( T_{\text{ord}} \) (Brown 1976; Nikitin and Tishin 1988; Tishin 1988).

Table 7.3 lists the maximum possible values of the magnetocaloric effect (\( \Delta T_{\text{max}} \)) at \( T = T_{\text{ord}} \), calculated by eq. (2.77) on the basis of \( \Delta S_M^{\text{max}} \) values. Also listed are the calculated values of the fields \( H_{\text{max}}(T_{\text{ord}}) \), in which the MCE is different from \( \Delta T_{\text{max}} \) by at most 1%. As one can see, an initial temperature rise of 100 K leads the MCE to increase by a factor 1.5–2. Such behavior of \( \Delta T_{\text{max}} \) corresponds to the functional dependence \( \Delta T \sim T \), as follows from eq. (2.77), since the factor \( (\Delta S_M/C_{p,H}) \) tends to a constant when \( H \) tends to infinity. The analysis made by Tishin (1990a) shows that the \( \Delta T_{\text{max}} \) value in the series of heavy RE metals is directly proportional to the product \( g_J J T_{\text{ord}} \).

From the classic point of view, the change of \( S_M \) value is usually related to the rotation of the magnetic moment vectors under influence of the magnetic field (i.e., the \( S_M \) decreases with increasing magnetization in classic magnetic materials). It has been experimentally established that the value of \( \Delta S_M \) measured in 60 kOe in rare-earth metals and their alloys in the vicinity of their magnetic phase transition totals approximately 8 to 10% of \( \Delta S_M^{\text{max}} \) (Tishin 1988). Moreover, the magnetization of Gd at the Curie point practically does not change in 100 to 300 kOe (Ponomarev 1986). The MCE value measured in 100 kOe in Gd equals 19 K (Dan’kov et al. 1998). But from Tishin’s (1990a and 1998c) calculations it follows that \( \Delta T_{\text{max}} \) in Gd is expected to be 234 K at \( T = T_C \). Thus, it appears that for most of the sample’s temperature increase one has to take account of paraprocesses (occurring in the region where the sample has already single domain structure and the atomic magnetic moments are mostly aligned parallel to the field). So the change of the MCE and the magnetic entropy is clearly determined not only by rotation of the magnetization vectors. This means that the experimental data can not be explained within the classic theory, which assumes the magnetic entropy decrease to occur at the expense of the rising order of the magnetic moments in the system. Thus, the use of a probability (quantum mechanical) approach to the entropy seems to be the right choice. This means that the magnetic entropy (and consequently the sample temperature) continues to change even in the region of the paraprocess, just because of the fact that the probability of atomic magnetic moment deflection from the field direction (due to the heat fluctuations) remains non-zero even in high magnetic fields. It is possible that the values of \( \Delta S_M \) (which have been observed in
rare-earth intermetallic compounds by Gschneidner et al. (1994a, 1994b)) are large due to suppression of spin heat fluctuations in the low temperature region.

Since the influence of $T_D$ on the MCE was not sufficiently studied yet, neither theoretically nor experimentally, it is of interest to define numerically the general rules of the phenomena. In general, the relation between the MCE and the entropy change is well known. To investigate the impact of the Debye temperature on the MCE we need to take into account the effect of the temperature on the lattice entropy (it is worth noting that the concept of total entropy as a sum of different parts can be used only for magnetic materials with localized magnetic moment, like REM). The entropy of a solid is known to increase significantly when the Debye temperature decreases. For instance, it is easy to show that at 300 K a decrease of the Debye temperature from 184 K (Gd) to 50 K leads to a lattice entropy ($S_L$) increase of about 33 J/mol K (70%). When the Debye temperature increases from 184 K to 500 K this leads to an $S_L$ change of only approximately 23 J/mol K (50%). It is well known that the maximum possible value of the magnetic entropy change can be defined as $\Delta S_{\text{max}} = -R \ln(2J + 1)$ (see eq. (2.70)). So, from one point of view the maximum MCE is limited by the total quantum number and the measurement temperature. On the other hand, in general the MCE can vary due to the change of magnetic, lattice and electronic contributions to the heat capacity. The electronic part of the heat capacity gives a constant contribution to the heat capacity and does not change the MCE if $T = \text{const}$. The character of magnetic contributions to the heat capacity change (generally a decrease for ferromagnets) under exposure of a field is quite complicated and can be predicted only in general terms.

Tishin's (1998c) calculations show, that the change in $T_D$ can significantly influence the magnetocaloric effect value. Consequently, a change in the Debye temperature has a different impact on the MCE value in the low- ($T < 200–230$ K) and high-temperature range. However, the problem of what are the ways and how the Debye temperature can be changed in real magnetic materials still remains quite insufficiently researched.

From the qualitative point of view, the Debye temperature can be treated as the rigidity of the crystal lattice. The rigidity of a lattice can be changed. For instance, one may change the fabrication process by making it amorphous or by the other processing means. Tishin (1998c) proposed that the Debye temperature can be effected significantly by addition of different elements to magnetic compounds. For example, additions of C, N or B are known to lead to a unit cell volume increase (swelling) of a magnetic material.

7.2. Rare earth alloys

7.2.1. Tb–Gd alloys

The MCE in Tb$_x$Gd$_{1-x}$ alloys was investigated by Nikitin et al. (1979b, 1980, 1981, 1988b). The alloys with $x > 0.94$ are examples of easy-plane ferromagnets with their hard magnetization direction along the $c$-axis (Nikitin et al. 1980). Such magnetic materials display a spin reorientation transition with the appearance of a magnetization component along the hard axis below some temperature.

The temperature dependences of the MCE measured in Tb$_x$Gd$_{1-x}$ alloys in fields applied in the basal plane (easy plane) have maxima near the Curie point (Nikitin et al. 1981). The MCE values measured along the $b$-axis are given in table 7.4.
The measurements along the hard \( c \)-axis revealed more complex MCE behavior. The temperature dependence of the MCE in the \( \text{Tb}_{0.2}\text{Gd}_{0.8} \) alloy is shown in fig. 7.13 (curves 1 and 2). A maximum for the positive MCE can be observed near \( T_C = 282 \) K, as in the case of \( H \) directed along the \( b \)-axis. However, as the sample is cooled down, a sign change of the MCE takes place below \( T_C \), where it becomes negative. The sign inversion temperature shifts towards lower temperatures in higher fields. Near \( T_C \) the MCE behavior is correlated with the temperature dependences of the magnetization (see fig. 7.13 and eq. (2.16)). For \( H = 60 \) kOe the \( \sigma(T) \) curve has a form usually observed for ferromagnets and the MCE displays a maximum. For \( H = 10 \) kOe there is a maximum in the \( \sigma(T) \) curve. The maximum appears due to the ordering of the magnetic moments in the basal plane in fields which are not high enough to orient them along the \( c \)-axis below \( T_C \). The maximum in the \( \Delta T(T) \) curve for \( \Delta H = 10 \) kOe is observed at the temperature where \( \partial \sigma / \partial T \) is negative and has a maximum value (see curves 2 and 4 in fig. 7.13). The negative MCE corresponds to positive \( \partial \sigma / \partial T \). The behavior of the temperature and field dependences of the MCE in \( \text{Tb}_{0.2}\text{Gd}_{0.8} \) for magnetization along the \( c \)-axis near \( T_C \) were discussed by Nikitin et al. (1981) in the framework of the Landau theory of the second-order transitions.

The reasons for the appearance of a negative MCE in Tb–Gd alloys in the low temperature range in fields applied along the hard axis were considered by Nikitin et al. (1988b).

The total MCE was presented as consisting of three contributions:

\[
\Delta T \approx -\frac{T}{C_{H,p}} \left[ \frac{\partial I_s}{\partial T} H \cos \Theta + \frac{\partial K_1}{\partial T} \left( \sin^2 \Theta - 1 \right) \right. \\
\left. + I_{RR} \left( \frac{\partial I_{\text{Tb}}}{\partial T} I_{\text{Gd}} + \frac{\partial I_{\text{Gd}}}{\partial T} I_{\text{Tb}} \right) \left( \cos^2(\Theta_{\text{Tb}} - \Theta_{\text{Gd}}) - 1 \right) \right],
\]

