MAGNETIZATION OF IRON GARNETS OF HEAVY RARE EARTH ELEMENTS IN FIELDS UP TO 240 kOe

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The magnetization of iron garnets of yttrium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, and ytterbium was measured at temperatures between 78 and 300° K in fields up to 240 kOe. The effective exchange interaction fields acting on the rare earth ions due to the neighboring iron sublattices and the magnetic moments of the rare earth ions in the garnets are determined on the basis of the data obtained. A field-induced transition to a noncollinear phase is observed in gadolinium, terbium, dysprosium, and holmium iron-garnets. It is shown that in the indicated temperature range the magnetic properties of these four garnets can be described in the collinear and noncollinear phases by molecular field theory involving a temperature-independent magnetic moment for the rare earth ion. The state of the rare earth ion in the other rare-earth garnets studied depends on temperature in this temperature range.

IN spite of a huge amount of research, many important features of the magnetic properties of rare-earth ferrites with the garnet structure (REIG) are still unexplained.

In particular, the state of the rare-earth ion in the crystal structure of the garnet and the effect of temperature and magnetic field upon it have not been determined conclusively. The magnitudes of the exchange interactions of the rare earth ion with the iron sublattices are not known very well. Finally, there is great interest in the field-induced noncollinear magnetic structures in REIG, the existence of which was predicted theoretically[1-5] and has been observed experimentally.[5-11]

For a more complete understanding of the magnetic behavior of REIG it is necessary to investigate them in fields comparable with the effective exchange fields that act on the rare-earth ions ($\sim 10^5$ Oe). In the present work, we studied the magnetic properties of iron garnets of heavy rare earth elements in fields to 240 kOe.

As has been shown in numerous papers (see, for example,[12]), a rare earth iron garnet ($R_3Fe_5O_{12}$) can be represented as consisting of three magnetic sublattices: two formed by the magnetic moments of iron ions in tetrahedral (d) and octahedral (a) sites, and a sublattice formed by the magnetic moments of the rare-earth ions arranged in dodecahedral (c) sites. Between the magnetic moments of iron in the a and d sublattices there is a strong negative interaction, as a result of which in a number of cases it is possible to think of a single resultant iron sublattice with moment $M_{Fe} = M_d - M_a$. The ordering in the rare earth sublattice is created as a result of a weaker negative exchange interaction between the rare-earth and iron sublattices; the interaction within the rare-earth sublattice is small and may be neglected.

In the molecular-field approximation, Clark and Callen[5] have shown that noncollinear magnetic structures arise in REIG over a certain interval of magnetic fields ($H_1 \leq H \leq H_2$) as a result of the competition of the exchange interaction between the rare-earth and resultant iron sublattices and the applied magnetic field. The values of the critical fields $H_{1,2}$ are given by

$$\frac{H_{1,2}(T)}{I_{mol}} \pm M_{Fe} = M_{R_0} B_S\left[\frac{\mu_R}{kT}(H_{1,2}(T) \pm I_{mol} M_{Fe})\right]. \qquad (1)$$

Here the plus sign refers to the field H_1, the minus sign to H_2; μ_R is the magnetic moment of the rare earth ion; $M_{R_0} = 3\mu_R$ is the magnetic moment of the rare-earth sublattice at 0° K per $R_3Fe_5O_{12}$ molecule; I_{mol} is the coefficient of the molecular field acting on the magnetic moments of the rare-earth ions due to the resultant iron sublattice. The coefficient I_{mol} is related to the coefficients of the exchange interactions I_{ex}^{cd} and I_{ex}^{ca} between the rare earth and iron a and d sublattices by the relation

$$I_{mol} = \frac{H_{mol}^c}{M_{Fe}} = \frac{2S\mu_B}{\mu_R}\frac{H_{ex}^c}{M_{Fe}} = \frac{2S\mu_B}{\mu_R}\frac{I_{ex}^{cd}}{1 - M_a/M_d}, \qquad (2)$$

where S is the spin of the rare earth ion. In Eq. (2), it is taken into account that in REIG we have $I_{ex}^{cd} \gg I_{ex}^{ca}$.[13] As the results of[14,15] show, Eq. (2) explains the temperature dependence of the "effective" molecular field coefficient I_{mol} in REIG when I_{ex}^{cd} and I_{ex}^{ca} are independent of temperature.

