Magnetocaloric effect in compounds of rare-earth metals with iron

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The temperature dependence of the magnetocaloric effect (ΔT effect) is studied for the compounds YFe_2, $ErFe_2$, YFe_3, and $HoFe_3$ in the temperature range from 78 to 600°K. For the compounds $ErFe_2$ and $HoFe_3$ there is a discontinuous change of sign of the ΔT effect at the compensation point T_c. The behavior of the isotherms $\Delta T(H)$ indicates the development of noncollinear magnetic structures in the immediate vicinity of T_c. On the basis of the ΔT-effect data, the paraprocess susceptibility, and the specific heat, an estimate is made of the effective exchange field acting on the rare-earth ions in $ErFe_2$ and $HoFe_3$.

The magnetic properties of compounds of rare-earth metals with iron are at present being studied intensively[1-3]. To explain the magnetic behavior of these substances, it is necessary to study in them also nonmagnetic effects that are dependent on peculiarities of their magnetic structure; in particular, it is of interest to study the magnetocaloric effect, which is very sensitive to the paraprocess and to angular configurations. In the present communication, we shall present the results of an investigation of the magnetocaloric effect in the compounds $ErFe_2$, YFe_2, $HoFe_3$, and YFe_3. These compounds were obtained in the laboratory of E. M. Savitskiĭ, in the A. A. Baĭkov Institute of Metallurgy of the USSR Academy of Sciences. The technology of specimen preparation and the method of measurement were described earlier[2-4]. The x-ray and metallographic analysis established the single-phase character of the specimens.

Figures 1 and 2 show the results of the measurements of the magnetocaloric effect (ΔT-effect). One notices that the ΔT-effect is positive over the whole temperature interval for YFe_2 and YFe_3, whereas for $ErFe_2$ and $HoFe_3$ there is a change of sign of the effect near the magnetic compensation point T_c (490° K and 389° K respectively). The ΔT-effect is positive for $T < T_c$ and negative for $T > T_c$. At the Curie point Θ_f, for all the specimens studied, there is a maximum of the positive ΔT-effect.

In order to explain the behavior of the magnetocaloric effect, it is necessary to take account of the magnetic and neutron-diffraction data[1-3,5], according to which the compounds YFe_2 and YFe_3 are ferromagnetic, with a single magnetic sublattice (the yttrium ion has no magnetic moment), whereas $ErFe_2$ and $HoFe_3$ consist of two magnetic sublattices (rare-earth and iron) whose magnetic moments are oriented antiparallel. The ΔT-effect observed in $ErFe_2$ and $HoFe_3$ consists of a ΔT_1-effect, due to the iron sublattice, and a ΔT_2-effect, due to the rare-earth sublattice ($\Delta T = \Delta T_1 + \Delta T_2$). According to thermodynamics[6]

$$\Delta T_1 = -\int_0^H \frac{T}{C_{H,V}} \left(\frac{\partial \mathbf{I}_1}{\partial T}\right)_{H,V} d\mathbf{H}, \quad (1)$$

$$\Delta T_2 = -\int_0^H \frac{T}{C_{H,V}} \left(\frac{\partial \mathbf{I}_2}{\partial T}\right)_{H,V} d\mathbf{H}, \quad (2)$$