(7.6)
### TABLE 7.4

Ordering temperatures $T_N$ or $T_C$, temperature of the maximum in the $\Delta T(T)$ curves ($T^{\text{T}}_{\text{max}}$), temperature of the maximum in the $\Delta S_M(T)$ curves ($T^{\text{S}}_{\text{max}}$) and maximum values of $\Delta S_M$ (at $T = T^{\text{S}}_{\text{max}}$) and $\Delta T$ (at $T = T^{\text{T}}_{\text{max}}$) induced by a magnetic field change for the rare earth alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T_C; T_N$, K</th>
<th>$T^{\text{T}}_{\text{max}}$, K</th>
<th>$\Delta T$, K</th>
<th>$\Delta H$, kOe</th>
<th>$T^{\text{S}}_{\text{max}}$, K</th>
<th>$-\Delta S_M$, J/mol K</th>
<th>$\Delta H$, kOe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd$<em>{0.3}$Tb$</em>{0.7}$</td>
<td>253$^a$ 252$^b$</td>
<td>9.1$^b$($lb$) 60$^b$</td>
<td>252$^a$</td>
<td>0.4$^a$($lc$) 12$^a$</td>
<td>252$^a$</td>
<td>0.4$^a$($lc$) 12$^a$</td>
<td>252$^a$</td>
</tr>
<tr>
<td>Gd$<em>{0.6}$Tb$</em>{0.4}$</td>
<td>271$^a$ 270$^b$</td>
<td>8$^b$($lb$) 60$^b$</td>
<td>270$^a$</td>
<td>0.8$^a$($lc$) 12$^a$</td>
<td>270$^a$</td>
<td>0.8$^a$($lc$) 12$^a$</td>
<td></td>
</tr>
<tr>
<td>Gd$<em>{0.8}$Tb$</em>{0.2}$</td>
<td>282$^a$ 281$^a$</td>
<td>2.2$^a$($lb$) 60$^a$</td>
<td>281$^a$</td>
<td>2.2$^a$($lc$) 60$^a$</td>
<td>281$^a$</td>
<td>2.2$^a$($lc$) 60$^a$</td>
<td></td>
</tr>
<tr>
<td>Gd$<em>{0.2}$Ho$</em>{0.8}$</td>
<td>160$^d$ 160$^d$</td>
<td>$\approx 7^d$ 60.2$^d$</td>
<td>160$^d$</td>
<td>$\approx 7^d$ 60.2$^d$</td>
<td>160$^d$</td>
<td>$\approx 7^d$ 60.2$^d$</td>
<td>160$^d$</td>
</tr>
<tr>
<td>Gd$<em>{0.4}$Ho$</em>{0.6}$</td>
<td>194$^d$ 194$^d$</td>
<td>$\approx 9^d$ 60.2$^d$</td>
<td>194$^d$</td>
<td>$\approx 9^d$ 60.2$^d$</td>
<td>194$^d$</td>
<td>$\approx 9^d$ 60.2$^d$</td>
<td>194$^d$</td>
</tr>
<tr>
<td>Gd$<em>{0.6}$Ho$</em>{0.4}$</td>
<td>230$^d$ 230$^d$</td>
<td>$\approx 9.5^d$ 60.2$^d$</td>
<td>230$^d$</td>
<td>$\approx 9.5^d$ 60.2$^d$</td>
<td>230$^d$</td>
<td>$\approx 9.5^d$ 60.2$^d$</td>
<td>230$^d$</td>
</tr>
<tr>
<td>Gd$<em>{0.8}$Ho$</em>{0.2}$</td>
<td>268$^d$ 268$^d$</td>
<td>$\approx 10^d$ 60.2$^d$</td>
<td>268$^d$</td>
<td>$\approx 10^d$ 60.2$^d$</td>
<td>268$^d$</td>
<td>$\approx 10^d$ 60.2$^d$</td>
<td>268$^d$</td>
</tr>
<tr>
<td>Gd$<em>{0.2}$Er$</em>{0.8}$</td>
<td>125$^d$ 125$^d$</td>
<td>$\approx 4^d$ 60.2$^d$</td>
<td>125$^d$</td>
<td>$\approx 4^d$ 60.2$^d$</td>
<td>125$^d$</td>
<td>$\approx 4^d$ 60.2$^d$</td>
<td>125$^d$</td>
</tr>
<tr>
<td>Gd$<em>{0.4}$Er$</em>{0.6}$</td>
<td>168$^d$ 168$^d$</td>
<td>$\approx 7^d$ 60.2$^d$</td>
<td>168$^d$</td>
<td>$\approx 7^d$ 60.2$^d$</td>
<td>168$^d$</td>
<td>$\approx 7^d$ 60.2$^d$</td>
<td>168$^d$</td>
</tr>
<tr>
<td>Gd$<em>{0.6}$Er$</em>{0.4}$</td>
<td>220$^d$ 220$^d$</td>
<td>$\approx 8^d$ 60.2$^d$</td>
<td>220$^d$</td>
<td>$\approx 8^d$ 60.2$^d$</td>
<td>220$^d$</td>
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<td>0.3$^i$($lc$) 60$^i$</td>
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<td>7$^i$($lc$) 60$^i$</td>
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<td>135$^f$</td>
<td>3.7$^f$($lc$) 60$^f$</td>
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<td>3.7$^f$($lc$) 60$^f$</td>
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<td>0.7$^k$ 13$^k$</td>
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<td>0.7$^k$ 13$^k$</td>
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<td>1.7$^k$ 13$^k$</td>
<td>207$^k$</td>
<td>1.7$^k$ 13$^k$</td>
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<td>1.7$^k$ 13$^k$</td>
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<td>2.1$^k$ 13$^k$</td>
<td>218$^k$</td>
<td>2.1$^k$ 13$^k$</td>
<td>218$^k$</td>
<td>2.1$^k$ 13$^k$</td>
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<tr>
<td>Er$<em>{0.8}$La$</em>{0.2}$</td>
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<td>0.8$^l$ 10$^l$</td>
<td>44$^l$</td>
<td>0.8$^l$ 10$^l$</td>
<td>44$^l$</td>
<td>0.8$^l$ 10$^l$</td>
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where Θ is the angle between the total spontaneous magnetization vector \( \vec{I}_s \) and the c-axis, \( K_1 \) is the anisotropy constant, \( I_{RR} \) is the exchange integral for the indirect interaction between the Tb and Gd magnetic moments, \( I_{TB} \) and \( I_{GD} \) are the magnetizations of the Tb and Gd sublattices, respectively; \( \Theta_{TB} \) and \( \Theta_{GD} \) are the angles between the sublattice magnetization vectors \( \vec{I}_{TB} \) and \( \vec{I}_{GD} \) and the c-axis. The first term, calculated by eq. (2.16), is due to the variation of exchange interaction inside the Tb and Gd sublattices (\( H \cos \Theta \) is the projection of the field on the magnetization vector \( \vec{I}_s \)), i.e., the paraprocess. The second term in eq. (7.6) is due to the rotation of \( \vec{I}_s \) from the basal plane to the c-axis against anisotropy forces. The last term describes the variation of the exchange interaction between Tb and Gd magnetic sublattices, which leads to a change of the angle between \( \vec{I}_{TB} \) and \( \vec{I}_{GD} \) and the formation of a noncollinear magnetic structure.

The calculations by eq. (7.6) on the basis of experimental data for the Tb\(_{0.2}\)Gd\(_{0.8}\) alloy showed that for \( \Delta H = 60 \text{ kOe} \) the anisotropy contribution to the MCE (the second term in eq. (7.6)) is negative and its absolute value increases up to the temperature of the spin-reorientation transition near 223 K (where a magnetization component along the c-axis appears) and then remains constant (approximately \(-4 \text{ K}\)). The contribution from the paraprocess is positive and has substantial values near the Curie temperature. At \( T = 223 \text{ K} \) it reaches a value of about 4.3 K. The last term in eq. (7.6) is small and negative below 223 K. The total MCE calculated as a sum of these three contributions is in good accordance with experimentally measured negative MCE below 223 K for \( \Delta H = 60 \text{ kOe} \) (Nikitin et al. 1988b).

7.2.2. Gd–Dy, Gd–Ho and Gd–Er alloys

The MCE in polycrystalline Gd–Ho and Gd–Er alloys was investigated by Nikitin et al. (1985b).

According to magnetization studies in Gd–Ho alloys a PM–FM transition at the Curie temperature \( T_C \) takes place if the Gd concentration exceeds 75 at.\% and a HAFM structure exists between \( T_C \) and \( T_N \), if the Gd concentration lies in the interval from 13 to 75 at.\% (Fujii et al. 1976). In Gd\(_{0.8}\)Ho\(_{0.2}\) a maximum in the \( \Delta T(T) \) curve was found caused by the PM–FM transition. In the alloys with higher Ho concentrations a high-temperature MCE maximum related with the HAFM–PM transition at \( T_N \) was observed. In Gd\(_{0.2}\)Ho\(_{0.8}\) a broad MCE maximum occurs in the temperature interval from 40 to 140 K (for \( \Delta H = 20 \text{ kOe} \)), which is associated with the HAFM–FM transition. In fields \( H > H_{cr} \) this maximum disappears. Tishin (1990d) determined \( \Delta S_M(T) \) curves for the Gd\(_{0.8}\)Ho\(_{0.2}\)

<table>
<thead>
<tr>
<th>Measurements on single crystals (the direction of magnetic field is shown in parenthesis)</th>
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<tbody>
<tr>
<td>** In J/kg K</td>
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</table>

References:

(a) Nikitin et al. (1981)
(b) Nikitin et al. (1988b)
(c) Nikitin et al. (1980)
(d) Nikitin et al. (1985b)
(e) Tishin (1990d)
(f) Smaili and Chahine (1996)
(g) Smaili and Chahine (1997)
(h) Nikitin (1989)
(i) Nikitin and Tishin (1989)
(j) Tishin (1988)
(k) Nikitin et al. (1989c)
(l) Zimm (1994)
alloy on the basis of magnetization measurements and eq. (2.71). The $\Delta S_M$ maximum was found near $T_C$ for $\Delta H = 10$ kOe.

Gd–Er alloys exhibit more complex magnetic structures (Bozorth 1967; Millhouse and Koehler 1970; Fujii et al. 1976). Below $T_N$, AFM structures are observed if the Er concentration exceeds 30 at.%, but they are more complicated than simple helicoidal. As in Er, spin oscillations along the $c$-axis take place. The complex magnetic structures cause the appearance of maxima in the $\Delta T(T)$ curves at $T_N$ and $T_C$, where a transitions from AFM to a ferromagnetic spiral-type structure occurs. In the Gd$_{0.8}$Er$_{0.2}$ alloy the MCE maximum is due to the PM–FM transition, and for the others investigated alloys it is due to an AFM–ferromagnetic spiral transition. The magnetic entropy change $\Delta S_M$ was calculated from the magnetization data for Gd$_{0.84}$Er$_{0.16}$ alloy by Tishin (1990d) and for Gd$_{0.9}$Er$_{0.1}$ and Gd$_{0.69}$Er$_{0.31}$ alloys by Smaili and Chahine (1996). The MCE and $\Delta S_M$ values for Gd–Ho and Gd–Er alloys are presented in table 7.4.

