Working substances for magnetic refrigerators

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The possibility of using alloys of heavy rare earth metals based on gadolinium for magnetic refrigeration in the room temperature range is theoretically investigated in this paper. The appropriate calculations are carried out using the molecular field approximation. The applicability of the theory is verified by experiment for the polycrystalline alloys $Gd_{0.84}Er_{0.16}$ and $Gd_{0.80}Ho_{0.20}$. The most promising complex refrigerants for narrow ($\Delta T_c \approx 20$ K) and broad ($\Delta T_c \approx 40$ K) Ericsson type magnetic cycles are determined. It is shown that the use of refrigerants composed of two rare earth alloys produces a gain in the magnetic entropy change, ΔS_M, of $\approx 20\%$, compared to refrigerants composed of one alloy. Subsequent increases in the number of alloys in the refrigerant do not result in a noticeable increase in ΔS_M.

Keywords: refrigeration; magnetic cooling; magnetic fields; rare earth metals

Nomenclature

B	Magnetic field (T)
$B_J(X)$	Brillouin function
g_J	Spectroscopic splitting factor
$I(B, T)$	Magnetization (e.m.u. cm^{-3})
J	Total angular moment
N	Number of spins
S_M	Magnetic part of entropy (J mol^{-1} K^{-1})
ΔS_M	Magnetic entropy change (J mol^{-1} K^{-1})
$\Delta S_M \Delta T_c / B$	Specific refrigerant capacity (J mol^{-1} T^{-1})
T	Absolute temperature (K)
T_{col}	Temperature of object to be refrigerated (K)
T_{hot}	Heat receiver temperature (K)
ΔT_c	Change in temperature from hot to cold end of cycle (K)

Greek letters

θ_c	Curie temperature (K)
θ_D	Debye temperature (K)
μ_B	Bohr magneton (J T^{-1})
μ_{eff}	Effective magnetic moment (μ_B)
μ_o	Saturation magnetic moment per rare earth ion (μ_B)

The search for effective working substances for magnetic refrigerators is one of the most important areas for further improvement in overall refrigerator structure. The ability to use a working body in a refrigerator depends on several of its physical and chemical properties, namely, a large magnetic entropy change, ΔS_M, by the application of an external magnetic field, considerable heat conduction, a suitable Debye temperature, θ_D, etc. The problems involved with selecting working bodies suitable for machines operating in the temperature range above 20 K have been discussed in detail[1–10]. Two important areas are under study in the search for refrigerants for Ericsson type cycles. One of these involves the use of ferromagnetic refrigerators with large ΔS_M values (i.e. large values of g_J and J) and with a pronounced ability to vary Curie temperature by replacing magnetic ions. Research done in this area (see, for instance, References 3–8) has shown that the most promising refrigerants are of the RM_2 type (where R = rare earth metal and M = 3d metal) intermetallic compounds and the compound EuS. These refrigerants have good heat conduction[5] and the complex laminated structures associated with their base can show large ΔS_M values over a wide temperature range[3,4,6–8]. The other option[2,9] is to use the helicoidal antiferromagnetism–ferromagnetism phase transition observed in heavy rare earths when an external magnetic field is applied. Thus, in dysprosium in which the maximum field for the helicoidal state is 1.1 T, a sharp increase of specific refrigerant capacity, $\Delta S_M \Delta T_c / B$, is observed in fields $B \lesssim 1$ T. With $B = 1.1$ T in dysprosium, $\Delta S_M \Delta T_c / B \approx 20$ J mol^{-1} T^{-1}.

In recent years research in the room temperature range has attracted special attention. The move in this direction started with a publication by Brown[10]. Brown had created a magnetic refrigerator operating in the temperature range $\Delta T_c = 47$ K, with a magnetic field of

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7 T. The working body (900 g of gadolinium) consisted of plates 1 mm thick with gaps between them for regeneration liquid to pass through, and its motion was reciprocating. The rotor scheme of the refrigerator was also noteworthy.