Calculations[5] show that in REIG a field-induced noncollinear structure can exist only below a certain critical temperature T_{cr}. For REIG with a compensation point, this temperature is somewhat higher, but close to the compensation temperature T_{comp}. At helium temperatures, the critical fields of most REIG exceed 500 kOe but sharply fall to zero near the compensation temperature. Above T_{cr} the transition from collinear ferrimagnetism to collinear ferromagnetism occurs without the emergence of angular structures by means of a paraprocess of the antiferromagnetic type.[16]

When $H \leq H_1$ (ferrimagnetic collinear structure) and $H \geq H_2$ (ferromagnetic collinear structure), the magnetization of the rare earth sublattice is

$$M_R(T,H) = M_{R_0}R_S\left[\frac{\mu_R}{kT}|H \pm I_{mol}M_{Fe}|\right]. \quad (3)$$

Here the plus sign pertains to the ferrimagnetic phase below the compensation temperature and the minus sign to the ferrimagnetic phase above the compensation temperature and to the ferromagnetic phase.

In the angular phase the magnetization of the rare earth sublattice does not depend on field:

$$M_R(T) = M_{R_0}B_S\left[\frac{\mu_R I_{mol}M_{Fe}}{kT}\right]. \quad (4)$$

In the temperature interval we investigated ($T \leq 300°$ K) the magnetization of the iron sublattice M_{Fe} may be considered as independent of field, since the exchange field acting on the iron sublattice ($H_{ex}^{da} = 5 \times 10^6$ Oe) is an order of magnitude greater than the field we applied ($H = 2 \times 10^5$ Oe).

The total magnetization of the REIG in the collinear phases equals the algebraic sum of the magnetizations of the iron and rare-earth sublattices, and in the angular phase, as shown in[5], it depends linearly on the field:

$$M_{tot} = H/I_{mol}. \quad (5)$$

Thus, in the isotherms of the magnetization for $H = H_{1,2}$, one should see breaks corresponding to the transition from a Brillouin function to a linear dependence. The size of these breaks becomes very much smaller as the temperature is raised, and close to the compensation point, where critical fields are now experimentally attainable, high relative measurement precision is required to detect them. Hence, other means of determining the critical fields have been suggested (Faraday effect,[6] absorption spectra,[10] magnetocaloric effect,[7,9] etc.). In[11] we proposed the magnetostriction effect. When the angular structure emerges, the magnetic moments of the sublattices are turned away from the field direction. If one measures, for example, the longitudinal striction, then when the angular structure forms a component of transverse striction of opposite sign arises. This leads to anomalies in the field dependence of the magnetostriction.

Measurements of magnetization and magnetostriction were carried out on polycrystalline samples of iron garnets of heavy rare-earth elements in pulsed magnetic fields up to 240 kOe (pulse length ~ 8 μ sec) over the temperature interval 78—300° K. The magnetization was measured by the induction method.[17] External piezoelectric pickups were used for the magnetostriction measurements.[18] Experimental error was 5—7% for magnetization, 10—12% for the magnetostriction.

Since our measurements were in pulsed fields, the magnetization process could not be considered isothermal. The character of the process (isothermal, adiabatic, polytropic) is determined by the heat transfer time $\tau \approx Cr^2/\lambda$ (C is the specific heat, r is the radius of the sample, λ is the heat-transfer coefficient). Under our conditions $\tau = 10^{-1}$ sec, i.e., much longer than the time of the pulse. Consequently the process of magnetization is adiabatic.

As was shown in[7], it follows from the general formula for the magnetocaloric effect

$$dT = \frac{T}{C_M}\left(\frac{\partial H}{\partial T}\right)_M dM \quad (6)$$

that the temperature increment is zero in the angular phase during adiabatic magnetization. From this same formula, using the above relations for the magnetization of the rare-earth sublattice, it is easy to obtain the change of temperature of the REIG during adiabatic magnetization in the collinear phases:

$$\ln\frac{T_H}{T} = \frac{3k}{C}\int_{z_0}^{z} B_S'(z)\,z\,dz, \quad (7)$$

where T_0 is the temperature in zero field, T_H is the temperature in field H, $z = \mu_R(H \pm I_{mol}M_{Fe})/kT$, C_M is the lattice heat capacity per molecule. From this formula, using the data on heat capacity from[19], it is easy to find the temperature increase during adiabatic magnetization and to take its effect on the magnetization into account. Calculations show that with our measurement accuracy it is possible to neglect the influence of the magnetocaloric effect at room temperature; however, it becomes important when the temperature is lowered.

