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Alloys of the Fe – Rh system as a new class of working material for magnetic refrigerators

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The temperature dependences of initial magnetic permeability, specific heat capacity and magnetocaloric effect in annealed and quenched samples of $Fe_{49}Rh_{51}$ alloys near the antiferromagnetic – ferromagnetic (AF – F) first-order phase transition have been investigated. The application of a magnetic field of about 2 T to a quenched sample of this alloy at 308.2 K causes a temperature drop of 12.9 K under adiabatic conditions. The magnetocaloric temeprature changes were combined with zero-field specific heat data to construct $T-S$ and $T-\Delta(S_m + S_e)$ diagrams for various heat-treated samples of $Fe_{49}Rh_{51}$ alloys and on the basis of these diagrams the refrigerant capacity of alloys was evaluated. The value of the refrigerant capacity of a quenched sample of the alloy at a field of 1.95 T is 135.22 J kg^{-1} T^{-1}. This value is significantly greater than the refrigerant capacities of well known magnetocaloric materials. The possibility of using the AF – F transition in FeRh alloys for magnetocaloric refrigeration is assessed.

Keywords: refrigeration; magnetic cooling; first order magnetic transition

Nomenclature

c	Specific heat capacity (J kg^{-1} K^{-1})
B	Magnetic field (T)
L	Inductance of coil with sample (H)
L_0	Inductance of coil without sample (H)
m	Mass (kg)
Q	Quantity of heat (J)
S	Total entropy (J kg^{-1} K^{-1})
S_m	Magnetic part of entropy (J kg^{-1} K^{-1})
S_e	Electronic part of entropy (J kg^{-1} K^{-1})
$\Delta(S_m + S_e)$	Sum of magnetic and electronic entropy change (J kg^{-1} K^{-1})
ΔS_m	Magnetic entropy change (J kg^{-1} K^{-1})
T	Absolute temperature (K)
ΔT_c	Operation temperature region of cycle (K)
T_{hot}	Hot temperature of cycle (K)
T_{col}	Cold temperature of cycle (K)
Δt	Time interval (s)
W	Power (W)

Greek letters

Θ_c	Curie temperature (K)
μ_0	Initial magnetic permeability (arb. units)
ξ	Specific refrigerant capacity (J kg^{-1} T^{-1})

Nowadays an intensive search for materials suitable for use as the working body of magnetocaloric refrigerators is under way[1]. This is due to the fact that the potential for further significant increases in the efficiency of traditional thermomechanical refrigeration methods as a consequence of their own energy losses is essentially exhausted. In addition, these refrigeration methods often do not satisfy increasing operational requirements such as availability, compactness, environmental effects and safety.

Magnetic materials with appreciably field-induced entropy changes, ΔS_m, over a wide temperature region are of greatest interest from the viewpoint of use as a working body in magnetocaloric refrigerators.

From this point of view there are prospective materials with field-induced phase transitions[2], in which the magnetic properties exhibit anomalously high changes, which cause a considerable increase in magnetic entropy, ΔS_m, in comparison with other entropy components. In near equiatomic[3] alloys of the Fe–Rh system there is a field-induced antiferromagnetic–ferromagnetic first-order magnetic phase transition, which is accompanied by an entropy change of about 10 J kg^{-1} K^{-1}. In this connection the above mentioned

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alloys are of considerable interest. These alloys have great potential for engineering use, for example as working material for various thermomagnetic heat energy converters[4,5].

The antiferro–ferromagnetic transition in Fe–Rh alloys has been well investigated. However, up to the present there have not been enough experimental results on the thermomagnetic properties of these alloys. As has been theoretically shown[6], the application of a pulsed field under adiabatic conditions to an $Fe_{48}Rh_{52}$ alloy causes a temperature change $\Delta T = -(20 \pm 2)$ K at a temperature $T = 333$ K and $\Delta T = -(2 \pm 1)$ K at a temperature $T = 77$ K in a magnetic field $B = 30$ T.