The test data for such a device are described in Reference 11. The rotor used was made from porous gadolinium and rotated in a field $B = 1.2$ T generated by a permanent iron magnet. Under these conditions, refrigeration of 1 W was achieved per 3 K decrease below room temperature. Remarkable progress in creating such machines is reported in Reference 12. Theoretical aspects of magnetic refrigeration in the room temperature range and new working bodies for this temperature range are discussed in Reference 13. Investigations using gadolinium as a working body have been carried out by Nikitin *et al.*[14] and by Benford and Brown[15]. An experimental model of a magnetic refrigerator operating near room temperature was described by Nikitin *et al.*[14] and it has been reported that Astronautics Corporation is planning (in the 1990s) to produce magnetic refrigerators with gadolinium as the working body and an electromagnet as the source of field.

It should be noted that the idea of using gadolinium, with a Curie temperature, $\theta_c = 293$ K, as a working body for room temperature refrigerators is put forward as a practical proposal in all relevant reports, apart from those of Hashimoto and Shiimo[13] and Tishin[17]. It seems, however, that the circumstances for use are, to a certain extent, limited, as they allow only the left branch of the temperature dependence, ΔS_M, to be used for refrigeration. It is necessary to search for working bodies possessing qualities as good as (or better than) gadolinium but having Curie temperatures 15–20 K below 293 K. The molecular field theory was used to calculate the magnetic entropy change and refrigerant capacity of gadolinium–terbium alloys[17]. It is shown that these alloys are more effective working bodies than pure gadolinium. The conclusion was also drawn that by using weak magnetic fields from 0.1 to 1 T one may achieve high efficiency for a refrigerator operating in the room temperature range.

Thus, it was of interest to investigate the possibility of using the following rare earth alloys as working bodies: gadolinium–terbium (Gd–Tb), gadolinium–dysprosium (Gd–Dy), gadolinium–holmium (Gd–Ho), gadolinium–erbium (Gd–Er) and gadolinium–thulium (Gd–Tm). The magnetic properties of these alloys have been investigated in some detail[18].

In particular, Gd–Tb alloys were studied in detail by Nikitin in Reference 19. It was found that in alloys of more than 6 at% Gd only the paramagnetism–ferromagnetism transition is observed at the Curie temperature, θ_c. The rise in Curie temperature in Gd–Tb alloys with the rise in gadolinium concentration was also revealed by measuring magnetization and the magnetocaloric effect of poly- and monocrystalline samples[20]. It has been pointed out[19] that in these alloys the magnetic moment of absolute saturation, μ_o, with respect to the rare earth ion, increases linearly with terbium concentration.

The study of the magnetic properties of Gd–Dy alloys is dealt with in a great number of papers (see, for example, References 18, 19 and 21–24). It has been established that in alloys with a gadoliniun concentration of more than 50 at% the antiferromagnetic ordering is destroyed completely and the ferromagnetic structure is stabilized. It has been found that a small amount of dysprosium added to gadolinium results in the Curie temperature of the alloy being reduced almost linearly. The consideration of the paramagnetic properties of alloys by Levitin *et al.*[23] on the basis of the molecular field theory shows good agreement between theoretical and experimental dependences of the effective magnetic moment, μ_{eff}, on concentration. The concentration dependence, μ_o, in these alloys is described in Reference 18.

Gd–Ho alloys have been investigated by several workers[18,25–27]. It is proposed that these alloys are ferromagnetic provided that the gadolinium concentration in the alloy does not exceed 75 at%. The Curie temperature decreases linearly as holmium concentration is increased[18,27]. With more than 25 at% of holmium in the alloy a helicoidal and subsequently conical structure is observed. Data are available on the concentration dependence of the magnetic saturation moment per atom[18].

