

# Magnetic properties of compounds of rare-earth metals with iron, of the type $RFe_3$

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Magnetic investigations have been conducted on the compounds  $DyFe_3$ ,  $YFe_3$ ,  $HoFe_3$ , and  $ErFe_3$ , including measurements of the magnetization in fields up to 53 kOe and of the temperature dependence of the coercive force. The magnetic moment per  $RFe_3$  molecule and the temperature dependence of the spontaneous magnetization were determined; the Curie temperature was determined by a thermodynamic method. An anomaly of the coercive force was observed near the magnetic compensation temperature. The temperature dependence of the magnetic properties is due to the ferrimagnetic structure of these compounds, characterized by antiparallel orientation of the magnetic moments of the sublattices of iron ions and of rare-earth ions. The Curie temperature of compounds  $RFe_3$  increases markedly with increase of the spin of the rare-earth ion; this indicates an appreciable contribution from exchange interaction of the rare-earth ions with the iron ions.

Investigation of the magnetism of compounds of the rare-earth metals with iron makes it possible to study the interaction of two different types of magnetically active atoms. If in the rare-earth metals the 4f shell is screened by the higher-lying electronic layers, then in the iron the magnetically active 3d shell is not screened and is subject to the influence of the surroundings. The presence of just two antiparallel magnetic sublattices facilitates the interpretation of the magnetic properties of these substances and renders them suitable topics for the theory of magnetism. The high Curie temperatures of these materials, as well as of compounds of the rare-earth metals with cobalt, distinguish them favorably from other rare-earth alloys, which as a rule have low Curie points. This is of interest from the point of view of technical applications.

In the present communication, we present magnetic data for the compounds  $RFe_3$ , where  $R = Y, Dy, Ho, Er$ . Although the magnetic properties of these compounds have been studied by a number of authors<sup>[1-3]</sup>, there is nevertheless no quite complete interpretation of the peculiarities of the magnetic behavior of these substances. This is explained in part by the fact that in the series of investigations no complete complex of measurements was made, including measurements of the isotherms of the magnetization in a sufficiently strong magnetic field to permit determination of the spontaneous magnetization and of the magnetic moment per molecule of the compound; determination of the temperature behavior of the hysteretic properties; and accurate determination of the Curie point, which requires careful measurements of the field dependence of the magnetization near the Curie point.

In this research we have carried out such an investigation. The hysteretic properties—the coercive force and the residual magnetization—were measured by the ballistic method, with magnetization in the field of a solenoid, with maximum magnetic field 1700 Oe. Measurements in the temperature range 4.2–78°K were made in the magnetic field of a superconducting solenoid, up to 53 kOe, by means of a vibration magnetometer. Measurements in the temperature interval 78–

700°K were made by a balance method in the field of an electromagnet, up to 15 kOe.

Compounds  $RFe_3$  have been discovered by a number of authors in study of rare-earth-iron state diagrams<sup>[4-7]</sup>. Specimens of the alloys studied by us were melted in an arc furnace on a water-cooled copper hearth in a helium atmosphere. A homogenizing anneal, in a vacuum of  $10^{-3}$  mm of mercury, was performed at 850°C over a period of 200–300 hours. X-ray and metallographic analyses established that the specimens obtained were single-phase and had rhombohedral lattices.

The table summarizes the data obtained on the Curie temperatures  $\Theta$ , the compensation temperatures  $T_C$ , and the values of the absolute-saturation magnetization  $\sigma_0$ , of the coercive force  $H_C$ , and of the residual magnetization  $\sigma_r$ . There are also values obtained by calculation: the magnetic moment  $\mu_0$ , per molecule of the compound  $RFe_3$ , the magnetic moment  $\mu_{Fe}$  on the iron ion, and the magnetic moment  $\mu_R$  on the rare-earth ion. It is seen that the materials under study possess quite high Curie temperatures and average values of the coercive force, the residual magnetization, and the saturation magnetization.

The absolute-saturation magnetization was determined from the magnetization isotherms (see Fig. 1) at 4.2°K, measured in a field up to 53 kOe. The spontaneous magnetization at 4.2°K was found by extrapolation of the magnetization curve to  $H=0$  from the field range 30 to 50 kOe. The value of the magnetic moment (in Bohr magnetons) per molecule was calculated by the formula  $\mu_0 = A\sigma_0/N\mu_B$  ( $A$  is the molecular weight,  $N$  is Avogadro's number, and  $\mu_B$  is the Bohr magneton).