Experimental investigation of the magnetocaloric effect in these alloys is of unquestionable interest for obtaining valuable information about the nature of AF–F transformation and about the possibility of using them as a working material of magnetocooling devices.

In this paper results of the experimental investigation of initial magnetic permeability, specific heat capacity and magnetocaloric effect as a function of temperature for annealed and quenched samples of $Fe_{49}Rh_{51}$ alloys is presented. The experimental results of this paper were used to construct a $T-S$ diagram of Fe–Rh alloys, on the basis of which the refrigeration capacity of alloys was calculated. Also, the possibility of using binary and diluted by 3d, 4d and 5d transition element pseudobinary alloys of the Fe–Rh system as a working material of stage refrigerators over a wide temperature region also is discussed.

Samples and experimental technique

Alloys were prepared by induction melting of appropriate quantities of the constituents (99.98% pure Fe and 99.99% pure Rh) in an argon atmosphere. Samples with dimensions of $4 \times 14 \times 1.2$ mm^3 were cut from the polycrystalline $Fe_{49}Rh_{51}$ alloy. The samples were homogenized by annealing at a temperature of 1300 K under vacuum for 72 h followed by slow cooling to room temperature. One of the samples was then water-quenched from 1300 K to 278 K. Some thermomagnetic properties of $Fe_{49}Rh_{51}$ alloys have previously been reported.

The phase transition parameters at heating and cooling are determined by measuring the temperature dependence of inductance of a coil with a sample from the alloy being investigated. The initial magnetic permeability μ_o is obtained as a function of L/L_o, where L_o is the inductance of the coil without the magnetic sample and L is the inductance of the coil with the sample[8]. The temperature region between 'branch' points of thermal hysteresis in which antiferromagnetic and ferromagnetic phases coexist is taken as an AF–F transition region. The values of the direct (AF–F) and reverse (F–AF) transition temperatures are defined in this work as the points where the temperature changes of magnetic permeability respectively at heating and cooling of the alloy are sharpest.

Heat capacity measurements were taken by the standard direct current heat pulse method in a vacuum adiabatic calorimeter with continuous heating. The rate of temperature change in this experiment was $dT/dt = 0.003-0.01$ K s^{-1}. The experimental values of heat capacity were determined by the equation

$$c = \frac{dQ}{mdT} = \frac{Wdt}{mdT} = \frac{W}{m}\left(\frac{dT}{dt}\right)^{-1}$$

where W is the power heating the sample. To decrease accidental errors the specific heat measurements were taken at regular intervals $\Delta t = 300$ s and calculation of dT/dt was made by numerical differentiation from the formula

$$dT/dt = \frac{1}{10\Delta t}\,(-2T_{n-2} - T_{n-1} + T_{n+1}\,2T_{n+2})$$

where n is the index of the following experimental point[9]. Special attention was paid to excluding systematic errors in the specific heat measurements. With this purpose the heat capacity was measured from time to time by a discrete heating method[10]. Reasonable agreement between the discrete and continuous heating methods was obtained.

The magnetocaloric data were obtained by switching on the magnetic field while heating of the sample. During magnetocaloric measurements the sample was fastened in a vacuum chamber, which was centred between the poles of an electromagnet. The sample was heated by an external bifilar heater. The temperature at the centre of sample was measured with a copper–constantan thermocouple. With the purpose of excluding the influence of thermal hysteresis in the results of the magnetocaloric measurements, before each measurement the sample was transformed to the antiferromagnetic state by cooling to a temperature below 293 K. Then the sample was heated to the required temperature and with the switching on of the magnetic field the magnetocaloric effect was measured. This method of measuring allowed us to achieve complete reproduction of the results obtained.

