Investigation of the magnetic properties and NMR in spin-reorientation transitions in $DyFe_{0.998}Co_{0.002}O_3$ crystals

A. V. Zalesskiĭ, A. M. Kadomtseva,[1] A. M. Savvinov, M. M. Lukina,[1] G. L. Ovchinnikova,[1] and A. V. Abramov[1]

Crystallography Institute, USSR Academy of Sciences

(Submitted December 6, 1973)

Zh. Eksp. Teor. Fiz. **66**, 1798–1805 (May 1974)

The methods of torsion balances and NMR (of the Fe^{57} nucleus in domains) were used to study the phase transitions connected with the temperature reorientation of the spins in the *b c* and *a c* planes of rhombic $DyFe_{0.998}Co_{0.002}O_3$ crystals. The character of the phase transitions is established, and the singularities of the NMR intensities in the phase transitions, both in the absence and in the presence of an external constant field, are explained.

INTRODUCTION

The phenomenon of spin reorientation in rare-earth orthoferrites has recently been under intensive investigation by various methods (see, e.g., [1,2]). Nuclear magnetic resonance (NMR) was recently used to study the reorientation process in $TmFeO_3$ and $ErFeO_3$ [3,4]. It is of interest to compare NMR investigations of other orthoferrites in which transitions connected with spin reorientation are observed, and it is expedient to combine the NMR procedure with magnetic measurements performed on the same samples.

The purpose of the present paper was to investigate exhaustively the magnetic properties and NMR in $DyFe_{0,998}Co_{0,002}O_3$ crystals, the spin-reorientation transitions in which have not been investigated in detail before. According to the data of [3], when crystals having a similar composition are heated in a temperature interval convenient for experimental purposes (77—300°K), several transitions should be observed, namely, from the antiferromagnetic (AFM) to the weakly ferromagnetic (WFM) state with the appearance of a spontaneous moment **m** parallel to the rhombic axis (a transition analogous to the Morin point T_M in hematite), as well as transitions connected with the gradual reorientation of the spins from the state **m** ∥ a to **m** ∥ c.

SAMPLES AND MEASUREMENT PROCEDURE

The single crystals were grown from the solution in a melt of the compounds 40% PbO, 52% PbF_2, 8% B_2O_3 (molar percentages). The cobalt content was determined by an MK-2 x-ray spectral analyzer, using an external standard, with accuracy to 4%.

A qualitative analysis was also carried out to determine the content of fluorine ions in the investigated crystals, since the melts used to grow the crystals contained monovalent fluorine ions capable of replacing the oxygen ions in the perovskite structure. An URKh-3 analyzer revealed the presence of fluorine in the crystals, and this should have contributed to the entry of the divalent cobalt into the crystals.

The magnetic properties of individual single crystals several millimeters in size were measured with a magnetic torsion balance with an autocompensator. The NMR at the Fe^{57} nuclei (natural isotope content) was observed with the aid of a static-type microwave spectrometer made by DECCA. To obtain a sufficiently intense NMR signal, the single crystals used in the magnetic measurements were oriented in the same direction and glued together to form a single sample. The total weight of this composite sample was 4.9 g. The disorientation of the individual crystals was minimal with respect to the c axis (~1°). The disorientation relative to the a and b axes could reach several degrees.

In addition to the investigation of the magnetic properties and the NMR, we measured the relative change in the real part of the high-frequency susceptibility χ' at a frequency in the region of 36 MHz. To this end we used the same composite sample and the generator of the NMR spectrometer. The change of χ' was registered by measuring the frequency of the generator, whose coil was filled with the sample. The frequency was read continuously, with high accuracy, with the aid of a digital electron-counting frequency meter. In this method, the temperature dependence of the frequency is the sum of the monotonic temperature drift of the frequency of the generator with the empty coil and an additional frequency change due to the dependence of the χ' of the sample on the temperature. At temperatures where χ' increases, the generator frequency decreases because of the increased inductance of the coil.