The values of  $\mu_0$  agree well with the assumption that there are two antiparallel magnetic sublattices: the sublattice of iron ions and the sublattice of rare-earth ions. According to this model, which for  $HoFe_3$  is supported by neutron-diffraction data<sup>[8]</sup>, the resultant magnetic moment per molecule is  $\mu_0 = \mu_R - 3\mu_{Fe}$ . Starting with neutron-diffraction data for  $HoFe_3$ , we took the magnetic moment of the holmium ion to be  $\mu_R = 9.5\mu_B$ . From our measurements for  $HoFe_3$  we found  $\mu_0 = 4.4\mu_B$ .

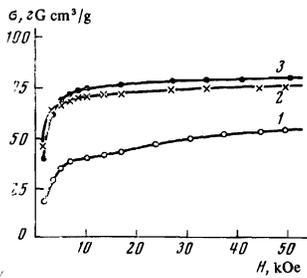


FIG. 1. Dependence of the magnetization  $\sigma$  on magnetic field at 4.2°K for the compounds  $\text{ErFe}_3$  (○),  $\text{HoFe}_3$  (×), and  $\text{DyFe}_3$  (●).

Hence it is easy to calculate for  $\text{HoFe}_3$  the magnetic moment per iron ion:  $\mu_{\text{Fe}} = 1.7\mu_{\text{B}}$ . This value agrees well with  $\mu_{\text{Fe}} = 1.68\mu_{\text{B}}$ , found from our measurements for  $\text{YFe}_3$ , and also with  $\mu_{\text{Fe}} = 1.83\mu_{\text{B}}$  for  $\text{GdFe}_3$ <sup>[3]</sup>. On the basis of these data, we took for all the compounds  $\text{YFe}_3$ ,  $\text{HoFe}_3$ ,  $\text{DyFe}_3$ , and  $\text{ErFe}_3$  the values  $\mu_{\text{Fe}} = 1.7\mu_{\text{B}}$ . Then the magnetic moment per rare-earth ion in the compounds  $\text{RFe}_3$  can be calculated by the formula  $\mu_{\text{R}} = \mu_0 + 3\mu_{\text{Fe}}$ .

As is seen from the table, these values are slightly smaller than the values of the magnetic moments of the free rare-earth ions; this is characteristic of many rare-earth alloys. Some deviation can be explained by the effect of the crystalline field on the orbital moment and by the superposed magnetization of the conduction electrons. Thus the original hypothesis about the ferromagnetism of these compounds is supported by the data on the magnetic moments.

Figure 2 shows, for the compounds studied, the temperature dependences of the spontaneous magnetization  $\sigma_{\text{S}}$ , of the susceptibility  $\chi_{\text{f}}$  in a strong magnetic field of 11 kOe, and of the coercive force  $H_{\text{C}}$ , measured in maximum magnetizing field 1700 Oe.

The spontaneous magnetization  $\sigma_{\text{S}}$  was found by extrapolation to  $H=0$  of the section of the  $\sigma(H)$  curve corresponding to the paraprocess. The Curie temperature  $\Theta$  and  $\sigma_{\text{S}}$  near the Curie point were determined by a thermodynamic method, by construction of the curves  $H/\sigma = f(\sigma^2)$ <sup>[9]</sup>. The Curie point according to this method is determined as the temperature where  $\sigma_{\text{S}} = 0$ . The possibility of use of this method for ferrimagnets fol-

lows from the thermodynamic theory of phase transitions of the second kind<sup>[10]</sup>. The methods previously used for determination of the Curie point of  $\text{RFe}_3$  compounds were very inaccurate; as a result, the values of the temperature  $\Theta$  differed in some cases by more than ten degrees.

From Fig. 2 it is seen that  $\sigma_{\text{S}}$  in  $\text{YFe}_3$  decreases monotonically on heating and on approach to the Curie point  $\Theta = 537^\circ\text{K}$ , as in a classical ferromagnet of the iron type. The absence of singularities on the  $\sigma_{\text{S}}(T)$  curve is due to the fact that the magnetic moment of the rare-earth sublattice is zero (yttrium has no magnetic moment). The susceptibility  $\chi_{\text{f}}$  has a maximum at the Curie point; the  $H_{\text{C}}(T)$  curve displays no anomaly in the temperature behavior.