Results and discussion

In *Figure 1* the temperature dependences of the initial magntic permeability in arbitrary units at heating and cooling of annealed and quenched samples of $Fe_{49}Rh_{51}$ alloys are plotted. The temperature regions of AF–F transitions for various treated samples are significantly different and are 298–374 K for annealed and 293–321 K for quenched samples of the alloy. On heating of the samples sharper temperature changes of permeability take place near the temperatures 342 K (for the annealed sample) and 313 K (for the quenched sample). These points are taken as zero-field critical temperatures of AF–F transitions, respectively, for the annealed and quenched samples. The widths of the thermal hysteresis of the AF–F transition are 10.5 K and 8.5 K, respectively, for the annealed and quenched samples.

The specific heat capacities of the annealed and quenched samples during heating as functions of temperature are shown in *Figure 2*. Particular peculiarities in the behaviour of the specific heat capacity of the samples should be noted. The values of the specific heat in the

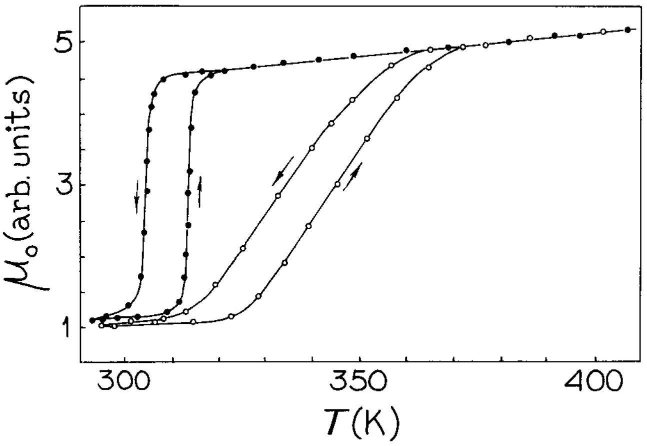

Figure 1 Temperature dependence of initial magnetic permeability of $Fe_{49}Rh_{51}$ alloy: (○) annealed sample; (●) quenched sample

AF phase near the transition point for both samples (460 J kg^{-1} K^{-1} for the annealed and 470 J kg^{-1} K^{-1} for the quenched samples) and at the capacity peak for the quenched sample (1630 J kg^{-1} K^{-1}) are significantly higher than those which were reported previously[11]. These results can be associated with the high quality of the samples.

The temperature at the heat capacity peak of the annealed sample is 334 K and the position of the peak of this sample is shifted by 8 K. This value is in rough agreement with the results of temperature dependence of magnetic permeability, where the transition point is at 342 K (see *Figure 1*). The quenched sample shows a prominent sharp peak at 313 K, which is an attractive fit to the data of permeability measurements (see also *Figure 1*).

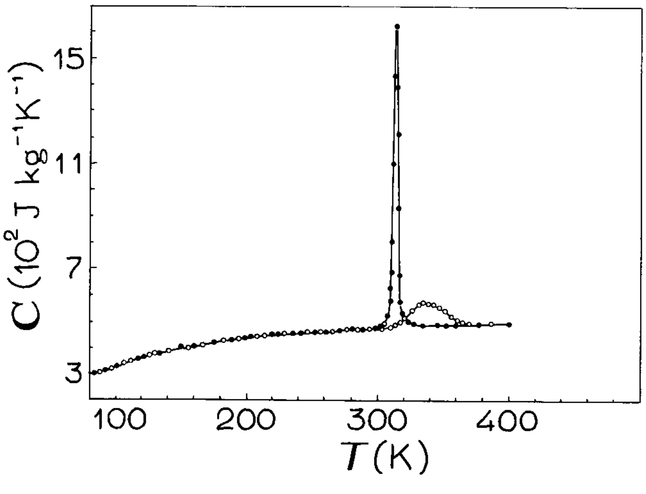

Figure 2 Temperature dependence of specific heat of $Fe_{49}Rh_{51}$ alloy: (○) annealed sample; (●) quenched sample