The points of magnetic phase transitions in Gd–Er alloys have been determined by various workers[18,25,27]. Neutron diffraction investigation of the composition of some of these allows has been described by Millhouse and Kochler[29]. On the basis of experimental data from the study of magnetic susceptibility, it has been shown[18] that in alloys with a gadoliniun concentration of more than 65% a ferromagnetic structure is stabilized, while other structures, such as helicoidal and conical, exist with lower gadolinium concentrations. The concentration dependence, μ_o, has also been reported on[18]. The magnetic properties and anisotropy of gadolinium alloyed with thulium have been examined by Okamoto *et al.*[30]. The present paper analyses the applicability of the alloys of gadolinium with other heavy rare earth metals for magnetic refrigeration in the room temperature range.

Experimental details

This paper presents experimental research on the rare earth polycrystalline alloys $Gd_{0.80}Ho_{0.20}$ and $Gd_{0.84}Er_{0.16}$. The alloys were prepared by an arc melting technique on a copper water-cooled hearth in a non-consumable tungsten electrode furnace, in an inert gas atmosphere. Annealing was performed in quartz ampules evacuated up to 10^{-4} mmHg for 20 h at 850°C. Chemical analysis was used to verify the composition of the alloys. An electric spark machine cut the ingots thus obtained. The measurements were made on columnar samples, of dimensions $1 \times 1 \times 4$ mm.

Magnetization was measured using a vibration magnetometer whose function and structure have been reported in detail elsewhere[31]. The magnetometer susceptibility was 2.0×10^{-3} e.m.u. The relative error of measuring the magnetic moment of the sample did not exceed 4%.

Theoretical model

The present paper uses the model of molecular field to determine the most promising alloys. The applicability of this model for gadolinium alloys has been verified on the experimentally investigated alloys, $Gd_{0.80}Ho_{0.20}$ and $Gd_{0.84}Er_{0.16}$. The theoretical basis of the molecular field approximation is systematically treated in a number of papers (see, for example, References 32–35). To calculate magnetization in this approximation one generally uses an expression of the type

$$I = NJg_J\mu_B B_J(X) \qquad (1)$$

where $B_J(X)$ is the Brillouin function.

The change of magnetic entropy, ΔS_M, as the field varies from 0 to B is described by the thermodynamic formula

$$\Delta S_M(B, T) = S_M(B, T) - S_M(0, T) = \int_0^B \left(\frac{\partial I}{\partial T}\right)_B \mathrm{d}B \qquad (2)$$

where $S_M(B, T)$ and $S_M(0, T)$ are magnetic parts of the entropy in field B and in the absence of the magnetic field, respectively. Relations (1) and (2) were used in this work for carrying out theoretical calculations.

The molecular field theory correctly describes the most essential magnetic properties of ferromagnets, such as the availability of spontaneous magnetization and its temperature dependence, the high temperature course of susceptibility and the heat capacity[34]. At the same time, it fails to describe accurately enough the amount of magnetization at low temperatures and in the immediate vicinity of θ_c. In addition, this theory predicts that the magnetic part of heat capacity vanishes above the Curie temperature[34], which is not the case in practice. Some of the above discrepancies can be avoided by using the Oguchi method, which describes pehomena relating to the existence of short-range magnetic order above θ_c[34]. The quantum phenomenological approach to this problem was used by Zvezdin *et al.*[35].

Results and discussion

The performances of magnetic refrigerators operating in the low temperature range is described in Reference 1. It is shown that increase in g_J results in a noticeable increase in the operating temperature range of such machines. Experiments to verify this statement[4] have indicated that the magnetic refrigerant $Gd_3Ga_5O_{12}$ ($g_J = 2$, $J = 7/2$) has larger absolute values of ΔS_M than the compound $Dy_3Al_5O_{12}$ ($g_J \approx 10$, $g_J = 1/2$) only at temperatures below 15 K. At $T > 15$ K the compound $Gd_3Ga_5O_{12}$ is less effective than $Dy_3Al_5O_{12}$.

