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Magnetocaloric Effect near the First-Order Phase Transitions in Compounds of Rare Earth and Transition Metals

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Abstract—The results of the calculations and the experimental values of the magnetocaloric effect (MCE) in a group of compounds that are promising for use in magnetic coolers are reported. In the materials studied, MCE reaches the largest values near the magnetic first-order phase transitions and is mainly determined by the evolving latent heat of the transition. Contributions of different processes, occurring at the first-order phase transitions, to the observed MCE value have been separated on the basis of the thermodynamic model.

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During the last decade, the magnetic materials exhibiting large values of the magnetocaloric effect (MCE) at temperatures close to room temperature have been actively investigated. The interest in this problem is due to the prospects of development of magnetic coolers with operating temperatures close to 300 K. Such devices can be used as household refrigerators or conditioners; they are characterized by low energy consumption and can operate without ecologically harmful gas coolants, such as freon [1].

The results of the investigations of the magnetic and thermal properties of different compounds were reviewed in [2–4]. In particular, it was established that the MCE values are maximum near magnetic phase transitions. When such a transition is a second-order phase transition and the effect of magnetic anisotropy can be neglected, the change in the magnetic part of the entropy of the system at the Curie temperature can be derived from the formula

$$\Delta S_m \approx -1.07 qR\left(\frac{g\mu_B JH}{kT_C}\right)^{2/3}, \quad (1)$$

where q is the number of magnetic ions per mol [5]. The corresponding change in temperature is calculated as

$$\Delta T = -\frac{T}{C_{p,H}}\Delta S_M. \quad (2)$$

Among the studied materials of such type, having a Curie temperature close to 300 K, the largest MCE values were observed for gadolinium: T_C = 294 K, ΔS = 4.5 J kg^{-1} K^{-1} at a change in field ΔH = 2 T, and ΔT = 4 K at a change in field ΔH = 1.4 T [4, 7]. It should also be noted that currently the term *magnetocaloric effect* can be considered as generally accepted for both magnetic-field-induced changes: adiabatic change in temperature and isothermal change in entropy.

Currently, the compounds in which first-order phase transitions can be induced by a magnetic field are of greatest interest since the latent heat of the transition evolved in this case increases the total change in temperature. Such materials as $Gd_5(Si_xGe_{1-x})_4$, $MnFe(P_xAs_{1-x})$, and $La(Fe_xSi_{1-x})_{13}$ are considered promising for use in magnetic coolers. In this paper, we report the results of comparative investigation of the MCE value in several samples of these three groups of

Curie temperatures and maximum MCE values

	T_C, K	ΔS, J kg^{-1} K^{-1}; ΔH = 2 T	ΔT, K; ΔH = 1.4 T
$Gd_5Si_{1.95}Ge_{2.05}$	262	14.5	2.3
$LaFe_{11.7}Si_{1.3}$	183	24	4
$LaFe_{11.2}Co_{0.7}Si_{1.1}$	269	12	2.4
$MnFe(P_{0.45}As_{0.55})$	306	14	4
$MnFe(P_{0.47}As_{0.53})$	296	12.5	3.4
$Mn_{1.1}Fe_{0.9}(P_{0.47}As_{0.53})$	292	21	4.2
Gd [7]	294	4.5	4

compounds. The table contains Curie temperatures and the corresponding maximum MCE values. The isothermal change in entropy was calculated from the formula

$$\Delta S = \int \frac{\partial I}{\partial T} dH. \quad (3)$$

The temperature derivative of the magnetization was calculated from the experimental data. The adiabatic change in temperature was measured directly [8, 9].

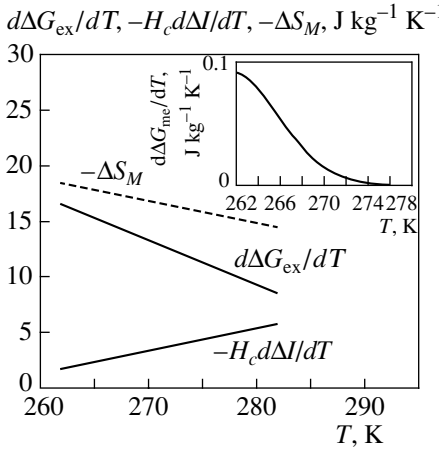
The following general regularities were observed: in all the compounds studied, except for $LaFe_{11.2}Co_{0.7}Si_{1.1}$, the phase transition from the ferromagnetic to the paramagnetic state is a first-order one. Destruction of magnetic ordering is accompanied by an anomaly of the thermal expansion coefficient, which is related to the sharp change in the spontaneous magnetostriction. In addition, in the $Gd_5Si_{1.95}Ge_{2.05}$ compound, the symmetry of the crystal structure also changes from orthorhombic to monoclinic. At temperatures exceeding the Curie temperature, application of a magnetic field with a strength exceeding $H_{cr}(T)$ leads to ferromagnetic ordering. This phase transition is a first-order one; it is accompanied by not only a sharp increase in magnetization but also a sharp change in the crystal structure parameters; in addition, the field dependences of the magnetization and magnetostriction have a wide field hysteresis. The temperature dependences of the MCE have a sharp maximum near the transition point. The field dependences of the MCE, measured at temperatures exceeding T_C, demonstrate a sharp increase only in magnetic fields exceeding $H_{cr}(T)$. On the basis of these results, it was concluded that the evolution of the latent heat of a transition induced by a magnetic field makes the main contribution to the MCE at temperatures close to T_C.

The contributions of different physical mechanisms to the MCE induced by the change in the entropy of the system at a first-order phase transition were separated with the use of the relations [6]

$$\Delta S_M^{tr} = -\left(\frac{\partial \Delta G_{ex}}{\partial T} + \frac{\partial \Delta G_{me}}{\partial T} + \frac{\partial \Delta G_a}{\partial T} - H_{cr}\frac{\partial \Delta I}{\partial T}\right), \quad (4)$$

$$\Delta T^{tr} = \frac{T}{C_{p,H}}\left(\frac{\partial \Delta G_{ex}}{\partial T} + \frac{\partial \Delta G_{me}}{\partial T} + \frac{\partial \Delta G_a}{\partial T} - H_{cr}\frac{\partial \Delta I}{\partial T}\right), \quad (5)$$

where G_{ex}, G_{me}, and G_a are the exchange, magnetoelastic, and anisotropic parts of the thermodynamic potential and H_{cr} is the critical field of the phase transition. The calculations performed with the use of the experimental data showed that the MCE in $Gd_5Si_{1.95}Ge_{2.05}$ is determined by more than 90% by the exchange component (see figure). Similar results were obtained for a number of materials [10]. Thus, we can conclude the following: in the compounds undergoing a magnetic first-order phase transition induced by a magnetic field, the MCE reaches maximum values at the transition temperature, and its value is related to the latent heat of the transition and is mainly determined by the change in the exchange energy at the transition.



Values of the entropy jump ΔS_M and individual terms entering Eq. (4), calculated for $Gd_5(Si_{1.95}Ge_{2.05})$. The phase-transition temperature in the absence of a magnetic field is 262 K.

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