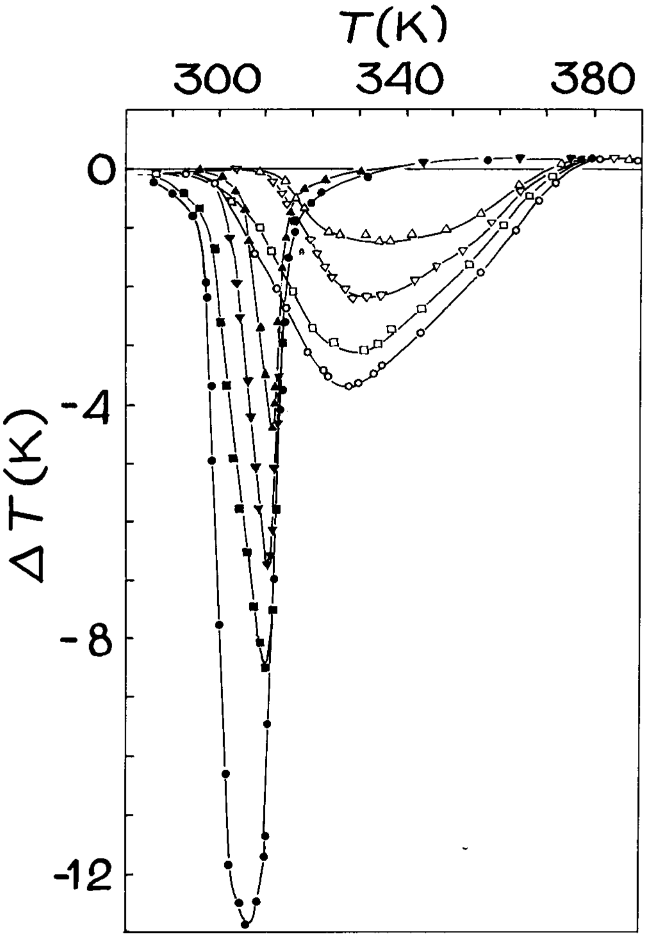

Figure 3 Temperature dependence of magnetocaloric effect for annealed (△, ▽, □, ○) and quenched (▲, ▼, ■, ●) samples of $Fe_{49}Rh_{51}$ alloy in various magnetic fields, *B*: (△, ▲), 0.65 T; (▽, ▼) 1.25 T; (□, ■), 1.7 T; (○, ●), 1.95 T

The magnetocaloric data for various heat treated samples of $Fe_{49}Rh_{51}$ alloy in applied fields of 0.65 T, 1.25 T, 1.7 T and 1.95 T are shown in *Figure 3* for the annealed and quenched samples. From *Figure 3* it will be obvious that in the AF phase and in the AF–F coexisting region on switching on of the magnetic field cooling of the samples takes place. With increasing initial temperature the magnetocaloric effect changes sign from negative to positive in the temperature regions of about 371–379 K and 336–337 K, respectively, for annealed and quenched samples, which indicates total transformation of the alloy to a ferromagnetic state. At temperatures above 389 K for the annealed and 337 K for the quenched samples up to 400 K the applied field becomes less effective in producing a temperature change. The Curie point of this alloy obtained from initial magnetic permeability measurements is 633 K. Regarding the temperature dependence of the magnetocaloric effect, a wide minimum for annealed and an extremely sharp minimum for quenched samples are observed. Our results indicate that the behaviour and value of the magnetocaloric effect are very sensitive both to heat treatment and the value of the applied field. With rising magnetic field the magnetocaloric minimum shifts to lower temperatures.

The results obtained in this paper can be interpreted in the following way. As is well known, the magnetic phase transition in Fe–Rh alloys can be initiated not only by increasing the temperature of the alloy, but also by applying a magnetic field to the alloy. The magnetic field, applied to the alloy in an AF state near the critical temperature induces the ferromagnetic state in it. The entropy of the Fe–Rh alloy consists of magnetic, electronic and lattice contributions. The band structure calculations[12,13] and low-temperature heat capacity experimental results[14–17] show significant increases of magnetic and electronic entropy during the AF–F transition in

Fe–Rh alloys. In consequence of the adiabatic conditions of the magnetocaloric experiment, at field-induced AF–F transition the lattice contribution of entropy decreases, and as a result the sample is cooled.