It was found that the maximum MCE value near $T_N$ is proportional to $T_N$ in Gd–Ho and Gd–Er alloys (Nikitin et al. 1985b). Since $T_N \sim G^{2/3}$, where $G = (gJ - 1)^2 J(J + 1)$ is de Gennes factor, $\Delta T(T_N)$ should be approximately proportional to $G^{2/3}$. Such a dependence (for an average de Gennes factor) was observed in Gd–Ho and Gd–Er alloys.

The magnetic entropy change $\Delta S_M$ for Gd–Dy alloys was calculated by Burkhanov et al. (1991) and Smaili and Chahine (1997) from the magnetization data. Maxima of $\Delta S_M$ were observed near the temperatures of transition from the paramagnetic to the magnetically ordered state. Their values are presented in table 7.4.

7.2.3. Tb–Y, Dy–Y and Tb–Dy alloys

According to neutron diffraction measurements, heavy REM-yttrium alloys order below $T_N$ in an antiferromagnetic structure of the same type that exists in the corresponding pure heavy REM (Koehler et al. 1963; Child et al. 1965). Magnetization measurements showed that in Tb$_x$Y$_{1-x}$ alloys a HAFM structure exists from helium temperatures to $T_N$ for $x = 0.1–0.63$. For $x \geq 0.835$ a HAFM–FM transition at $T_C$ takes place (Nikitin 1989). The easy and hard magnetization directions in Tb$_x$Y$_{1-x}$ alloys are the crystallographic $b$- and $c$-axis, respectively.

MCE measurements in Tb$_x$Y$_{1-x}$ alloys with PM–HAFM and HAFM–FM transitions were carried out in fields up to 16 kOe by Nikitin et al. (1977a, 1977b), Nikitin (1978), Nikitin and Andreenko (1981), Nikitin and Tishin (1989). A tricritical point $T_K$ was found in the phase diagram $H_{cr}(T)$ of the alloys. The $\Delta T(T)$ curves were analogous to those obtained for Dy (see fig. 7.7). Below $T_K$, jumps in the $\Delta T(H)$ curves were observed. The contributions to the MCE arising at the field-induced HAFM–FM transition at $H = H_{cr}$ were determined for Tb$_{0.835}$Y$_{0.135}$ alloy by Nikitin (1989). The MCE at the transition was obtained from the equation:

$$\frac{C_p,H \Delta T(H_{cr})}{T} = S_{HAFM} - S_{FM} = \left(\frac{\partial G_{FM}}{\partial T}\right)_p - \left(\frac{\partial G_{HAFM}}{\partial T}\right)_p,$$

where $G_{HAFM}$ and $G_{HAFM}$ are the Gibbs energy in the FM and HAFM states, respectively. The Gibbs energy in the corresponding magnetic phase was written down as:

$$G = F_{ex} + E_{me} + E_{K} - HI,$$
where $F_{ex}$ is the free energy of the exchange interaction between the basal planes, $E_{me}$ is the energy of the magnetoelastic interaction, $E^{b}_{A}$ is the basal plane anisotropy energy, and $I$ is the magnetization. From eqs (7.7) and (7.8) it follows that the MCE due to the HAFM–FM transition at $H = H_{cr}$ is:

$$\Delta T(H_{cr}) = \frac{T}{C_{p,H}} \left( \frac{\partial \Delta F_{ex}}{\partial T} + \frac{\partial \Delta E_{me}}{\partial T} + \frac{\partial \Delta E^{b}_{A}}{\partial T} - H_{cr} \frac{\partial \Delta I}{\partial T} \right),$$

(7.9)

where $\Delta$ denotes the change of the corresponding parameter across the transition ($\Delta I = I_{FM} - I_{HAFM}$). The calculations were made on the basis of experimental data on magnetostriction, anisotropy and magnetization and showed that for $T \gg 137 \text{ K} > T_{c}$ in Tb$_{0.835}$Y$_{0.135}$ the main contribution to $\Delta T(H_{cr})$ comes from interplane exchange and magnetoelastic energy changes. The last contribution is due to the giant magnetostriction across the field induced HAFM–FM transition. As the temperature increases, the role of this contribution decreases and the negative exchange and positive Zeeman contributions become prevalent. Near the tricritical temperature $T_{K} = 190 \text{ K}$ these contributions compensate each other and $\Delta T(H_{cr}) = 0$. The results of calculations are confirmed by experimental $\Delta T(H)$ curves.

Nikitin and Tishin (1989) measured the MCE in Tb$_x$Y$_{1-x}$ alloys in fields up to 60 kOe. The temperature dependence of the MCE in the Tb$_{0.1}$Y$_{0.9}$ alloy measured along the $b$-axis shows a maximum near the magnetic ordering temperature $T_N$. Upon cooling the MCE changes sign and becomes negative. When the field was applied along the $c$-axis the maximum of positive MCE near $T_N$ was broader than in the case of that $H$ was applied along the $b$-axis. At $T = 30 \text{ K}$ a MCE minimum was observed with $\Delta T = -0.17 \text{ K}$ at $\Delta H = 60 \text{ kOe}$. These data lead to the conclusion that application of a magnetic field along the $c$-axis results in a transformation of the magnetic structure. A ferromagnetic spiral seems to appear for the case that $H$ is applied along the $c$-axis, when the magnetization has a ferromagnetic component along the $c$-axis and its basal plane component remains helicoidal.

Figure 7.14 shows the temperature dependences of the MCE in Tb$_{0.63}$Y$_{0.37}$ alloy for $H$ applied along $b$-axis. When $\Delta H < 22 \text{ kOe}$ the MCE changes sign at low temperatures and displays a minimum with a value of $-0.6 \text{ K}$ at $T = 168 \text{ K}$ and $\Delta H = 15 \text{ kOe}$. In stronger fields ($\Delta H > 22 \text{ kOe}$), a negative MCE is not observed. This can be explained by the complicated temperature behavior of the MCE contribution arising from the destruction of the HAFM structure (see the magnetic phase diagram $H_{cr}(T)$ in the inset in fig. 7.14). Near $T_N$ the MCE is mainly controlled by the paraprocess and has a sharp maximum. The negative MCE in Tb$_{0.1}$Y$_{0.9}$ and Tb$_{0.63}$Y$_{0.37}$ alloys was explained by the authors by the field-induced distortion of the HAFM structure which reduces, in the initial stage, the magnetic ordering and increases the magnetic entropy. The MCE maximum values near $T_N$ in Tb$_x$Y$_{1-x}$ alloys are presented in table 7.4. The maximum $\Delta S_M$ values were calculated by eq. (2.77) on the basis of MCE and heat capacity data (Nikitin and Tishin 1989).

Tishin (1988) investigated the MCE in a Dy$_{0.7}$Y$_{0.3}$ single crystal in fields applied along the easy magnetization axis $a$. The MCE measurements made by a direct method for $\Delta H = 20–50 \text{ kOe}$ revealed two maxima: at $T = 70 \text{ K}$ and $T_N = 135 \text{ K}$, which were explained by the complicated character of the temperature dependence of the critical field
Fig. 7.14. Temperature dependences of the MCE in the Tb_{0.63}Y_{0.37} alloy in fields applied along the b-axis: (1) $\Delta H = 15$ kOe; (2) 20 kOe; (3) 25 kOe; (4) 35 kOe; (5) 45 kOe; (6) 60 kOe. The insert shows the magnetic phase diagram $H_{cr}(T)$ (Nikitin and Tishin 1989).

$H_{cr}(T)$. For $\Delta H \leq 20$ kOe temperature dependence of the MCE displays one maximum near $T_N$. Negative MCE values are observed in the temperature interval from 90 to 110 K for $\Delta H < 25$ kOe. By analogy with Dy, this was explained by the formation of a fan structure. The $\Delta T(H)$ curves are similar to those for Dy and provide evidence that the HAFM–FM transition is of the first order in the interval from 4.2 to 110 K. In the region from 65 to 135 K this transition occurs via an intermediate fan structure. The HAFM–fan transition is of the first order in the interval from 65 to 110 K and of the second order above 110 K, where no jumps were observed in $\Delta T(H)$ curves. At the tricritical point $T_K = 110$ K the MCE due to the destruction of the HAFM structure is equal to zero and because of this a minimum in the $\Delta T(T)$ curve was observed.

Nikitin et al. (1989c) measured the MCE in polycrystalline Tb$_x$Dy$_{1-x}$ alloys with $x = 0.25$; 0.5 and 0.75 by a direct method. The temperature dependences of the MCE for $\Delta H = 13$ kOe (the maximum $H_{cr}$ for Dy is about 10 kOe (Nikitin et al. 1991b)) in the alloys with $x \leq 0.5$ have two maxima and resemble those of the Gd–Ho alloys with high Ho content (see section 7.2.2). For Tb$_{0.5}$Dy$_{0.5}$ alloy the value of the high-temperature maximum at $T = 207$ K. For the latter, $\Delta T \approx 1.7$ K is larger than for the low-temperature maximum at $T = 175$ K ($\Delta T \approx 1.1$ K). For $x = 0.25$ the maxima are approximately equal. The authors related these maxima with the HAFM–FM and HAFM–PM transitions.
Field and temperature dependences of the magnetization characteristic of the presence of a HAFM structure were observed in a Tb$_{0.8}$Dy$_{0.5}$ single crystal by Bykhover et al. (1990). A minimum corresponding to the tricritical point $T_K$ was observed in the $\Delta T(T)$ curves obtained with $\Delta H = 13$ kOe for $x = 0.25$ (at $T \approx 190$ K) and for $x = 0.5$ (at $T \approx 200$ K). A negative MCE appears for $x = 0.25$ near 190 K and was related with the formation of a fan structure. The low-temperature MCE maximum disappears in strong magnetic fields.