Figure 1 shows the field dependence of the magnetization at 295 and 78° K. It is seen that the magnetization of yttrium iron garnet is independent of field, whereas the other REIG possess a large paraprocess due to the change of magnetization of the rare earth sublattice in the field. To compare the experimental data with the above theory, it is necessary to know the magnetic moment of the rare-earth ion μ_R and the molecular field coefficient I_{mol}. Usually (see, for example,[12]), I_{mol} is determined from the temperature dependence of the spontaneous magnetization of the rare-earth sublattice according to Eq. (3), and μ_R is found from the spontaneous magnetization at 0° K. However, this is possible

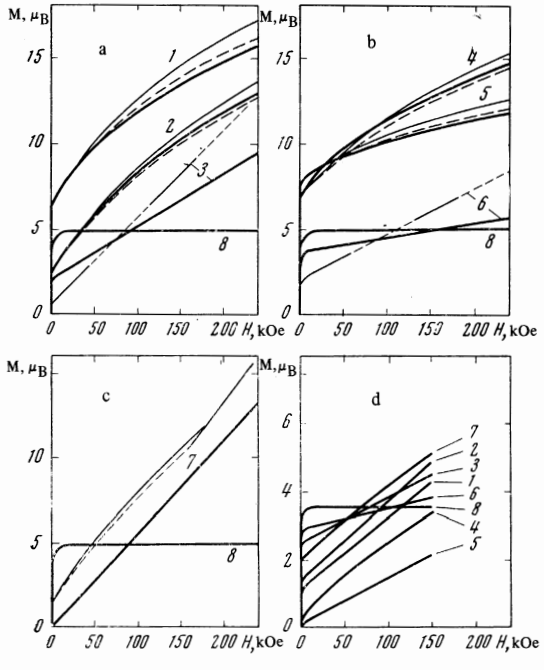

FIG. 1. Dependence of the magnetization of REIG on field at 78° K (a, b, c) and 295° K (d). Curve 1—$Dy_3Fe_5O_{12}$; 2—$Ho_3Fe_5O_{12}$; 3—$Tm_3Fe_5O_{12}$; 4—$Tb_3Fe_5O_{12}$; 5—$Gd_3Fe_5O_{12}$; 6—$Yb_3Fe_5O_{12}$; 7—$Er_3Fe_5O_{12}$; 8—$Y_3Fe_5O_{12}$. Heavy curves—experiment; light solid—theoretical dependence for an isothermal process; broken—theoretical dependence for an adiabatic process. (For the ferrite-garnets of Tm and Yb both theoretical curves coincide.)

only when there is a collinear magnetic structure at 0°K in the absence of field, and, in addition, the crystalline field does not affect the state of the rare-earth ion. These conditions are fulfilled for the gadolinium iron garnet because the trivalent gadolinium ion is in an S state and has no orbital momentum for the crystalline field to influence.[12]

There is information[20] that at low temperatures certain REIG have a noncollinear magnetic structure of the rare-earth sublattice in zero field. In addition, the crystal fields acting on the rare-earth ions in iron garnets split the energy levels of the free rare-earth ions into sublevels that are characterized by values of magnetic moment differing from the magnetic moment of the free ion. The magnitude of this splitting between sublevels in REIG amounts to 10—100 cm^{-1},[14,21,22] and it is obvious that thermal excitations both at nitrogen and room temperatures can affect the population of the sublevels and consequently the magnetic moments of the rare-earth ions. Hence the description of the temperature dependence of the magnetization of the rare-earth sublattice in iron garnets by means of Eq. (3) is, strictly speaking, not valid. However, in a certain interval of temperature for which the population of the sublevels is approximately the same, the Brillouin function will approximately describe the magnetization of the rare-earth sublattice. The value of μ_R may then differ from the corresponding value for the free trivalent ion. In this case μ_R can be determined from Eq. (3) if the spontaneous magnetization of the rare earth sublattice at a given temperature $M_R(T)$ and the molecular field coefficient I_{mol} are known.

Measurements in strong fields permit finding the molecular field coefficient experimentally without making any assumptions about the magnitude of μ_R. In fact, above the compensation temperature $M_{Fe} > M_R$ and the molecular field $H = I_{mol}M_{Fe}$ is antiparallel to the applied field. In fields $H \leq H_{mol}$ an increasing field leads to decreasing magnetic order in the rare-earth sublattice and when $H = H_{mol}$, we have $M_R = 0$, i.e., the total magnetization of the ferrite equals the magnetization of the iron sublattice M_{Fe}. Hence it follows that the external field in which the molar magnetizations of the yttrium iron garnet and the investigated REIG are identical equals the molecular field of the investigated REIG. The values of H_{mol} and μ_R that we determined in this fashion at 295°K are given in the table.