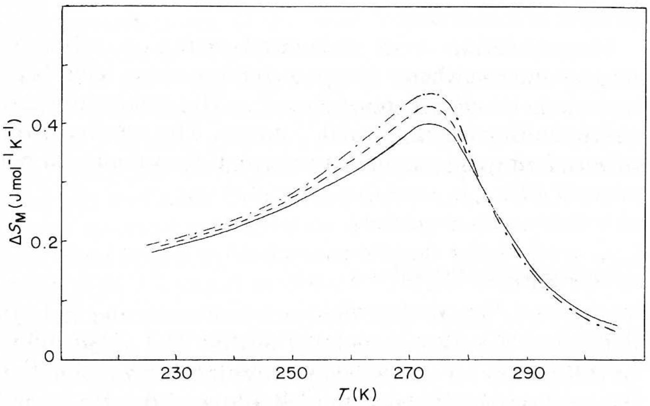

Figure 1 Theoretical temperature dependence, $\Delta S_M(T)$, with $g_J J = 7$, $\theta_c = 273$ K, $B = 1$ T: ——, $g_J = 1$, $J = 7$; – – –, $g_J = 1.5$, $J = 4.667$; – · –, $g_J = 2$, $J = 3.5$

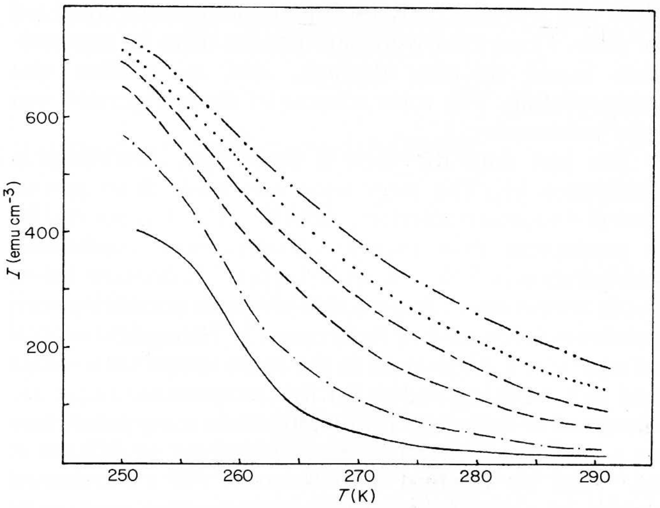

Figure 2 Temperature dependence of maganetization of polycrystalline alloy $Gd_{0.84}Er_{0.16}$ in various magnetic fields, *B*: ——, 0.1 T; – · –, 0.2 T; – – –, 0.4 T; –––, 0.6 T; · · ·, 0.8 T; – · · –, 1 T

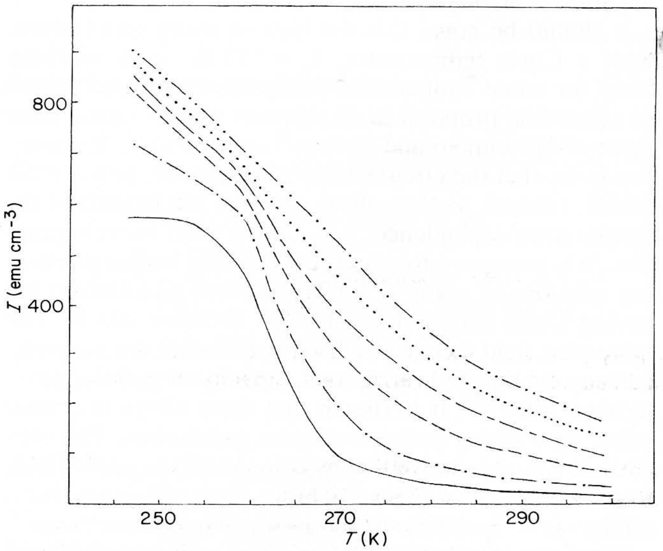

Figure 3 Temperature dependence of magnetization of polycrystalline alloy $Gd_{0.80}Ho_{0.20}$ in various magnetic fields. Key to curves as for *Figure 2*