7.2.4. Er–La alloys

The temperature dependences of the heat capacity and the MCE of the polycrystalline Er$_{0.8}$La$_{0.2}$ alloy were measured by Zimm et al. (1994) in fields up to 70 kOe. Only one maximum and one anomaly, characteristic for ferromagnets, were observed in the $\Delta T(T)$ and $C(T)$ curves, respectively. Magnetization measurements confirmed the ferromagnetic ordering in Er$_{0.8}$La$_{0.2}$. The maximum $\Delta T$ value obtained in the Er$_{0.8}$La$_{0.2}$ alloy is not much larger than that of Er (see tables 7.2 and 7.4).

On the basis of heat capacity data a magnetic entropy value of 111 J/kg K was calculated by eq. (2.76) when the integration was made from 0 to 100 K. This value corresponds to $J = 7.8$, being close to $J = 15/2$ for Er.

8. Magnetocaloric effect in nanocomposite systems

In this section we shall consider the experimental investigations of the MCE in various nanocomposite systems which have attracted attention in recent years.

Shao et al. (1996a, 1996b) studied the MCE in nanocomposite ribbons prepared by a copper-sheated rolling technique from Gd$_{0.85}$Tb$_{0.15}$, Gd$_{0.85}$Y$_{0.15}$ and Gd$_{0.75}$Zr$_{0.25}$ alloys. The arc-melted and homogenized alloys were resolidified into amorphous particles about 20 nm in diameter by melt-spinning. Then these particles were milled within a sealed agate bowl containing agate balls. This method allowed it to obtain powder particles finer than mesh size 360 nm. X-ray analyzes showed that the milling led to the formation of nanocrystallites of 10–20 nm size within the original amorphous particles, although part of them remained amorphous. The powder was packed into an annealed copper tube, sealed at both ends and then rolled into the copper sheated nanocomposite ribbon. The powder density in the ribbon was about 80% of that of the corresponding bulk alloy. The samples cut from the composite ribbons had the dimensions of $5 \times 5 \times 0.8$ mm.

Heat capacity measurements made on the ribbons in the temperature range of 280–310 K revealed an increase with a maximum mean value of 57.9% for Gd$_{0.85}$Y$_{0.15}$. On the other hand, the Curie temperature was reduced in the ribbons. Shao et al. (1996a) related these experimental facts with the large proportion of interface atoms arranged in disorder, which changed the interatomic distances and lowered the number of the nearest neighbors.

The MCE (and $\Delta S_M$) in nanosized Gd$_{0.85}$Y$_{0.15}$ ribbons was higher than in bulk material at temperatures above 240 K, see fig. 8.1. Such behavior is characteristic for superparamagnets (see fig. 2.4). At the same time no enhancement in the MCE was observed in the investigated Gd$_{0.85}$Tb$_{0.15}$ and Gd$_{0.75}$Zr$_{0.25}$ ribbons.

Investigation of magnetic and magnetocaloric properties of amorphous Dy$_{70}$Zr$_{30}$ and Dy$_{30}$Zr$_{70}$ allowed Giquere et al. (1999) to conclude that the materials can be considered as nanocomposites with interacting clusters.
Many investigations were devoted to the studies of the MCE (or the corresponding magnetic entropy change) in the nanocomposite compound Gd$_3$Ga$_{5-x}$Fe$_x$O$_{12}$ ($x < 2.5$), also known as gadolinium gallium iron garnet (GGIG). Results have been presented by McMichael et al. (1993b), Shull et al. (1993), and Shull (1993a, 1993b). It is a magnetic nanocomposite present as a single crystallographic phase which according to X-ray data has the gadolinium gallium garnet (Gd$_3$Ga$_5$O$_{12}$ (GGG)) structure. The magnetic properties change considerably after addition of Fe relative to GGG which has simple paramagnetic behavior above 1 K (McMichael et al. 1993a, 1993b; Numazawa et al. 1996). Magnetization measurements reveal superparamagnetic behavior for $0 \leq x \leq 2.5$ and ferromagnetic behavior for $x \geq 2.5$. It is supposed that the formation of magnetic nano-scaled clusters is due to Gd-Gd interactions of the superexchange type realized via the Fe atoms (Shull 1993). Ferromagnetic resonance and Mössbauer spectroscopy data confirm that GGIG consists of nano-sized magnetic clusters.

Figure 8.2 shows the magnetic entropy change after removal of 9 kOe, calculated by eq. (2.71) for GGIG with $x = 0, 1, 1.75, 2.5,$ and 5 on the basis of magnetization data. One can see an obvious increase of $\Delta S_M$ in the high-temperature region for increasing iron concentration. This is in qualitative agreement with theoretical results presented in fig. 2.2 under the assumption that higher iron concentration corresponds to larger cluster sizes. Extrapolation shows that samples with smaller $x$ will have larger $\Delta S_M$ values below 6 K. The intersections of the $\Delta S_M$ curves for $x \neq 0$ with the GGG curve occur at higher temperatures when $x$ increases, which was also predicted by theoretical calculations (see fig. 2.2). Measurements for $\Delta H = 50$ kOe showed that addition of iron to GGG did not cause such strong magnetic entropy changes as for $\Delta H = 9$ kOe, but the enhancement was still significant for temperatures above 9 K. It was established by Shull et al. (1993) that for $x = 1.75$ no hysteresis losses were observed.

McMichael et al. (1993a, 1993b) investigated $\Delta S_M(T)$ curves for rapidly solidified Nd$_{0.14}$(Fe$_{1-x}$Al$_x$)$_{0.8}$B$_{0.06}$ alloys ($x = 0; 0.1; 0.2$) for $\Delta H = 9$ kOe in the temperature range of 290–500 K. X-ray analyzes showed that the material, produced in the form of melt-spun ribbons, was structurally amorphous. $\Delta S_M(T)$ curves were calculated from magnetization data by eq. (2.71). Figure 8.3 shows that near the Curie temperatures (determined by differential scanning calorimetry) broad peaks of $\Delta S_M$ are observed. The
obtained results were interpreted in the framework of mean field calculations made for superferromagnets (see fig. 2.4). The experimental $\Delta S_M(T)$ curve for $x = 0.2$ was shown to be in good agreement with that calculated for cluster magnetic moments of about $20\mu_B$, corresponding to about 10 atoms of Fe. It was concluded that the magnetic structure of the alloy can be regarded as consisting of regions with local concentration fluctuations, rather than an assembly of distinct nanometersized magnetic particles dispersed in a nonmagnetic matrix. However, the magnetocaloric properties of these alloys display the characteristics predicted for superferromagnet nanocomposites.
Kokorin et al. (1984) studied the water quenched alloys \( \text{Cu}_{0.783}\text{Ni}_{0.13}\text{Fe}_{0.087} \) and \( \text{Cu}_{0.63}\text{Ni}_{0.22}\text{Fe}_{0.15} \). It was shown that the alloys were inhomogeneous solid solutions consisting of a nonmagnetic matrix with low concentration of Fe and Ni, and ferromagnetic inclusions rich in Fe and Ni, dispersed in the matrix. Mean dimension of the inclusions were 3–5 nm. Subsequent annealing of the samples at 773–973 K led to size increase of the inclusions. Also their number and the concentration of Ni and Fe in the inclusions increased.

According to magnetic susceptibility measurements \( \text{Cu}_{0.783}\text{Ni}_{0.13}\text{Fe}_{0.087} \) displays at some temperature (at about 77 K for the as-quenched state and at about 300 K for the annealed state) a transition to a spin-glass like state due to the interactions between the magnetic clusters (Kokorin and Perekos 1978). At this transition no \( \Delta T \) maximum was observed. At high temperatures, where the alloys displayed superparamagnetic behavior, a maximum of the MCE was found. This was attributed to the occurrence of ferromagnetic order inside the inclusions according to the second term in eq. (2.103). The maximum MCE value was \( \Delta T \approx 10^{-2} \) for \( \Delta H = 15 \) kOe at \( T \approx 750 \) K for the annealed state. The temperature of the \( \Delta T \) maximum corresponds to the Curie temperature of the magnetic particles in the material (628 K for the as-quenched state and 740 K for the annealed state).

The \( \text{Cu}_{0.63}\text{Ni}_{0.25}\text{Fe}_{0.15} \) alloy is characterized by stronger interactions between the magnetic inclusions. It displays a superferromagnetic type of order, occurring at a temperature \( T_1 \), which is close to the Curie temperature of the inclusions in the material. That is why the observed MCE (with a maximum value about 0.015 K for \( \Delta H = 15 \) kOe near 700 K) and the magnetic susceptibility anomaly approximately coincide on the temperature scale (Kokorin et al. 1984).