On the  $\sigma_{\text{S}}(T)$  curve for the compound  $\text{DyFe}_3$  there is a characteristic break at  $T_{\text{C}} = 535^\circ\text{K}$ , as if to mark a magnetic compensation temperature. For  $T < T_{\text{C}}$ , in this compound, the magnetic moment of the dysprosium sublattice is larger; for  $T > T_{\text{C}}$ , that of the iron sublattice. The susceptibility  $\chi_{\text{f}}$  has a maximum at the Curie point  $\Theta = 631^\circ\text{K}$ , due to the paraprocess. On the  $H_{\text{C}}(T)$  curve there appear a small plateau near  $T_{\text{C}}$  and a maximum at  $470^\circ\text{K}$ .

In the compound  $\text{HoFe}_3$ , the magnetic compensation point is quite sharply expressed at  $T_{\text{C}} = 393^\circ\text{K}$ . Here there occurs compensation of the magnetic moments of the holmium sublattice and of the iron sublattice. For  $T < T_{\text{C}}$  the magnetic moment of the holmium sublattice is larger than the magnetic moment of the iron sublattice; for  $T > T_{\text{C}}$ , smaller. There is a complicated behavior of the coercive force: in this compound, also near  $T_{\text{C}}$ , we detected two maxima on the  $H_{\text{C}}(T)$  curve (see Fig. 2).

As was shown in papers on rare-earth ferrite-garnets<sup>[11]</sup> and alloys<sup>[12]</sup>, an abrupt decrease of the coercive force right at the compensation point is due to the absence here of a spontaneous magnetization. On departure from  $T_{\text{C}}$  the coercive force increases because of the increase of  $\sigma_{\text{S}}$ : here  $H_{\text{C}}$  is determined by magnetization reversal of single-domain particles by the

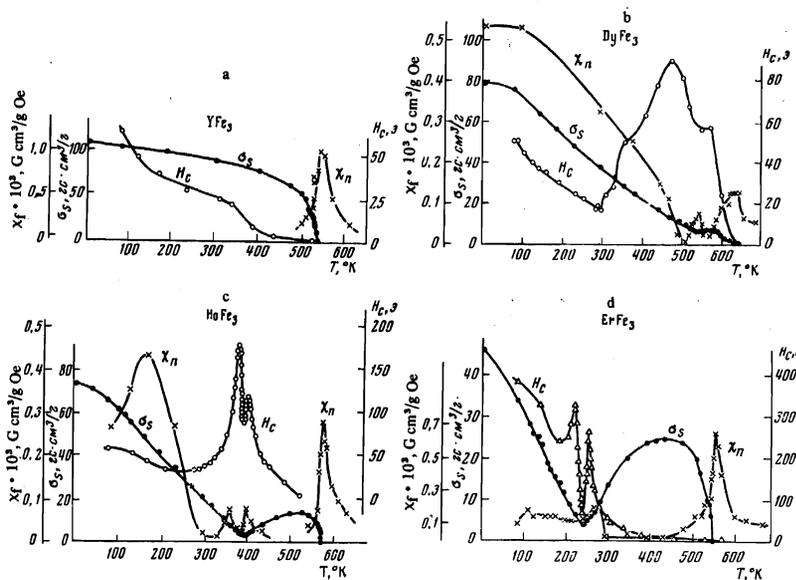


FIG. 2. Temperature dependence of the spontaneous magnetization  $\sigma_{\text{S}}$  (in  $\text{G}\cdot\text{cm}^3/\text{g}$ ), the coercive force  $H_{\text{C}}$ , and the susceptibility  $\chi_{\text{f}}$  (in  $\text{G}\cdot\text{cm}^3/\text{g}\cdot\text{Oe}$ ) in a strong field ( $H = 11$  kOe) for  $\text{YFe}_3$ ,  $\text{DyFe}_3$ ,  $\text{HoFe}_3$ , and  $\text{ErFe}_3$ .

paraprocess. Increase of  $H_C$  on approach to  $T_C$  from high and low temperatures occurs because of the predominance of magnetization reversal by irreversible rotation of the spontaneous magnetization. Here  $H_C \propto K/I_S$  ( $K$  is the magnetic anisotropy constant,  $I_S$  the spontaneous magnetic moment per unit volume); and a diminution of  $I_S$  as  $T \rightarrow T_C$  leads to an increase of  $H_C$ . If complete compensation of the sublattice magnetizations is absent, as in  $DyFe_3$ , then there is observed only a disturbance of the regular behavior of the  $H_C(T)$  curve: a maximum without splitting, or a step.