The present author has carried out similar calculations for the temperature range near 273 K. The results of the calculations for the case of $g_J J = 7$ are presented in *Figure 1*. The calculations show that both an increase of g_J and an increase of J do not lead to any noticeable increase in temperature range with large values of ΔS_M. At the same time, an increase in g_J results in a certain increase in the values of ΔS_M in the vicinity of θ_c. On the basis of the analysis made, it can also be concluded that it is the refrigerants possessing the largest values of $g_J J$ that are most promising in this case. The investigation has been concentrated on the alloys of gadolinium with other heavy rare earth metals, as larger values of μ_o are observed in such alloys than in pure gadolinium.

The experimental temperature dependences of magnetization of the polycrystalline alloys $Gd_{0.84}Er_{0.16}$ and $Gd_{0.80}Ho_{0.20}$ are plotted in *Figures 2* and *3*. The curves are of a typically ferromagnetic character with a sudden reduction in magnetization around θ_c in weak magnetic fields. Why these two particular alloys have been

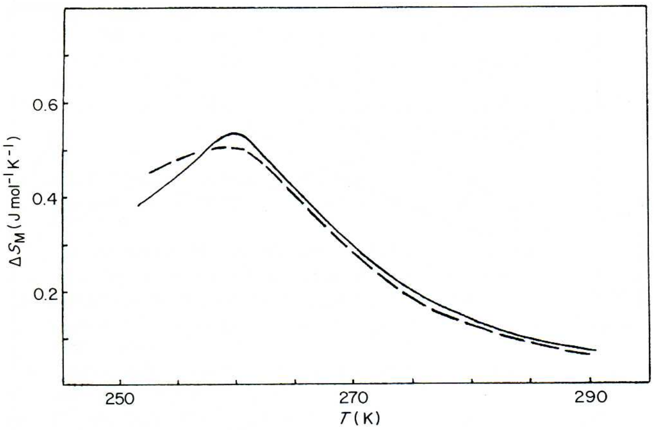

Figure 4 Temperature dependence of ΔS_M for alloy $Gd_{0.84}Er_{0.16}$ in a field of 1 T: – – –, theory; ——, experimental values

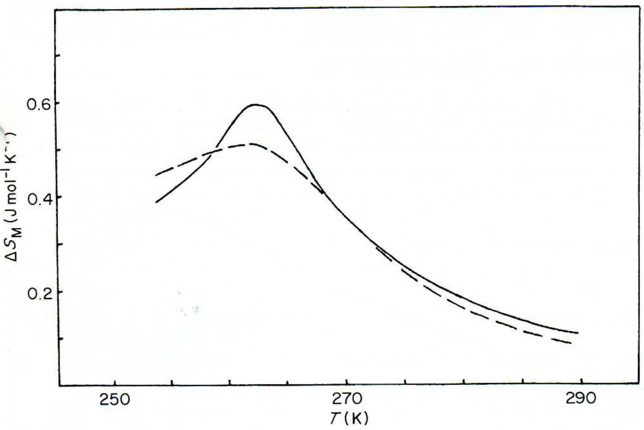

Figure 5 Temperature dependence of ΔS_M for alloy $Gd_{0.80}Ho_{0.20}$ in a field of 1 T: – – –, theory; ——, experimental values

chosen for the verification of the theoretical model will become clear from what follows.

The values of magnetization obtained have been used to calculate ΔS_M using Equation (2). Comparison of the results for empirical calculations (*Figures 4* and *5*) and theoretical dependences shows fairly good agreement. In fact, the final conclusions are not essentially affected by the negligible discrepancies in the vicinity of θ_c. The molecular field approximation is subsequently used to calculate the dependence of the magnetic entropy change on the temperature and magnetic field in ferromagnetic alloys of gadolinium with other rare earth metals.