In a real sample there are certain temperature regions in which the AF and F phases coexist[18]. This fact attests that in samples of alloys various sections with different critical temperatures and consequently with different critical fields exist. Each applied field induces a first-order transition only in those sections of the sample for which its value is equal to or greater than the critical field. In connection with this, with an increasing magnetic field new sections with lower critical temperatures are involved in AF–F transition, which causes increasing depths and widths of the magnetocaloric minimum and its shifting to lower temperatures. The magnetocaloric effect must be increased with further field increases. However, obviously there is a 'limiting' field which induces AF–F transition in the whole volume of the sample. Application of the 'limiting' magnetic field to a sample with AF–F transition must give the maximum magnetocaloric effect in the sample and with further increases of magnetic field (above the limiting field) the increase of the magnetocaloric effect stops.

It has been shown[19] that the rare earth gadolinium, with a Curie temperature $\Theta_c = 293$ K, is a reasonable working material for magnetocaloric refrigeration. The values of the positive magnetocaloric effect in gadolinium are 2.4 K and 4.4 K respectively for applied fields of 1 T and 2 T. The results of this investigation show that the magnetocaloric effect in quenched samples of $Fe_{49}Rh_{51}$ alloy reached large negative values: 6.9 K in a field of 0.65 T and 12.9 K in a field of 1.95 T. These values are significantly larger in comparison with the magnetocaloric effect in gadolinium. Up to the present a negative magnetocaloric effect of about 0.3 K in rare earth compounds in magnetic fields of 2 T has been observed[1].

From this point of view the refrigerant capacity of Fe–Rh alloys is of interest. On the basis of our magnetocaloric and heat capacity experimental results the $T-S$ diagram of Fe–Rh alloy was calculated. *Figure 4* shows the $T-S$ diagram for a quenched sample of $Fe_{49}Rh_{51}$ alloy over the entire measuring temperature range and for various applied fields: zero-field (curve 1); 0.65 T (curve 2); 1.25 T (curve 3); 1.7 T (curve 4) and 1.95 T (curve 5). The behaviour of isothermal entropy changes $\Delta(S_m + S_e)$ of annealed and quenched samples as a function of temperature is shown in *Figures 5* and *6* for various values of magnetic field.