Ion R^{3+}	Gd	Tb	Dy	Ho	Er	Tm	Yb
Spin S	7/2	3	5/2	2	3/2	1	1/2
Orbital momentum L	0	3	5	6	6	5	3
Magnetic moment of ion R^{3+}, $\mu_R = g_J = L + 2S$, μ_B	7	9	10	10	9	7	4
Magnetic moment of ion R^{3+} in REIG from measurements of magnetization at 0°K, [23] μ_B	7	7,7	7,3	6,7	5,1	2,1	1,7
Magnetic moment of ion R^{3+} in REIG from measurements of magnetization at 295°K, μ_B	7±0,4	8,4±0.5	9.1±0.6	8,7±0,6	8.0±0.5	5,6±0.4	3.3±0.3
Molecular field H_{mol} at 295°K, kOe	260±7	165±5	117±5	90±4	70±7	80±9	105±10
Exchange field H_{ex} at 0°K, kOe	283±8	244±7	233±10	215±12	200±20	240±22	378±30

The correctness of using the molecular field approximation with temperature independent rare-earth magnetic moment was checked by comparing the experimental field dependences of magnetization at 78°K with the calculated ones. For the calculations, the values of μ_R and I_{mol} determined at 295°K were used, with the dependence of I_{mol} on temperature taken into account (see Eq. (2)). As is seen from Fig. 1, satisfactory agreement is observed for the REIG of gadolinium, terbium, dysprosium, and holmium. The agreement for the REIG of erbium, thulium, and ytterbium is significantly worse. This shows that the effect of the crystal field on the rare-earth ions in the iron garnets increases with an increase in the relative contribution of the orbital momentum to the total ion angular momentum.

The magnetic moments calculated for room temperature of the rare-earth ions in the garnets of terbium, dysprosium, and holmium are somewhat less than the theoretical values for the free trivalent ions; however, they greatly exceed the magnitudes determined from the magnetic measurements at helium temperatures (see table). This means either that at low temperatures in REIG noncollinear magnetic structures occur in zero field, or that the effect of the crystal field is greatly diminished when the temperature is raised to 78°K.

Note that our data on the effective fields in the REIG of gadolinium, dysprosium, and ytterbium agree well with the results of others.[5,15] However, the effective field in the holmium iron garnet is according to our data 50% greater than that determined from Faraday effect measurements.[6] The reason for this is not yet clear.

The table also gives the values of the exchange fields acting on the rare-earth spins at 0°K, calculated from the experimental data using Eq. (2). It is seen that the exchange fields are about the same for all REIG and decrease somewhat as the atomic number of the rare-earth element increases. The exception is the ytterbium garnet, for which H_{ex} is much greater than for the others. This has already been mentioned in[14], where the exchange field action on Yb^{3+} in garnet was theoretically estimated from the splitting of the Kramers doublet.

In the REIG of gadolinium, terbium, dysprosium, and holmium we observed the emergence of an angular phase in field. Figure 2 shows the field dependence of the longitudinal magnetostriction of these garnets. At temperatures close to the compensation temperature, there are breaks at several places on the $\lambda(H)$ curves; as shown above, these are due to the emergence of angular structures.

In the REIG of dysprosium and holmium we were able to observe the occurrence of angular structures in the field also from the anomalies in the field dependence of the magnetization (Fig. 3). It is seen that above a certain field the magnetization curves are linear in field, as is indeed predicted by the theory of induced angular structures (see Eq. (5)).

In Fig. 4 are shown the temperature dependences of the critical fields for the transition to the noncollinear phase, determined from measurements of the longitudinal and transverse magnetostriction, as well as magnetization. The same figure shows the theoretical functions $H_{1,2}(T)$, calculated in the molecular field approximation from Eq. (1) for isothermal and adiabatic