9. Magnetocaloric effect in \( \text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4 \) alloys

The \( \text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4 \) alloys, some of which exhibit a large magnetocaloric effect, were investigated by Pecharsky and Gschneidner (1997a, 1997b, 1997c, 1997d). Three phase regions were found: the \( \text{Gd}_5\text{Si}_4 \)-based solid solution for \( 0.5 \leq x \leq 1 \), the \( \text{Gd}_5\text{Si}_4 \)-based solid solution for \( 0 \leq x \leq 0.2 \) (both these phases have an orthorhombic crystalline structure) and a ternary phase with the monoclinically distorted \( \text{Gd}_5\text{Si}_4 \) structure for \( 0.24 \leq x \leq 0.5 \). Magnetic and heat capacity measurements allowed to construct a magnetic phase diagram. The alloys with \( 0.5 \leq x \leq 1 \) have simple ferromagnetic structures with the Curie temperatures from 295 to 335 K. The alloys with \( 0 \leq x \leq 0.2 \) order in two steps: ferrimagnetically at the upper transition temperature and ferromagnetically at the lower one. The upper transition temperature is almost independent of composition (\( \sim 130 \) K), while the lower transition temperature decreases proportionally (down to 20 K) with decreasing \( x \). The ternary solid solution phase alloys \( (0.24 \leq x \leq 0.5) \) also order magnetically in two steps. Upon cooling they initially order at \( T_{c1} \) to form a ferromagnetic structure 1 with a low net magnetic moment and later the second transition to a ferromagnetic structure 2 (at \( T_{c2} \)) occurs. The difference between \( T_{c1} \) and \( T_{c2} \) for \( x = 0.24–0.5 \) is about 40 K. For all the alloys with \( x \leq 0.5 \) the high-temperature magnetic transition is of the second-order type and the lower one is the first-order transition. Heat capacity measurements showed that the first-order nature of the lower magnetic transition was preserved even in high magnetic fields (\( \sim 100 \) kOe).
The magnetic entropy change $-\Delta S_M$ (for $\Delta H = 50$ kOe) of Gd$_5$(Si$_{1-x}$Ge$_{1-x}$)$_4$ alloys with $x = 0-0.5$ was obtained by Pecharsky and Gschneidner (1997a) from the heat capacity and magnetization measurements. It was found that the main part of $\Delta S_M$ (about 90%) is associated with the lower temperature first-order magnetic transition which is due to the sharp change in magnetization at the transition temperature. Although the first-order transition is characterized by hysteresis, the magnetic structure changes back to ferromagnetic (or ferrimagnetic) and remnant magnetization becomes zero after removing of the magnetic field. The comparison, made by Pecharsky and Gschneidner (1997a) with other known high-$\Delta S_M$ materials (such as DyAl$_2$, GdAl$_2$, Gd$_{0.73}$Dy$_{0.27}$, Gd) showed that $\Delta S_M$ is 2–10 times larger in these Gd$_5$(Si$_{1-x}$Ge$_{1-x}$)$_4$ alloys ($x = 0–0.5$). For the alloys with $x > 0.5$ a substantial decrease of $\Delta S_M$ (about three times) was observed. The authors related it with the second-order nature of the paramagnetic–ferromagnetic transition taking place in these alloys.

The MCE of the alloys with $x = 0–0.5$ determined on the basis of heat capacity data is shown in fig. 9.1. The MCE exhibits peaks near the temperature of the first-order transition and reaches the value $\sim 18$ K for $x = 0.43$.

Pecharsky and Gschneidner (1997c) investigated the effect of substituting small amounts (up to 0.6 at.%) of Fe, Co, Ni, Cu, Ga, Al and C on $\Delta S_M$ and MCE in Gd$_5$(Si$_2$Ge$_2$). It was found that the substitution of Fe, Co, Ni and Cu led to the Curie temperature
increase with simultaneous $|\Delta S_M|$ decrease. The maximum value of $|\Delta S_M|$ found for Gd$_5$(Si$_{1.985}$Ge$_{1.985}$Ni$_{0.03}$) was $|\Delta S_M| \approx 12.4$ J/kg K for $\Delta H = 50$ kOe at $T \approx 296$ K. This was related by the authors with the loss of the first-order nature of the magnetic phase transition, which was confirmed by magnetization measurements. The addition of carbon and aluminum acted similarly as Fe, Co, Ni and Cu, leading to the elimination of the first-order transition and to conditions for the occurrence of a giant MCE. Addition of Ga in an amount of 0.33 at.% preserved the first-order nature of the lower magnetic transition in Gd$_5$(Si$_2$Ge$_2$) and increased its temperature from $T_c \approx 276$ K to about 286 K. The $-\Delta S_M$ value for Gd$_5$(Si$_{1.985}$Ge$_{1.985}$Ga$_{0.03}$) was $\approx 17.6$ J/kg K at $T \approx 286$ K and the maximum $\Delta T$ value was about 14.8 K at $T \approx 292$ K for $\Delta H = 50$ kOe, which is almost the same as in Gd$_5$(Si$_2$Ge$_2$) alloy. The substitution of 0.67 at.% Ga shifted the magnetic ordering temperature to higher temperatures of about 300 K, but led to the loss of the giant MCE (the maximum value of $|\Delta S_M|$ was about 9.5 J/kg K at $T \approx 300$ K). It should be noted that the heat capacity measurements of Gd$_5$(Si$_{1.985}$Ge$_{1.985}$Ga$_{0.03}$) showed that the lower and upper magnetic transitions merged between 50 and 75 kOe into the single second-order transition at temperatures above 320 K.

10. Magnetocaloric effect in amorphous materials

The magnetic properties and $\Delta S_M$ were examined in R$_{0.7}$TM$_{0.3}$ ($R =$ Gd, Tb, Dy and Er; TM = Fe and Ni) and Gd$_{0.65}$Co$_{0.35}$ amorphous alloys by Liu et al. (1996a). The melt spanning was used to form ribbons 30–40 µm thick and 20 mm wide. The amorphism of the samples was confirmed by X-ray diffraction analysis. The heat capacity was measured for Gd$_{0.7}$Ni$_{0.3}$, Er$_{0.7}$Fe$_{0.3}$ and Gd$_{0.65}$Co$_{0.35}$ and used to calculate $\Delta S_M(T)$ and $\Delta T(T)$ curves by the method described in section 3.3. For other alloys $\Delta S_M$ was obtained on the basis of magnetization data.

Magnetic and the Mössbauer measurements showed, that below the Curie temperature the investigated alloys ordered ferromagnetically for R = Gd and displayed complex non-collinear magnetic structures for anisotropic R ions. The magnetic moment of the 3d ions was small or did not exist, so the magnetothermal properties were determined by the R magnetic subsystem. The coercivity near $T_C$ was negligible even in the alloys with anisotropic R ions, although magnetic saturation was not achieved in these alloys in high magnetic fields. The Curie temperatures of the alloys, obtained from magnetization measurements, are shown in table 10.1.

The $\Delta S_M(T)$ and $\Delta T(T)$ curves for Gd$_{0.7}$Ni$_{0.3}$, Er$_{0.7}$Fe$_{0.3}$ and Gd$_{0.65}$Co$_{0.35}$ alloys are presented in fig. 10.1. One can see that the curves have broad maxima with relatively low heights near $T_C$. The zero-field heat capacity measurements showed that a $\lambda$-type anomaly at $T_C$ is absent in these alloys. Such behavior in these amorphous materials was explained by the authors by the broad character of magnetic phase transition due to fluctuations of the exchange integrals resulting from the structural disorder. Calculations of the temperature dependences of the heat capacity made by the authors for various degrees of exchange integral fluctuations in the framework of MFA, confirmed this proposition.

Further investigations of the magnetothermal properties of amorphous R–TM alloys were made by Liu et al. (1996b) on R$_{0.7}$(Fe$_{x}$Ni$_{1-x}$)$_{0.3}$ ($R =$ Gd and Dy) melt-spun ribbons. It was found that the addition of Fe led to an increase of $T_C$ from 130 to 300 K for
<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T_C$, K</th>
<th>$T_{T_{\text{max}}}$, K</th>
<th>$\Delta T$, K</th>
<th>$\Delta H$, kOe</th>
<th>$T_{S_{\text{max}}}$, K</th>
<th>$-\Delta S_M$, J/mol K</th>
<th>$\Delta H$, kOe</th>
</tr>
</thead>
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<tr>
<td>Dy$<em>{0.7}$Fe$</em>{0.3}$</td>
<td>108$^a$</td>
<td>$\approx 40^a$</td>
<td>$3.7^a$</td>
<td>$80^a$</td>
<td>$\approx 108^a$</td>
<td>0.93$^a$</td>
<td>$10^a$</td>
</tr>
<tr>
<td>Er$<em>{0.7}$Fe$</em>{0.3}$</td>
<td>35$^a$</td>
<td>$\approx 35^a$</td>
<td>$2^a$</td>
<td>$40^a$</td>
<td>$\approx 35^a$</td>
<td>12.2$^a$</td>
<td>$80^a$</td>
</tr>
<tr>
<td>Gd$<em>{0.7}$Ni$</em>{0.3}$</td>
<td>130$^a$</td>
<td>$\approx 125^a$</td>
<td>$3.3^a$</td>
<td>$80^a$</td>
<td>$\approx 130^a$</td>
<td>5$^a$</td>
<td>$40^a$</td>
</tr>
<tr>
<td>Dy$<em>{0.7}$Ni$</em>{0.3}$</td>
<td>35$^b$</td>
<td>$\approx 125^b$</td>
<td>$1.8^b$</td>
<td>$40^b$</td>
<td>$\approx 130^b$</td>
<td>11$^b$</td>
<td>$70^b$</td>
</tr>
<tr>
<td>Gd$<em>{0.65}$Co$</em>{0.35}$</td>
<td>180$^a$</td>
<td>$\approx 210^a$</td>
<td>$2.8^a$</td>
<td>$80^a$</td>
<td>$\approx 200^a$</td>
<td>3.6$^a$</td>
<td>$80^a$</td>
</tr>
<tr>
<td>Gd$<em>{0.7}$Fe$</em>{0.12}$Ni$_{0.18}$</td>
<td>$\approx 185^b$</td>
<td>$\approx 210^a$</td>
<td>$2.1^a$</td>
<td>$40^a$</td>
<td>$\approx 200^b$</td>
<td>2.6$^b$</td>
<td>$40^b$</td>
</tr>
<tr>
<td>Fe$<em>{0.9}$Zr$</em>{0.1}$</td>
<td>$\approx 237^c$</td>
<td>$\approx 237^c$</td>
<td></td>
<td></td>
<td>$\approx 130^b$</td>
<td>7.6$^b$</td>
<td>$70^b$</td>
</tr>
<tr>
<td>Fe$<em>{0.89}$Ni$</em>{0.009}$Zr$_{0.1}$</td>
<td>$\approx 255^c$</td>
<td>$\approx 275^c$</td>
<td></td>
<td></td>
<td>$\approx 263^c$</td>
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<tr>
<td>Fe$<em>{0.88}$Ni$</em>{0.018}$Zr$_{0.1}$</td>
<td>$\approx 275^c$</td>
<td>$\approx 275^c$</td>
<td></td>
<td></td>
<td>$\approx 272^c$</td>
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<td>$14^c$</td>
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<tr>
<td>Fe$<em>{0.87}$Ni$</em>{0.027}$Zr$_{0.1}$</td>
<td>$\approx 288^c$</td>
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<td></td>
<td></td>
<td>$\approx 276^c$</td>
<td>12.5$^c$</td>
<td>$14^c$</td>
</tr>
<tr>
<td>Fe$<em>{0.855}$Al$</em>{0.045}$Zr$_{0.1}$</td>
<td>$\approx 303^c$</td>
<td>$\approx 303^c$</td>
<td></td>
<td></td>
<td>$\approx 292^c$</td>
<td>12.5$^c$</td>
<td>$14^c$</td>
</tr>
<tr>
<td>Fe$<em>{0.855}$Si$</em>{0.045}$Zr$_{0.1}$</td>
<td>$\approx 315^c$</td>
<td>$\approx 315^c$</td>
<td></td>
<td></td>
<td>$\approx 300^c$</td>
<td>12.5$^c$</td>
<td>$14^c$</td>
</tr>
<tr>
<td>Fe$<em>{0.855}$Sn$</em>{0.045}$Zr$_{0.1}$</td>
<td>$\approx 310^c$</td>
<td>$\approx 310^c$</td>
<td></td>
<td></td>
<td>$\approx 298^c$</td>
<td>12.5$^c$</td>
<td>$14^c$</td>
</tr>
<tr>
<td>Fe$<em>{0.855}$Co$</em>{0.045}$Zr$_{0.1}$</td>
<td>$\approx 315^c$</td>
<td>$\approx 315^c$</td>
<td></td>
<td></td>
<td>$\approx 307^c$</td>
<td>12.5$^c$</td>
<td>$14^c$</td>
</tr>
<tr>
<td>Fe$<em>{0.855}$Si$</em>{0.15}$B$_{0.1}$</td>
<td>$\approx 286^c$</td>
<td>$\approx 286^c$</td>
<td>$0.11^d$</td>
<td>$10^d$</td>
<td>$\approx 645^d$</td>
<td>$645^d$</td>
<td>$10^d$</td>
</tr>
</tbody>
</table>