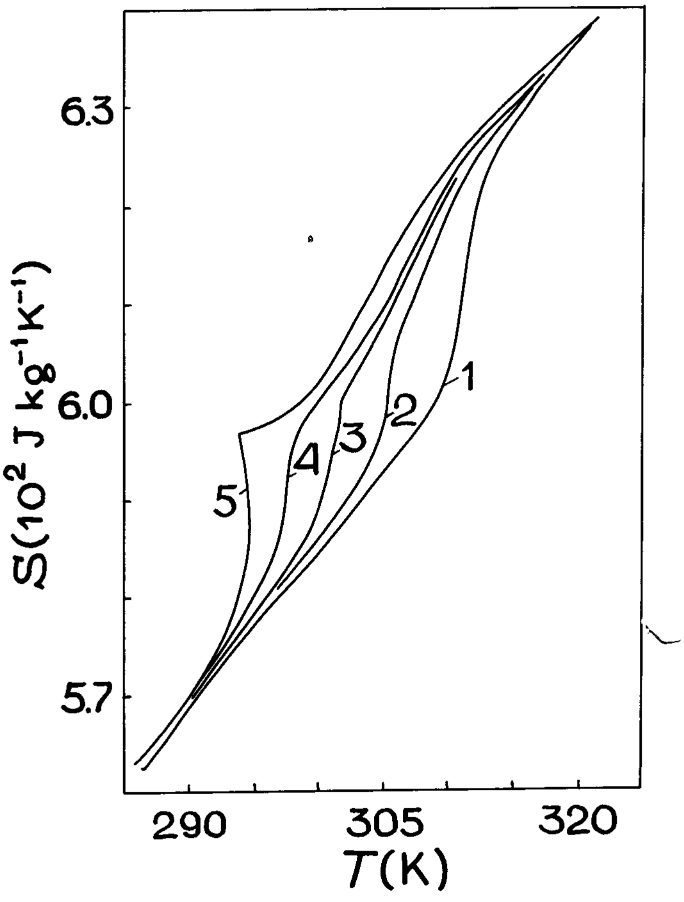

Figure 4 Temperature dependence of entropy of quenched $Fe_{49}Rh_{51}$ alloy in various magnetic fields, B: 0 T (curve 1); 0.65 T (curve 2); 1.25 T (curve 3); 1.7 T (curve 4); 1.95 T (curve 5)

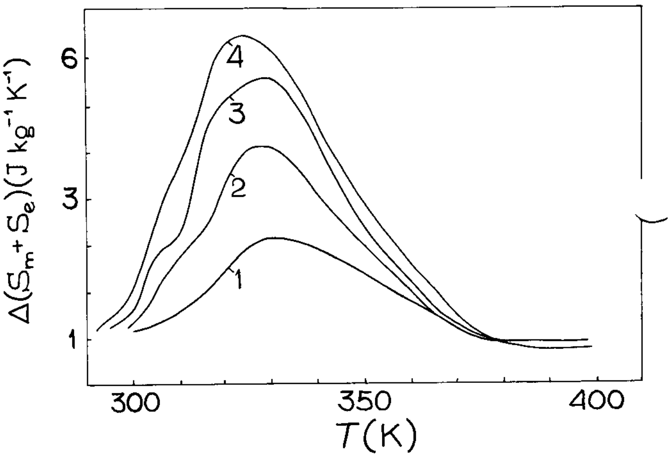

Figure 5 Temperature dependence of $\Delta(S_m + S_e)$ for annealed $Fe_{49}Rh_{51}$ alloy in various magnetic fields, *B*: 0.65 T (curve 1); 1.25 T (curve 2); 1.7 T (curve 3); 1.95 T (curve 4)

For optimization of stage magnetocooling cycles the refrigerant capacity of $Fe_{49}Rh_{51}$ alloy was estimated. The refrigerant capacity of $Fe_{49}Rh_{51}$ alloys is given by the following equation

$$\xi = \frac{\Delta(S_m + S_e)\Delta T_c}{B}$$

where $\Delta(S_m + S_e)$ is the change in the sum of magnetic and electronic entropy, $\Delta T_c = T_{hot} - T_{col}$ is the operational temperature region of the cycle, T_{hot} is the hot temperature, T_{col} is the cold temperature of the cycle and H is the applied magnetic field. The numerical results of the refrigerant capacity calculations for annealed and quenched samples of $Fe_{49}Rh_{51}$ alloy and for $Gd_{0.59}(Gd_{0.9}Dy_{0.1})_{0.41}$[20] are shown in *Table 1*.

It is clear that using $Gd_{0.59}(Gd_{0.9}Dy_{0.1})_{0.41}$ provides a significant amount of refrigeration capacity and a wide temperature range. However, the higher values of the refrigeration capacity of $Fe_{49}Rh_{51}$ alloys in easily achieved fields show that alloys of the Fe–Rh system are promising candidates for a magnetic refrigerant for stage magnetic refrigerators.