where I_1 and I_2 are the magnetizations of the iron and rare-earth sublattices respectively (the resultant magnetization is $\mathbf{I} = \mathbf{I}_1 + \mathbf{I}_2$). In the case of YFe_2 and YFe_3, we have $\Delta T_2 = 0$, $\partial I_1/\partial T < 0$, and $\Delta T_1 > 0$; that is, in these substances there is a positive magnetocaloric effect due to a paraprocess of ferromagnetic type, since here the application of a magnetic field leads to an increase of the magnetic order[4]. For the ferromagnets $ErFe_2$ and $HoFe_3$ at $T < T_c$, the magnetic moment of the rare-earth sublattice is directed along the field and increases with increase of the field, so that $\Delta T_2 > 0$, whereas the moment of the iron sublattice is directed opposite to the field and decreases with increase of the field (a paraprocess of antiferromagnetic type[4]), so that $\Delta T_1 < 0$. For $T < T_c$ there is a net positive ΔT-effect, since ΔT_2 is larger in absolute value than ΔT_1 because of the fact that the magnetic moment of the rare-earth sublattice changes more rapidly with temperature and field, at low temperatures, than does the moment of the iron sublattice[2,3]. For $T > T_c$ in $ErFe_2$ and $HoFe_3$, the magnetic moment of the iron sublattice is directed along the field ($\Delta T_1 > 0$), whereas the moment of the rare-earth sublattice is directed opposite to the field. Here an increase of field leads to ordering of the iron sublattice and disordering of the rare-earth sublattice (paraprocess of antiferromagnetic type), so that $\Delta T_1 > 0$ and $\Delta T_2 < 0$. The net ΔT-effect is nega-

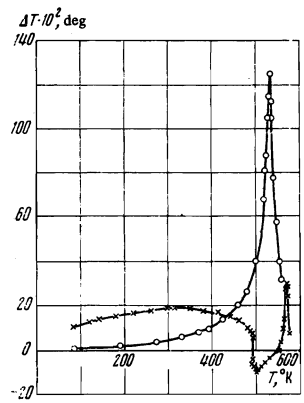

FIG. 1

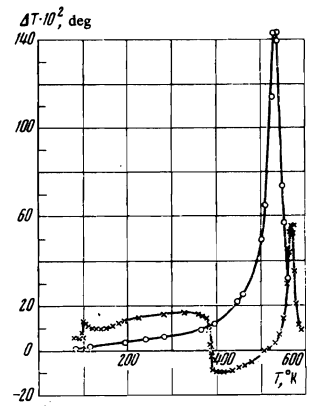

FIG. 2

FIG. 1. Temperature dependence of the magnetocaloric effect for the compounds YFe_2 (O) and $ErFe_2$ (X) in external field 15.8 kOe.

FIG. 2. Temperature dependence of the magnetocaloric effect for the compounds YFe_3 (O) and $HoFe_3$ (X) in external field 15.8 kOe.

tive, since ΔT_2 is larger in absolute value than ΔT_1. The values and signs of ΔT_1 and ΔT_2 can be determined from equations (1) and (2).

Mössbauer-effect investigations on iron nuclei[7] in compounds of the type RFe_2, where R is a heavy rare-earth ion, have shown that in these compounds the magnetic moment μ_{Fe} of the iron sublattice varies no more than 10% with respect to the presence of one or another rare-earth ion. Magnetic and neutron-diffraction data[1-3,5] also indicate a change of μ_{Fe} by no more than 15% in a series of compounds RFe_2 or RFe_3. It may therefore be assumed that likewise the magnetocaloric effect ΔT_1 due to the iron sublattice, far from the Curie point, is in first approximation the same in all the compounds RFe_2 and RFe_3. This enables us to estimate the magnetocaloric effect ΔT_2 due to the rare-earth sublattice, for $ErFe_2$ and $HoFe_3$, from the relation $\Delta T_2 = \Delta T - \Delta T_1$. Thus at temperature 300°K and for H = 15.8 kOe one can obtain in $ErFe_2$ the value $\Delta T_2 = \Delta T - \Delta T_1 = 0.19° + 0.04° = 0.23°$, and in $HoFe_3$ the value $\Delta T_2 = 0.17° + 0.07° = 0.24°$K (see Figs. 1 and 2). Knowing ΔT_2, we estimate the value of the effective field H_{e2} acting on the rare-earth ion, according to the formula of molecular-field theory for ferrimagnets in a collinear phase at temperatures far from the Curie point[8]:

$$H_{e2}=\frac{g_2 J_2}{2s_2}\frac{C_v}{\chi_2 H}\Delta T_2, \qquad (3)$$

where s_2 and J_2 are the spin and total magnetic moments, respectively, of the rare-earth ion, χ_2 is the molar susceptibility of the rare-earth sublattice, and C_V is the specific heat. From our measurements, $\chi_2 = 0.028$ in $ErFe_2$ and 0.04 in $HoFe_3$. On substituting in formula (3) the values found above for ΔT_2 and χ_2, the field H = 15.8 kOe, the known values of g_2, J_2, and s_2, and also $C_V = 24$ cal/deg mol (for $ErFe_2$ and $HoFe_3$)[1)], we found $H_{e2} \approx 1.6 \times 10^6$ Oe and $H_{e2} \approx 1.0 \times 10^6$ Oe, respectively, for $ErFe_2$ and $HoFe_3$.

The effective field acting within the iron sublattice can be estimated from the values of the Curie points Θ_f of the ferromagnets YFe_2 and YFe_3 by the formulas of molecular-field theory[8]:

$$H_{e1}=3k\Theta/2\mu_B(s_1+1)\approx(7.5-8)\cdot10^6 \text{ Oe}.$$

Here k is Boltzmann's constant, $s_1 = \frac{1}{2}$ to 1, and μ_B is the Bohr magneton. Compounds of the type RFe_2 and RFe_3 possess a maximum value of the field H_{e2} acting on the rare-earth ion, as compared with other types of rare-earth ferro- and antiferromagnets (for example, in rare-earth iron-garnets $H_{e2} \sim 3 \times 10^5$ Oe[10], in rare-earth orthoferrites $H_{e2} \approx 10^4$ Oe[11]). The large magnitude of the field H_{e2} causes magnetic ordering of the rare-earth sublattice at high temperatures and is responsible for the huge magnetostrictive deformations ($\lambda \sim 10^{-3}$) at room temperature in some compounds of the type RFe_2 and RFe_3[12].

As was shown earlier[13,14], the magnetocaloric effect in rare-earth iron garnets is a very sensitive indicator for the occurrence of angular configurations of the sublattice magnetizations. Near the compensation temperature the values of the critical fields H_{cr} at which there occurs a transition to a noncollinear structure decrease abruptly. It was therefore of interest to investigate the behavior of the magnetocaloric effect of the compounds $ErFe_2$ and $HoFe_3$ in the immediate vicinity of their magnetic compensation points (see Figs. 3 and 4). The ΔT-effect in the region $T < T_c$ is positive and increases

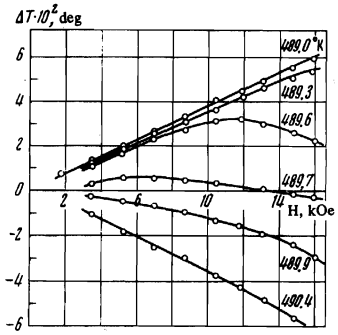

FIG. 3

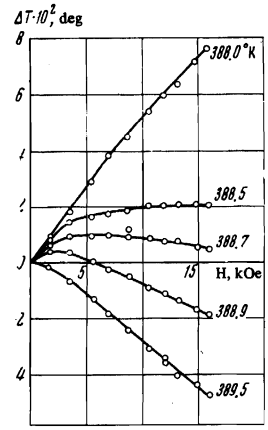

FIG. 4

FIG. 3. Dependence of the magnetocaloric effect on external field H in the immediate vicinity of the compensation temperature, for the compound $ErFe_2$.