*a* In kJ/m$^3$ K

References:
(a) Liu et al. (1996a)
(b) Liu et al. (1996b)
(c) Maeda et al. (1983)
(d) Belova et al. (1984)

Gd$_{0.7}$(Fe$_x$Ni$_{1-x}$)$_{0.3}$ alloys and from 35 to 110 K for Dy$_{0.7}$(Fe$_x$Ni$_{1-x}$)$_{0.3}$ alloys for $x$ varied from 0 to 1. Gd-based alloys showed zero hysteresis in the whole temperature range, and in Dy-based alloys the coercive force decreased with increasing temperature and became zero near $T_C$. In the low temperature range, the Dy$_{0.7}$Ni$_{0.3}$ alloy displayed a peak in the temperature dependence of the magnetization in weak magnetic field. This is characteristic for spin glass behavior (the peak was located at $\sim 20$ K for $H = 2$ kOe).

The magnetic entropy change $\Delta S_M$ was determined from the magnetization data and the MCE was estimated using $\Delta S_M$ and zero field heat capacity data in conjunction with eq. (2.77). Broad maxima were observed in the $\Delta S_M(T)$ curves near $T_C$ for both the Gd- and the Dy-based alloys. The results for Gd$_{0.7}$Fe$_{0.12}$Ni$_{0.18}$ and Gd$_{0.7}$Ni$_{0.3}$ alloys are pre-
Fig. 10.1. Temperature dependence of $-\Delta S_M$ (a) and MCE (b) induced by $\Delta H = 80$ kOe in Gd$_{0.7}$Ni$_{0.3}$ (1), Er$_{0.7}$Fe$_{0.3}$ (2) and Gd$_{0.65}$Co$_{0.35}$ (3) amorphous alloys (Liu et al. 1996a).

The substitution of Fe for part of the Ni led to broadening of the $\Delta S_M$ maximum with a simultaneous reduction of its value: 31% for Gd$_{0.7}$(Fe$_x$Ni$_{1-x}$)$_{0.3}$ and 12% for Dy$_{0.7}$(Fe$_x$Ni$_{1-x}$)$_{0.3}$ for a variation of $x$ from 0 to 0.4 and $\Delta H = 70$ kOe. It should be noted, that in Dy$_{0.7}$Ni$_{0.3}$ below 10 K positive $\Delta S_M$ values were induced by the application of a magnetic field. The authors explained this as an artificial effect caused by spin-glass magnetization behavior in this temperature interval. The $\Delta S_M$ broadening was related with the additional concentration fluctuations and further broadening of the exchange integral distribution arising from the substitution of Fe for part of the Ni. The MCE in Gd$_{0.7}$Ni$_{0.3}$ was determined on the basis of $\Delta S_M$ calculated from magnetization data. It was larger than that calculated by Liu et al. (1996a) from the heat capacity measurements, see table 10.1.

Maeda et al. (1983) studied the magnetic properties of amorphous (Fe$_{1-x}$Ni$_x$)$_{0.9}$Zr$_{0.1}$ ($x = 0, 0.01, 0.02, and 0.03$) and (Zr$_{0.95}$M$_{0.05}$)$_{0.9}$Zr$_{0.1}$ ($M = Al, Si, Ga, Ge, and Sn$) alloys, prepared by melt-spinning and piston anvil-quenching techniques. Magnetic fields up to 70 kOe were used. The $\Delta S_M(T)$ curves, obtained on the basis of these data, showed a broad maximum near the Curie temperature $T_C$. The maximum $\Delta S_M$ values and $T_C$ are presented in table 10.1. The values of $T_C$ and $\Delta S_M$ increased with increasing $x$. The atomic number of the $M$ element in the (Fe$_{0.95}$M$_{0.05}$)Zr$_{0.1}$ alloys had a small influence on the maximum $\Delta S_M$ value.

Belova et al. (1984) measured directly the MCE of a melt-spun ferromagnetic amorphous Fe$_{0.05}$Co$_{0.7}$Si$_{0.15}$B$_{0.10}$ ribbon. In the $\Delta T(T)$ curve a maximum with the value of $\Delta T = 0.11$ K was observed near $T_C = 645$ K for $\Delta H = 10$ kOe. In the temperature range from 390 to 465 K an additional $\Delta T$ anomaly was found, which was related by the authors with the temperature dependence of the local anisotropy constant.
Fuerst et al. (1994) prepared Gd$_x$Ag$_{1-x}$ ($x = 0.50; 0.70; 0.75; 0.77; 0.80; 1$) alloy ribbons by melt spinning in order to form a system containing small magnetic particles. X-ray diffraction and transmission electron microscopy analysis showed that the Gd ribbons consist of hexagonal Gd grains 0.5 $\mu$m in size. With decreasing $x$ the amount of an amorphous Gd–Ag component increased. Gd$_{0.755}$Ag$_{0.225}$ ribbons contained 100 $\AA$ sized Gd grains embedded in an amorphous matrix with composition Gd$_{0.5}$Ag$_{0.5}$. A similar picture was observed for $x = 0.7$. In Gd$_{0.5}$Ag$_{0.5}$ ribbons crystalline GdAg grains (with a mean diameter of about 100 $\AA$) but no gadolinium grains were found. From magnetization measurements $\Delta S_M(T)$ curves were calculated with the help of eq. (2.71) for $\Delta H = 9$ kOe. The Gd ribbon exhibited a $\Delta S_M$ maximum (with a value of about 2.5 J/kg K) near 290 K, which is lower than that for bulk Gd (about 3 J/kg K, as measured by the authors). For $0.7 \leq x \leq 0.8$ two broad $\Delta S_M$ maxima were observed, one near 280 K, and another in the interval 100–120 K. Their heights were 1.25, 0.75 and 0.1 J/kg K for the high-temperature maximum and 0.25, 0.6, 0.9 J/kg K for the low-temperature maximum for $x = 0.8, 0.775, and 0.7$, respectively. The authors related the former maximum with the $T_C$ of the 100 $\AA$ sized particles of Gd and the latter maximum with the $T_C$ of the ferromagnetic amorphous Gd$_{0.5}$Ag$_{0.5}$ alloy.

11. Magnetic refrigeration

In this section the possible utilization of magnetic materials in refrigeration technology will be briefly considered. At present only rare earth magnetic materials were recognized as appropriate for these purposes. According to Barclay (1994), the rare earth materials can be used in gas cycle refrigerators as passive regenerators. In magnetic refrigerators they can be applied as working materials (bodies) in externally regenerated or non-regenerative cycles. They can also serve as active magnetic regenerative refrigerators (AMRR). The main attention here will be paid to heavy rare earth metals and their alloys.

11.1. Passive magnetic regenerators

A regenerator serves to expand a refrigerator temperature span, since the temperature span produced by the adiabatic process itself is insufficient to achieve the desired temperature (especially in the case of magnetic materials). With the help of a regenerator the heat is absorbed from or returned to the working material at the various stages of a regenerative thermodynamical cycle.