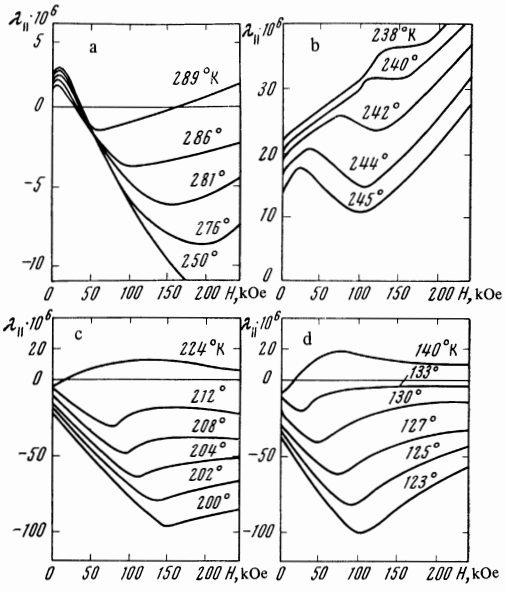

FIG. 2. Dependence of the longitudinal magnetostriction of REIG on field near the compensation temperature. a–$Gd_3Fe_5O_{12}$, b–$Tb_3Fe_5O_{12}$, c–$Dy_3Fe_5O_{12}$, d–$Ho_3Fe_5O_{12}$.

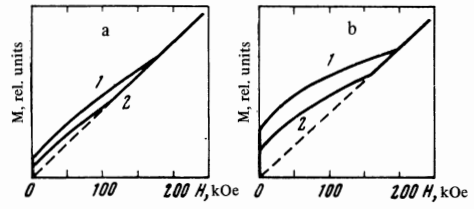

FIG. 3. Dependence of magnetization of REIG on field near the compensation temperature. a–$Dy_3Fe_5O_{12}$, curve 1–200°K, curve 2–210°K; b–$Ho_3Fe_5O_{12}$, curve 1–100°K, curve 2–113°K.

processes. Experiment and theory agree, except that the theoretical values are systematically too high. The reason for this is unknown. Of course, the theory assumes an isotropic ferrimagnetic with zero magnetic anisotropy. Inclusion of anisotropy leads to some change in the phase diagram,[24] as well as to the fact that the transition to the noncollinear phase may become a first-order phase transition, whereas with zero anisotropy it is a second-order phase transition.[25] Although the anisotropy of the garnets is relatively small in the temperature interval we investigated, it can affect the magnitude of the critical fields in the immediate vicinity of the compensation point.

Thus, our measurements of magnetization and magnetostriction in fields to 240 kOe have shown that in the temperature interval 78–300°K the magnetic properties of the REIG of gadolinium, dysprosium, terbium, and holmium in the collinear and noncollinear phases can be described approximately by molecular field theory with a temperature-independent magnetic moment for the rare-earth ion. The state of the rare-earth ion in the REIG of erbium, thulium, and ytterbium changes significantly with temperature in this temperature interval.

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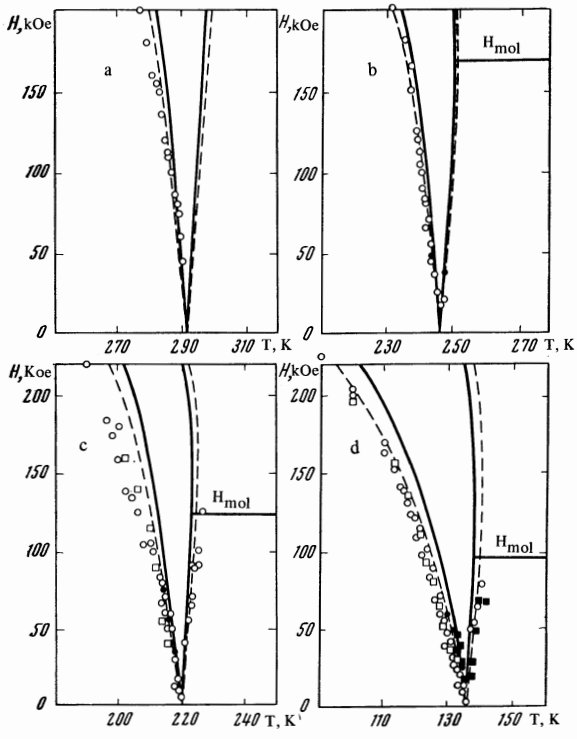

FIG. 4. Dependence of the critical fields of REIG on temperature. a–$Gd_3Fe_5O_{12}$; b–$Tb_3Fe_5O_{12}$; d–$Ho_3Fe_5O_{12}$. Points–experiment: open circle, from longitudinal magnetostriction; solid circle, from transverse magnetostriction; open square, from magnetization; solid square, from Faraday effect. [6] Solid curves–theoretical dependence for an isothermal process; broken curves–theoretical dependence for an adiabatic process.

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