It follows from *Figures 4* and *5* that the value of ΔS_M remains large over a considerable temperature range. Due to this fact, one may expect gadolinium alloys to be successfully used for magnetic refrigeration. Calculations of $\Delta S_M(T, H)$ show that for magnetic refrigerators operating over the narrow temperature ranges of $T_{hot} \approx 293$ K and $T_{col} \approx 273$ K, the use of even one alloy will achieve values of $\Delta S_M \approx 0.35$ J mol^{-1} K^{-1} at $B = 1$ T (see *Table 1*).

The ability to use gadolinium alloys over wider temperature ranges is demonstrated in *Figures 6–9*. *Table 2* shows the values of ΔS_M in a field of 1 T for ideal Ericsson type cycles operating over a temperature range 253–293 K, and using various rare earth alloys. The values of ΔS_M obtained in this case are much lower than while operating over narrow temperature ranges.

Table 1 Theoretical values of ΔS_M for ideal Ericsson type magnetic cycles in refrigerators operating in the temperature range $T_{hot} \approx 293$, $T_{col} \approx 273$ K ($B = 1$ T)

Number	Composition	ΔS_M (J mol^{-1} K^{-1})
1	$Gd_{0.88}Tb_{0.12}$	0.35
2	$Gd_{0.94}Dy_{0.06}$	0.35
3	$Gd_{0.97}Ho_{0.03}$	0.33
4	$Gd_{0.98}Er_{0.02}$	0.32

Table 2 Theoretical values of ΔS_M for ideal Ericsson type magnetic cycles in refrigerators operating in the temperature range $T_{hot} \approx 293$, $T_{col} \approx 253$ K ($B = 1$ T)

Number	Composition	ΔS_M(J mol^{-1} K^{-1})
1	$Gd_{0.85}Tb_{0.15}$	0.26
2	$Gd_{0.88}Dy_{0.12}$	0.26
3	$Gd_{0.96}Er_{0.04}$	0.25
4	$Gd_{0.97}Ho_{0.03}$	0.27

It is possible to obtain larger values of ΔS_M for the above cycles by using various methods. In cases where the working body consists of several separate parts, such as plates[10] or foil, each of these parts can be prepared from a definite alloy. The specific weight of each of the required alloys can be changed by either varying the number of plates made from that alloy or the plate thickness. Each part of such a compound working body will be most effective in a certain temperature range.

Roubeau, Steyert and Barclay put forward the idea of using a magnetic refrigerator in which the ordering temperature varies along the refrigeration column. Series of local cycles can be arranged along the column. Wood and Potter[33] proposed the use of a porous ferromagnetic refrigerator with this arrangement. To construct such a body is, however, a technically complex task.

A somewhat diffferent approach has been under development in recent years[1,3,4], where the working body is prepared as a complex laminated structure, as follows. The container is filled with layers of a powder (say $RAl_{2.2}$, where R stands for a rare earth metal), whereupon it undergoes pressing and sintering treatment. This process enabled Hashimoto *et al.*[4] to bring the operating temperature range down to 40 K ($\Delta S_M \approx 5$ J mol^{-1} K^{-1}, $B = 5$ T). The form of the dependence $\Delta S_M(T)$ in this temperature range was close to a horizontal line.

A similar method for making refrigerants can also be used for the gadolinium alloys under discussion in the present paper. The components of the working body are prepared using the zone melting method and are thus given the required shape. They can even undergo grinding at the joints and treatment of the assembled body with pressing and continuous annealing.

Analysis shows that the use of a complex working body for the case of $T_{hot} = 293$ and $T_{col} = 273$ K enables one to achieve the value of $\Delta S_M \approx 0.36$ J mol^{-1} K^{-1} at $B = 1$ T. The optimal situation is approached with a working body consisting of the two alloys $Gd_{0.95}Tb_{0.05}$ and $Gd_{0.73}Tb_{0.27}$ in the ratio 0.75:0.25. The results of the calculations for the temperature range $T_{hot} = 293$ K and $T_{col} = 253$ K for the case of complex working bodies are presented in *Figures 6–9*.