The temperature dependence of  $\chi_f$  in  $HoFe_3$  is of quite complicated nature. Near the Curie point  $\Theta = 570^\circ K$ , there occurs a maximum due to an intense paraprocess. At low temperatures  $\sim 140^\circ K$  there is a maximum, which by analogy with the rare-earth ferrite-garnets can be explained by the destruction of long-range magnetic order in the rare-earth sublattice<sup>[13]</sup>. Near  $T_C$  two maxima occur on the  $\chi_f(T)$  curve, at approximately the same temperatures as on the  $H_C(T)$  curve. As in the case of the coercive force, the complicated temperature behavior of  $\chi_f$  is caused by singularities of the phase transition at  $T_C$ , and possibly by occurrence of a non-collinear configuration in the field.

In the compound  $ErFe_3$ , magnetic compensation is observed at  $T_C = 240^\circ K$ . Here there occurs a strong diminution of  $\sigma_S$ . Such a temperature behavior of  $\sigma_S$  also indicates ferrimagnetic ordering in this compound; the erbium sublattice and the iron sublattice have different temperature behaviors, and this leads to the occurrence of a compensation temperature at a comparatively low temperature. The susceptibility  $\chi_f$  has, as usual, a maximum at the Curie point. On the curve of temperature variation of the coercive force there occur, as in  $HoFe_3$ , two maxima near the compensation temperature.

On analysis of the data on the values of the Curie temperatures of the compounds  $RFe_3$  (see table), it can be noted that there appears here a regularity characteristic of many rare-earth compounds. Namely, the Curie temperature increases monotonically in the series of rare-earth compounds with increase of the value of the spin  $S$ , from erbium to dysprosium. The Curie temperature, as is well known, is determined by the exchange interaction, which, other things being equal, is larger, the larger the forces of the interacting atoms. Therefore the observed increase of  $\Theta$  with increase of the spin indicates an appreciable contribution of the exchange interaction of the sublattice of rare-earth ions with the iron sublattice. The Curie temperature of  $DyFe_3$

and  $ErFe_3$  differ by  $85^\circ$ . But the exchange interaction between the iron ions is the strongest, since for the compound  $YFe_3$ , where  $\mu_R = 0$ , the Curie point  $\Theta = 537^\circ K$  is quite high.

Thus the results of the investigation of the magnetic properties of compounds of the type  $RFe_3$  allow us to draw the following basic conclusions:

1. The values of the magnetic moments per molecule can be explained on the basis of the assumption that two magnetic sublattices are present: a sublattice of rare-earth ions and a sublattice of iron ions. The magnetic moments of the sublattices are oriented antiparallel.
2. The temperature behavior of  $\sigma_S$ ,  $H_C$ , and  $\chi_f$  is due to the ferrimagnetic structure of these substances.
3. The Curie temperatures of these compounds increase appreciably with increase of the spin of the rare-earth ion; this indicates an appreciable contribution from the exchange interaction of the rare-earth ions with the iron ions.

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Composition	$H_C$ , °K	$T_C$ , °K	$\sigma_S$ , G cm <sup>3</sup> /g	$\mu_{Fe}^I/\mu_B$	$\mu_{Fe}^{II}/\mu_B$	$\mu_R/\mu_B$	$\epsilon J$	$H_C, O_e$ at 300°K	$\sigma_r$ , G cm <sup>3</sup> /g
DyFe <sub>3</sub>	631	535	78	4.6	1.7	9.7	10	21	1.6
HoFe <sub>3</sub>	570	393	73.5	4.4	1.7	9.6	10	34	0.95
ErFe <sub>3</sub>	546	240	46	2.8	1.7	7.9	9	50	0.47
YFe <sub>3</sub>	537	—	110	5.06	1.68	0	0	4	0.5

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