Table 1 Thermodynamic parameters of iron–rhodium and gadolinium–dysprosium alloys (B, magnetic field; T_{hot} and T_{col}, hot and cold temperature of cycle, respectively; $\Delta T_c = T_{hot} - T_{col}$, the operating temperature region of the cycle; $\Delta(S_m + S_e)$, entropy change in cycle and $\xi = \Delta(S_m + S_e)\Delta T_c/B$, specific refrigeration capacity of alloys)

Composition	B (T)	T_{hot} (K)	T_{col} (K)	ΔT_c (K)	$\Delta(S_m + S_e)$ (J kg^{-1} K^{-1})	ξ (J kg^{-1} T^{-1})
$Fe_{49}Rh_{51}$ (annealed sample)	1.95	347.7	309.0	38.7	3.23	64.10
	1.70	345.3	313.0	32.3	3.18	60.42
	1.25	345.8	316.0	29.8	2.47	58.88
	0.65	355.5	317.0	28.5	1.02	44.72
$Fe_{49}Rh_{51}$	1.95	312.2	295.0	17.2	15.33	135.22
	1.70	312.4	299.2	13.2	13.31	103.35
	1.25	312.5	303.0	9.5	12.00	101.79
	0.65	312.5	307.5	5.0	9.30	71.54
$Gd_{0.59}(Gd_{0.9}Dy_{0.1})_{0.41}$^{a}	1.50	293.0	273.0	20.0	3.25	44.67

^{a}Data from Reference 20

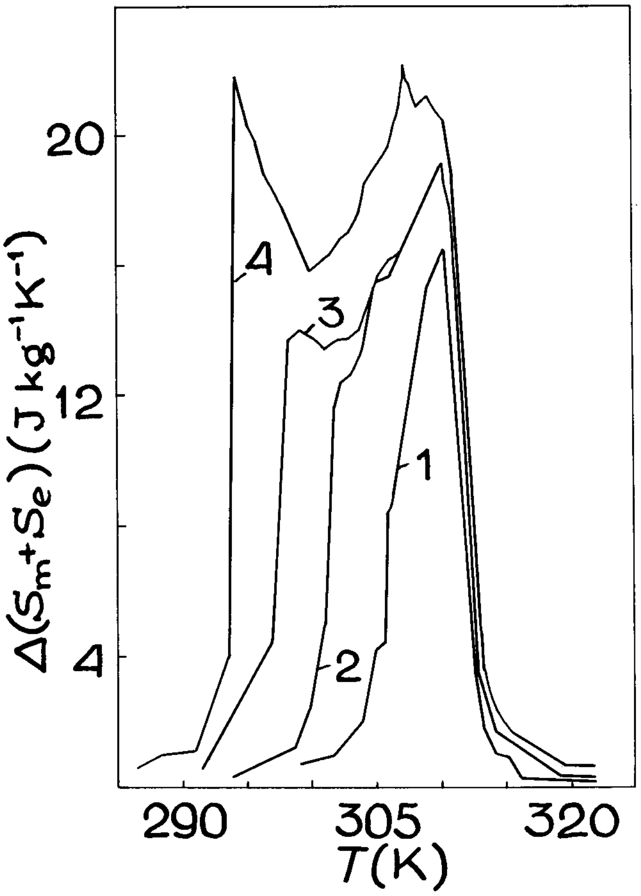

Figure 6 Temperature dependence of $\Delta(S_m + S_e)$ for quenched $Fe_{49}Rh_{51}$ alloy in various magnetic fields, B: 0.65 T (curve 1); 1.25 T (curve 2); 1.7 T (curve 3); 1.95 T (curve 4)

The idea of using alloys of the Fe–Rh system as working materials in stage magnetic refrigerators over a wide temperature region and at easily achieved magnetic fields is based on the fact that the AF–F transition temperature is very sensitive not only to changes of Rh component from 47 to 63 at% but also to diluting alloys of the Fe–Rh system by 3d, 4d and 5d transition elements[21].

Conclusions

From experimental results it is shown that transformation of the magnetic structure of Fe–Rh alloys from antiferromagnetic to ferromagnetic is accompanied by heat absorption which is typical of first-order magnetic transitions. The results obtained in this paper show that alloys of the Fe–Rh system have a significant entropy reserve, which may be strongly changed by a low enough magnetic field over a wide temperature range. This offers strong possibilities of using Re–Rh alloys as a working material for stage magnetic refrigerators.

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