In the low-temperature region the heat capacity of conventional regenerators in cryogenic refrigerators essentially decreases, since the lattice heat capacity of a solid is proportional to $T^3$ and the electronic heat capacity in metals is proportional to $T$ (see eqs (2.64) and (2.66)). In the refrigerators used for cooling of helium gas this leads to a rapid decrease of the refrigerator effectiveness because below $\approx 10$ K the volume heat capacity (the capacity per unit volume) of compressed helium increases. Buschow et al. (1975) proposed rare earth compounds as a possible solution of this problem. The statement of these authors was based on the fact that in rare earth compounds the low magnetic ordering temperatures and the associated heat capacity peaks can be combined with relatively high magnetic contributions to the volume heat capacity. Practical constructions of
the passive magnetic regenerators using Er$_3$Ni compound appeared after investigations of heat capacity of various R–Ni compounds made in Japan by Hashimoto and coworkers (see section 6.2). Kuriyama et al. (1990) and Sahashi et al. (1990) used Er$_3$Ni in a two-stage Gifford–McMahon (G–M) refrigerator as the low-temperature stage regenerator. Later ErNi$_{0.9}$Co$_{0.1}$, ErNi$_{0.8}$Co$_{0.2}$, Er$_{0.9}$Yb$_{0.1}$Ni alloys and their combinations with Er$_3$Ni were used as regenerators (Kuriyama 1994; Hashimoto et al. 1995; Satoh et al. 1996; Takashi et al. 1997). The use of passive magnetic regenerators allowed it to reach 4.2 K and to increase the cooling power in G–M refrigerators. Long et al. (1995a, 1995b) investigated heat capacity of the Er$_x$Dy$_{1-x}$Sb and RNiGe (R = Gd, Dy, Er and Y) compounds which can be suitable to regenerators in G–M refrigerators. The suggestion to use Nd (ordering temperature 20 K) as a regenerator was made by Chafe et al. (1997).

### 11.2. Magnetics refrigerators

In magnetic refrigerators nonregenerative Carnot cycle is used in conjunction with the magnetic type regenerative Brayton, Ericsson, and AMR (active magnetic regenerator) cycles (Barclay 1994).

The Carnot cycle with a temperature span from $T_{\text{cold}}$ to $T_{\text{hot}}$ is shown by the rectangle ABCD in the total entropy–temperature ($S$–$T$) diagram in fig. 11.1. The heat $Q$, corresponding to the load during one cycle of refrigeration, equals to $T_{\text{cold}}\Delta S_M$, where $\Delta S_M = S_2 - S_1$. Increasing the temperature span beyond a certain optimal value leads to a significant loss of efficiency as point C in fig. 11.1 tends to point G and the cycle becomes narrow. The temperature span of the Carnot cycle for a given $T_{\text{cold}}$ and $H$ is limited by the distance AG in fig. 11.1 (i.e., by the MCE at $T = T_{\text{cold}}$ and the field change from 0 to $H$), when $Q$ becomes zero. At temperatures above 20 K the lattice entropy of
solids strongly increases, which leads to a decrease of the Carnot cycle area (see rectangle abcd in fig. 11.1). That is why applications of the Carnot-type refrigerators are restricted to temperatures region below 20 K.

Magnetic refrigerators operating at higher temperatures have to employ other thermodynamic cycles, including processes at constant magnetic field. Such cycles, as distinct from the Carnot cycle, allow to use the area between the curves $H = 0$ and $H \neq 0$ in the $S$-$T$ diagram more fully. The rectangles AFCE and AGCH presents the Ericsson and Brayton cycles, respectively. The two cycles differ in the way the field change is accomplished, isothermally in the Ericsson cycle and adiabatically in the Brayton cycle. Realization of isofield processes in both of these cycles requires heat regeneration.

An example of magnetic refrigerator using the regenerative magnetic Ericsson cycle is the device proposed by Brown (1976), see fig. 11.2. The regenerator consists of a vertical column with fluid (0.4 dm$^3$, 80% water and 20% alcohol). The magnetic working material immersed in the regenerator consists of 1 mol of 1 mm thick Gd plates, separated by screen wire to allow the regeneration fluid to pass through in the vertical direction. The working material is held stationary in a water-cooled electromagnet while the tube containing the fluid oscillates up and down.

The first stage (fig. 11.2(a)) is isothermal magnetization, with the regenerator in its lowest position, so that the working material is at its top. Then, at constant field ($H = 70$ kOe), the regenerator tube is moved upwards (fig. 11.2(b)). The field is then reduced and cooling occurred (fig. 11.2(c)). At the last stage the working material passes back through the regenerator (fig. 11.2(d)). Then the cycle is repeated. If initially the regenerator fluid is at room temperature, after about 50 cycles the temperature at the top can reach $+46^\circ$C and

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**Fig. 11.2.** Magnetic refrigerator using the Ericsson cycle. A solid circle indicates that the field is switched on (Brown 1976).
Fig. 11.3. Construction of an AMR refrigerator operating near room temperature (Zimm et al. 1998).

The temperature at the bottom can reach \(-1^\circ\text{C}\). The temperature gradient in this device is maintained in the regenerator column.

In the AMR refrigerator the magnetic working material and regenerator are joint in one unit. The idea of such device was proposed by Barclay and Steyert (1982a). In this case the temperature gradient exists inside the working material and such cycle cannot be described by a conventional gas cycle analogue (Hall et al. 1996). The theory of the AMR cycle was developed by Barclay and Steyert (1982a), DeGregoria (1992), Hall et al. (1996) and Johnson and Zimm (1996). Initially it was found that the reversible AMR cycle requires a linear increase of the MCE with increasing temperature in the working material (see Reid et al. 1994). Then it was argued that this requirement is not necessary and only definite boundary conditions should be fulfilled on the cold and hot ends of the regenerator (Hall et al. 1996). The AMR refrigerators were demonstrated to operate in cryogenic temperature regions (Wang et al. 1995) and near the room temperature (Green et al. 1990; Zimm et al. 1998).

Let us consider the AMRR construction created by Zimm et al. (1998), which is shown in fig. 11.3. A magnetic field up to 50 kOe was provided by a helium cooled superconducting solenoid working in the persistent mode. Two beds, each composed of 1.5 kg of Gd spheres, were used as the AMR. The spheres had a diameter between 150 and 300 μm and were made by a plasma-rotating electrode process. The beds were by turns moved in
and out of the dewar bore with a magnetic field. Water was used as a heat transfer fluid. The working cycle of the device started with water cooling by blowing it through the demagnetized bed located inside the magnetic area (bottom position in fig. 11.3). Then the water passed through the cold heat exchanger picking up the thermal load from the cooling object. After this the water was blown through the magnetized bed located in the magnetic field area where it absorbed the heat evolved due to the MCE. Next the water passed through the hot heat exchanger, giving up the heat absorbed from the magnetized bed. The cycle was finished by removing of the magnetized bed from the magnet and replacing it by the demagnetized one. During the movement of the beds the water flow was stopped. One cycle takes a minimum of 6 s (0.17 Hz). Such a device, working at 0.17 Hz with the field of 50 kOe in the room temperature range with the temperature span of 5 K, provided a cooling power of 600 watts (which is about 100 times better than in previous constructions) with a maximum efficiency of 60% that of the Carnot process.

11.3. Working materials for magnetic refrigerators

As was mentioned above, refrigerators without regeneration, working with a Carnot cycle can be used below 20 K. For these purposes, oxides with low magnetic ordering temperature temperatures such as R₂Ga₅O₁₂ and RAIO₃ were proposed (Barclay and Steyert 1982b; Hashimoto 1986; Kuz’min and Tishin 1991, 1993b). Barclay and Steyert (1982b) showed that among various gadolinium oxide compounds the gadolinium gallium garnet is the most suitable one as a working material for magnetic refrigerators in the temperature range between 2 and 20 K. Kuz’mín and Tishin (1991, 1993b) and Kimura et al. (1995) have devoted their investigations to rare earth orthoaluminates with perovskite structure. From the MFA calculations made by Kuz’min and Tishin (1991) it was shown that DyAlO₃ and GdAlO₃ are the most advantageous compounds among the orthoaluminates. DyAlO₃ is more efficient in weak and moderate fields, while GdAlO₃ is better within the strong field region. An ErAlO₃ single crystal was found to be a promising material for temperatures below 20 K, as shown by magnetization measurements of Kimura et al. (1995). According to theoretical calculations made by Tishin and Bozkova (1997) some success can also be expected from the DyₓEr₁₋ₓAlO₃ orthoaluminates.

A possible construction of a magnetic refrigerator working below 20 K and utilizing the strong anisotropy of a DyAlO₃ single crystal was proposed by Kuz’min and Tishin (1991), see fig. 11.4. DyAlO₃ has μₑffective = 6.88 μB along [0 1 0] direction (b-axis) and μeffective = 0.8 μB along [0 0 1] direction (c-axis) (Kolmakova et al. 1990). The working material, having the shape of a cylinder cut along the [1 0 0] direction (a-axis), rotates from the b-axis to the c-axis. The rotation causes demagnetization and, consequently, cooling due to the MCE. The device allows the use of a short-circuited superconducting solenoid for producing the field, which can significantly reduce its weight. The advantages of this design is its simplicity and the possibility of miniaturization.

Daudin et al. (1982) suggested a solid solution between DyVO₄ and Gd₃Ga₅O₁₂ as a working material for use in an Ericsson cycle in the low-temperature range. Tomokiyo et al. (1985) proposed Dy₃Ga₅O₁₂ to be used in an Ericsson cycle below 20 K.