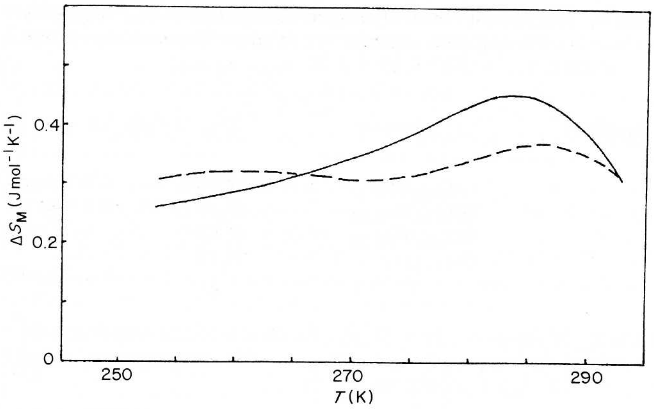

Figure 6 Theoretical temperature dependence of ΔS_M in a field of 1 T for: ——, alloy $\mathrm{Gd_{0.85}Tb_{0.15}}$; – – –, complex refrigerant $\mathrm{(Gd_{0.90}Tb_{0.10})_{0.78}\ (Gd_{0.40}Tb_{0.60})_{0.22}}$

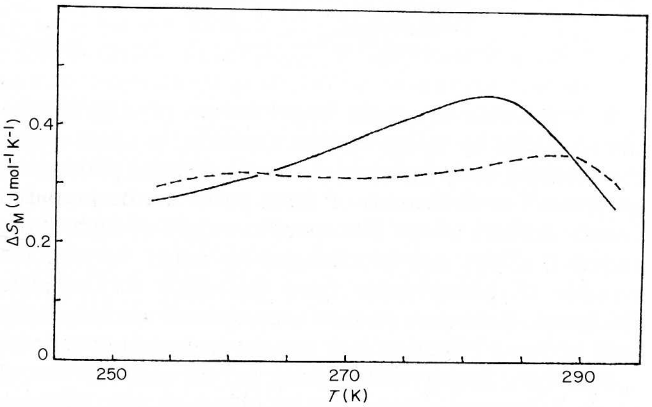

Figure 7 Theoretical temperature dependence of ΔS_M in a field of 1 T for: ——, alloy $\mathrm{Gd_{0.88}\ Dy_{0.12}}$; – – –, complex refrigerant $\mathrm{(Gd_{0.67}Dy_{0.33})_{0.24}\ (Gd_{0.97}Dy_{0.03})_{0.76}}$

The comparison made above of theoretical and experimental results enables one to see whether the calculated dependences, $\Delta S_M(T)$, obtained are close to the real values. As seen from *Figure 8*, the alloy $\mathrm{Gd_{0.84}Er_{0.16}}$ may form part of one of the complex refrigerants. For this reason it has been chosen for experimental study. The alloy $\mathrm{Gd_{0.80}Ho_{0.20}}$ is fairly similar to $\mathrm{Gd_{0.77}Ho_{0.23}}$ which forms part of another refrigerant (see *Figure 9*). The calculations show that the largest value of $\Delta S_M = 0.30$ can be obtained for the complex refrigerant made from $\mathrm{Gd_{0.90}Tb_{0.10}}$ and $\mathrm{Gd_{0.40}Tb_{0.60}}$ in the ratio 0.78:0.22. This result can be accounted for in the following way.

Holmium has the largest value of $g_J J$ in the series of rare earth metals. Hence, the alloys of gadolinium with holmium may, at first sight, seem most promising. However, since the temperature of the antiferromagnetism–paramagnetism phase transition in holmium is 135 K, the present paper has been concerned with alloys containing it in small quantities. The main contribution to the value of $g_J J$ in these alloys was made by gadolinium.