FIG. 4. Dependence of the magnetocaloric effect on external field H in the immediate vicinity of the compensation temperature, for the compound $HoFe_3$.

with increase of field, but on attainment of a certain critical value of the field it begins to decrease. On increase of the temperature this decrease of the ΔT-effect becomes stronger, and ultimately it leads to a change of sign of the ΔT-effect. For $T > T_c$ the magnetocaloric effect acquires a negative sign. The behavior of the ΔT-effect near T_c was more complicated in the substances studied than in the rare-earth iron garnets, where on development of angular configurations there was a saturation of the ΔT-effect and the isotherms $\Delta T(H)$ experienced a break. In the compounds $ErFe_2$ and $HoFe_3$ we did not observe the abrupt break that determined the values of H_{cr} in iron garnets; but the general change of the $\Delta T(H)$ curves indicates the occurrence in these compounds of a noncollinear structure in the immediate vicinity of the magnetic compensation temperature. It is seen from Figs. 3 and 4 that on heating, with approach to T_c the change of character of the $\Delta T(H)$ curves begins at weaker fields; this indicates that with approach to T_c the critical fields decrease. But in contrast to the iron garnets, above the compensation temperature we did not detect an increase of the critical fields.

In closing, we express our thanks to Professor K. P. Belov for his attention to the research and for discussion of the results, and also to V. F. Terekhova and V. E. Kolesnichenko for preparation of the specimens for the investigation.

[1)]The specific heat was measured by the "flash method" [9] in the laboratory of B. A. Strukov, with accuracy 5-7%.

[1] E. Burzo, Z. Angew. Phys. **32**, 127 (1971).
[2] K. P. Belov, S. A. Nikitin, A. M. Bisliev, E. M. Savitskiĭ, V. F. Terekhova, and V. E. Kolesnichenko, Zh. Eksp. Teor. Fiz. **64**, 2154 (1973) [Sov. Phys.-JETP **37**, 1086 (1973)].
[3] K. P. Belov, A. M. Bisliev, S. A. Nikitin, and V. E. Kolesnichenko, Fiz. Met. Metalloved. **34**, 470 (1972) [Phys. Met. Metallogr. **34**, No. 3, 19 (1972)].
[4] K. P. Belov, E. V. Talalaeva, L. A. Chernikova, and V. I. Ivanovskiĭ, Zh. Eksp. Teor. Fiz. Pis'ma Red. **7**, 423 (1968) [JETP Lett. **7**, 331 (1968)].

[5] J. M. Moreau, C. Michel, M. Simmons, T. J. O'Keefe, and W. J. James, J. Phys. (Paris) **32**, Suppl., C1-670 (1971).
[6] S. V. Vonsovskiĭ, Magnetizm (Magnetism), "Nauka", 1971.
[7] K. N. R. Taylor, Adv. Phys. **20**, 551 (1971).
[8] K. P. Belov and S. A. Nikitin, Phys. Status Solidi **12**, 453 (1965).
[9] W. J. Parker, R. J. Jenkins, C. P. Butler, and G. L. Abbott, J. Appl. Phys. **32**, 1679 (1961).
[10] K. P. Belov, S. A. Nikitin, E. V. Talalaeva, L. A. Chernikova, T. V. Kudryavtseva, V. V. Tikhonov, and V. I. Ivanovskiĭ, Zh. Eksp. Teor. Fiz. **61**, 1101 (1971) [Sov. Phys.-JETP **34**, 588 (1972)].
[11] K. P. Belov and A. M. Kadomtseva, Magnitnye i kristallokhimicheskie issledovaniya ferritov (Magnetic and Crystallochemical Investigations of Ferrites), Izd. MGU, 1971.
[12] A. E. Clark and H. S. Belson, Phys. Rev. **B5**, 3642 (1971).
[13] K. P. Belov, L. A. Chernikova, E. V. Talalaeva, R. Z. Levitin, T. V. Kudryavtseva, S. Amadesi, and V. I. Ivanovskiĭ, Zh. Eksp. Teor. Fiz. **58**, 1923 (1970) [Sov. Phys.-JETP **31**, 1035 (1970)].
[14] A. K. Zvezdin and V. M. Matveev, Izv. Akad. Nauk SSSR Ser. Fiz. **36**, 1441 (1972) [Bull. Acad. Sci. USSR Phys. Ser. **36**, 1278 (1972)].

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