Initial studies in the room temperature range were carried out by Brown (1976), who used gadolinium as a working material in his magnetic refrigerator (see section 11.2).
should be noted that in almost all of the earlier studies it was proposed to use Gd \((T_C = 293\text{ K})\) as a working material for room temperature refrigerators. However, in the case of Gd only the left part of the \(\Delta S_M(T)\) curve is used. It is therefore desirable to search for working materials possessing performances as good as (or better than) Gd but having the Curie temperatures 15–20 K below 293 K. The suggestion to use binary and more complicated rare-earth alloys as a working bodies for the room temperature region was made by Tishin (1990d).

For the application in the ideal Ericsson magnetic regenerator cycle a magnetic working material should have a magnetic entropy change \(\Delta S_M\) that is constant in the cycle temperature span. As a quantitative criterion of efficiency of the working material, the maximum refrigerant capacity \((\Delta S_M \Delta T_{\text{cyc}})_{\text{max}}\) with \(\Delta T_{\text{cyc}} = T_{\text{hot}} - T_{\text{cold}}\) was used by Wood and Potter (1985). This corresponds to a cycle area in the \(S-T\) plane that is maximized for a given material, provided \(\Delta S_M\) is constant over the whole cycle. In real cycles, however, the latter condition is usually violated. Irreversible processes in the real cycles are not taken into account in the proposed estimation. A reasonable value of the refrigerant capacity that might be realized in a real cycle of magnetic refrigerators is, according to Wood and Potter (1985), about half of the computed value.

The maximum refrigerant capacity as defined above apparently depends on the value of the magnetic field. To optimize refrigerator performance and cost by choosing the proper field value, one may use the specific maximum refrigerant capacity \((\Delta S_M \Delta T_{\text{cyc}})_{\text{max}}/H\) corresponding to a field change from 0 to \(H\). Figure 11.5 shows the theoretical field dependences of the specific maximum refrigerant capacity for Tb–Gd alloys (Tishin 1990a). \(\Delta S_M\) curves for the Tb–Gd alloys were calculated on the basis of MFA (Tb–Gd alloys with Gd contents higher than 6 at.% order ferromagnetically). It can be seen that with increasing Tb content, the specific maximum refrigerant capacity increases throughout the range of magnetic fields. A sharp decrease in the refrigerant capacity with the field decrease begins only for \(H \leq 10\text{ kOe}\). Analysis of the data has led to two important conclusions (Tishin 1990a): (1) the use of Tb–Gd alloys as magnetic refrigerators near room temperature is more effective than the use of pure Gd; (2) Gd and its alloys with Tb have a high
specific refrigerant capacity over a wide range of fields from 10 to 60 kOe, which enables one to construct magnetic refrigerators in which relatively weak fields are used.

Investigations in the room temperature region were continued by Tishin (1990d) with ferromagnetic alloys Gd–Tb, Gd–Dy, Gd–Er and Gd–Ho of high Gd concentration. Their $\Delta S_M(T)$ curves were measured and calculated on the basis of MFA. These binary alloys have the Curie temperatures close to room temperature. It was shown that Gd–Tb and Gd–Dy alloys are the most promising ones as working materials.

Further progress in optimizing magnetic refrigerators can be achieved using complex working bodies consisting of several parts, such as plates of foil, each prepared from a certain alloy. The specific weight of each of the required alloys can be changed by varying either the number of plates made from that alloy or the plate thickness. Roubeau, Steyert and Barclay put forward the idea of using a magnetic refrigerator in which the ordering temperature varies along the refrigeration column. Wood and Potter (1985) proposed the use of a porous ferromagnetic refrigerant with such an arrangement.

Tishin (1990d) showed that for a complex working material made from Gd$_{0.9}$Tb$_{0.1}$ and Gd$_{0.4}$Tb$_{0.6}$ in the ratio of 0.78:0.22 the value $\Delta S_M = 0.3$ J/mol K for $\Delta H = 10$ kOe can be achieved in the temperature interval from 255 to 295 K. Burkhanov et al. (1991) carried out an experimental study of Gd–Dy alloys and revealed that a complex working material consisting of 59% Gd and 41% Gd$_{0.9}$Dy$_{0.1}$ is the most promising refrigerant for the room temperature region. The effective Curie point of this complex material is below room temperature and $\Delta S_M$ reaches a value of 0.8 J/mol K at 10°C.

Rare earth alloys which can be used as working materials for magnetic refrigeration in the temperature interval from 20 to 250 K have also been extensively studied (Tishin 1990e, 1990f). A comparison of the refrigerant capacity of AFM rare earth metals and alloys with the results of Wood and Potter (1985) showed that the materials where the AFM structure was destroyed by a relatively small magnetic field were often more advantageous.
than ferromagnets. According to the temperature dependence of $\Delta S_M$ (see fig. 7.5) the rare earth metals are efficient within certain narrow temperature intervals. Thus, Ho is the most suitable for cycles from 20 to 135 K, where its refrigerant capacity reaches 129 J/mol for $H = 60$ kOe. Er is good enough for the range from 20 to 85 K, where its refrigerant capacity is 72 J/mol for $H = 60$ kOe. For Dy ($\Delta S_M \Delta T_{cyc})_{max} = 87.3$ J/mol in the temperature interval from 100 to 190 K. The specific maximum refrigeration capacity was considered by Tishin (1990f) who showed that Dy is a promising working material for refrigerators using relatively small ($\approx 10$ kOe) magnetic fields, whereas Ho is advantageous for $H \geq 50$ kOe.

The results discussed above show that the problem of finding magnetic materials capable of working in a cycle with a wide temperature span can most advantageously be solved by using alloys of rare earth metals. With this end in view the Gd–Ho, Gd–Er, Gd–Tb and Gd–Dy alloys were studied by Nikitin and Tishin (1988). Figure 11.6 shows the maximum refrigeration capacity of these alloys for $H = 60$ kOe as a function of Gd content. Whereas Gd–Dy alloys were found to be best for the room temperature range (see above), Gd–Ho are preferable at lower temperatures. Thus, for fixed Ericsson cycle parameters, $T_{hot} = 300$ K, $T_{cold} = 20$ K and $H = 60$ kOe, a maximum refrigeration capacity of 60.5 J/mol is shown by Gd$_{0.8}$Ho$_{0.2}$ alloy. Therefore this alloy can be recommended as a working material for a magnetic refrigerator operating from room temperature down to 20 K.

Still better results in the range from 20 to 300 K can be achieved using a complex working body. The best results were achieved with Ho, Tb$_{0.5}$Dy$_{0.5}$ and Gd$_{0.6}$Tb$_{0.4}$, working in the intervals 20–135, 135–215, and 215–300 K, respectively. In this case ($\Delta S_M \Delta T_{cyc})_{max} = 269$ J/mol (Tishin 1990c, 1990f).

Fig. 11.6. Dependence of maximum refrigerant capacity of: (1) Gd$_x$Ho$_{1-x}$; (2) Gd$_x$Tb$_{1-x}$; (3) Gd$_x$Dy$_{1-x}$ and (4) Gd$_x$Er$_{1-x}$ on Gd content $x$ ($H = 60$ kOe) (Nikitin and Tishin 1988).
Hashimoto (1986, 1991) proposed for the magnetic Ericsson cycle with a temperature span from 10 to 80 K the use of complex magnetic materials consisting of RA12 intermetallic compounds (R = heavy rare earth metal). A layered material with the composition ErAl2, HoAl2 and Ho0.5Dy0.5Al2 in a molar ratio of 0.312: 0.198: 0.490 had an almost constant $\Delta S_M$ value of about 3 J/mol K in the temperature range from 10 to 45 K for $\Delta H = 50$ kOe. A similar result was obtained for a complex sintered material of the same composition. $\Delta S_M$ in the complex sintered material composed of the (Gd0.9Dy0.1)3Al2 and Gd3Al2 compounds which can be used near room temperatures was studied by Chang et al. (1998). A promising result was obtained below 35 K by Tomokiyo et al. (1986) using RNi2 compounds (R = Dy, Ho, Er).

Pecharsky and Gschneidner (1997a, 1997b) proposed the use of the alloys Gd5(Si$_x$Ge$_{1-x}$)$_4$ (see section 9) with large MCE as working materials for magnetic refrigerators. It was shown that the temperature of the MCE maximum can be easily tuned between 30 and 275 K by changing $x$. Adding Ga led to an increase of the MCE maximum temperature to about 290 K. A comparison of the refrigerant capacity of some of Gd5(Si$_x$Ge$_{1-x}$)$_4$ alloys with other magnetic materials used as refrigerants showed that the former possesses 25–70% more capacity than the latter (Gschneidner et al. 1998). (Gd$_{1-x}$Er$_{x}$)NiAl is another promising working material for temperatures below 60 K. It has table-like $\Delta T(T)$ and $\Delta S_M(T)$ curves in a wide interval as discussed in section 6.2 (Korte et al. 1998a).

Reid et al. (1994) considered the working body required for an AMR refrigerator with a temperature span from 100 to 300 K. As it was noted above, initially it was supposed that in an AMR refrigerator the working material should have a MCE increasing linearly with the rising temperature. To achieve this it was proposed to use a layered material consisting of Gd for the range 270–300 K, Tb for the range 220–240 K and Dy for the range of 170–185 K. No appropriate materials were suggested for the other temperature intervals. A possible physical mixing with a magnetic material diluted by aluminum particles to achieve the best $\Delta T(T)$ profile was also discussed.

Thus, we have considered the passive and active magnetic refrigerators and working materials which can be used for their operation. Concluding, it is evident that magnetic cooling is a promising technology for use in the refrigeration industry and will be one of the important markets for the rare earth industry in the near future. At the same time it is necessary to note that magnetic materials with large MCE value could be also utilized for the creation of novel types of heat pumps. These magnetic heat pumps could operate using thermodynamic cycles analogous to those used in magnetic refrigerators and could be, in some cases, more effective than conventional heat pumps. However, the works in this direction is currently practically absent.

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