The situated is reversed in the alloys of gadolinium with terbium since the temperature of the antiferromagnetism–paramagnetism phase transition in terbium is close to the temperature range under consideration. Thus, the value of $g_J\ J$ of terbium makes a considerable contribution to the value of $g_J J$ for an alloy and these alloys are, to all appearances, the most promising.

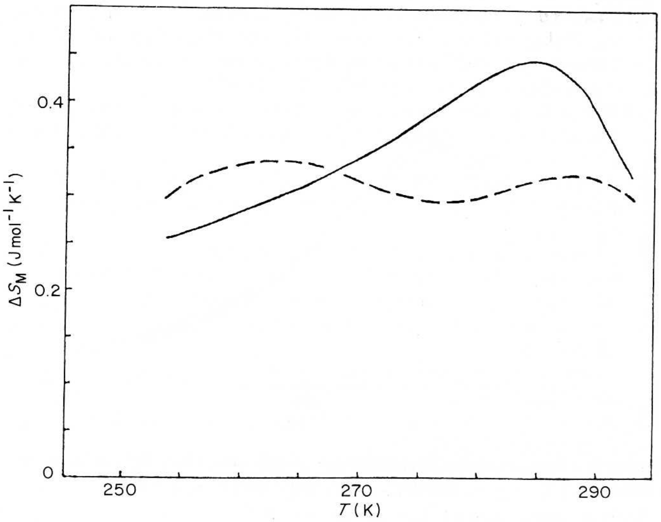

Figure 8 Theoretical temperature dependence of ΔS_M in a field of 1 T for: ——, alloy $\mathrm{Gd_{0.96}Er_{0.04}}$; – – –, complex refrigerant $\mathrm{(Gd_{0.84}Er_{0.16})_{0.32}\ (Gd_{0.98}Er_{0.02})_{0.68}}$

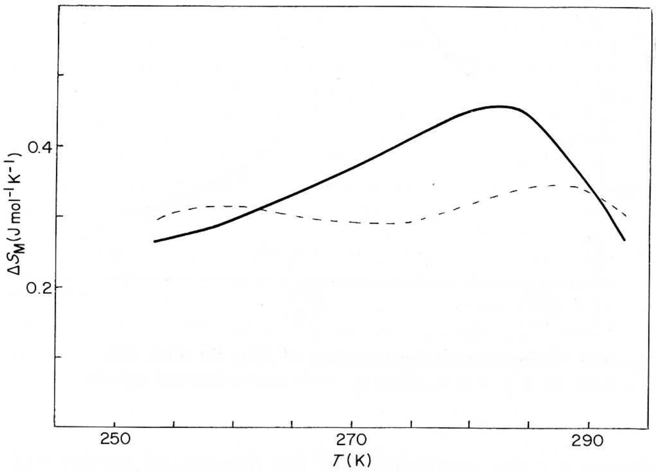

Figure 9 Theoretical temperature dependence of ΔS_M in a field of 1 T for: ——, alloy $\mathrm{Gd_{0.97}Ho_{0.03}}$; – – –, complex refrigerant $\mathrm{(Gd_{0.77}Ho_{0.23})_{0.25}\ (Gd_{0.97}Ho_{0.03})_{0.75}}$

The calculations carried out for working bodies consisting of three or more alloys allow one to conclude that this does not lead to any noticeable increase in the value of ΔS_M over either a narrow or a wide temperature range. The results of the present calculations also indicate that the use of more complex working bodies, consisting of gadolinium alloys with various rare earth metals, is unlikely to lead to any noticeable increase in ΔS_M. Thus, the use of alloys of rare earth metals for magnetic refrigeration seems quite promising. The utilization of one mole of these alloys in real Ericsson type magnetic cycles will, it appears, enable one to pump over $Q_c = \Delta S_M T_{col} \gtrsim$ 38 J per cycle from 253 to 293 K at $B = 1$ T.

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