RESULTS OF INVESTIGATION OF THE MAGNETIC PROPERTIES

The magnetic measurements have shown that single-crystal $DyFe_{0,998}Co_{0,002}O_3$ at $T < 140°K$ is an antiferromagnet with antiferromagnetism vector **l** parallel to the b axis. When heated near $T_M = 140°K$, the crystal goes over into the WFM state (b—c reorientation) with **l** ∥ c and with the appearance of a perpendicular spontaneous moment **m** ∥ a due to the onset of noncollinearity of the spins. With further temperature rise, the spin becomes reoriented from **l** ∥ c to **l** ∥ a (c—a reorientation), causing a rotation of **m** from the a axis to the c axis. At 300°K and above, **m** is parallel to the c axis of the rhombic crystal. Figure 1 shows the temperature dependence of the specific magnetization $\sigma = m/\rho$ (ρ is the density) measured along the axes a and c, while Fig. 2 shows the dependence of the angle θ_0 between the equilibrium direction of **m** ("easy" axis) and the rhombic axis c. The values of σ and θ_0 were obtained from the torque curves with allowance for the torque due to the anisotropy of the paramagnetic susceptibility of the dysprosium ions. The torque due to the anisotropy of the susceptibility of the rare-earth ions was determined from the torque curves plotted in the same plane for single crystals of the non-substituted dysprosium orthoferrite.

As seen from Figs. 1 and 2, the reorientation of the spins to the b axis, accompanied by a WFM-AFM transition at $T_M = 140°K$, occurs practically jumpwise,

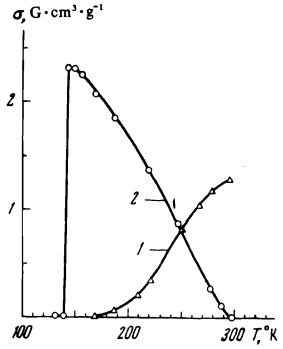

FIG. 1

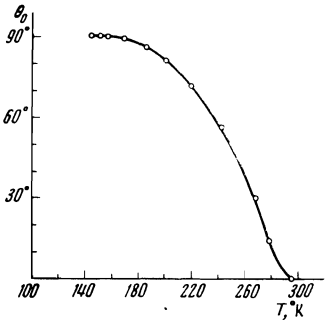

FIG. 2

FIG. 1. Temperature dependence of the specific sponteneous magnetization σ, measured along the axes c (curve 1) and a (curve 2), respectively, for a single crystal of $DyFe_{0.998}Co_{0.002}O_3$.

FIG. 2. Dependence of the angle θ_0 between m and the c axis on the temperature.

whereas the spin reorientation in the ac plane is effected via a smooth rotation of the spins in a wide temperature interval from 170 to 300°K.

From the torque curves plotted in the planes ac and ab we determined the signs of the corresponding second anisotropy constants K_2 and K_2'. It turned out that K_2, corresponding to anisotropy in the ac plane, is positive in the entire temperature interval. On the other hand, from the torque curves near T_M for the ab plane it follows that $K_2' < 0$.

The torque curves at $T < T_M$, where the crystal is antiferromagnetic, reveal abrupt anomalies at sufficiently large values of the projection of the magnetic field H on the a axis; these anomalies are connected with the transition of the crystal from the AFM to the WFM state. The dependence of the AFM → WFM transition temperature on H, determined by this method, is shown by the circles in Fig. 3.

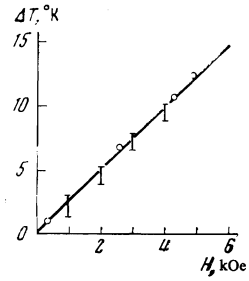

FIG. 3. Shift of AFM-WFM transition temperature under the influence of a field H ∥ a. The bars show the transition interval as obtained from measurement of χ' and of the NMR intensity, while the circles show the results of the magnetic measurements.

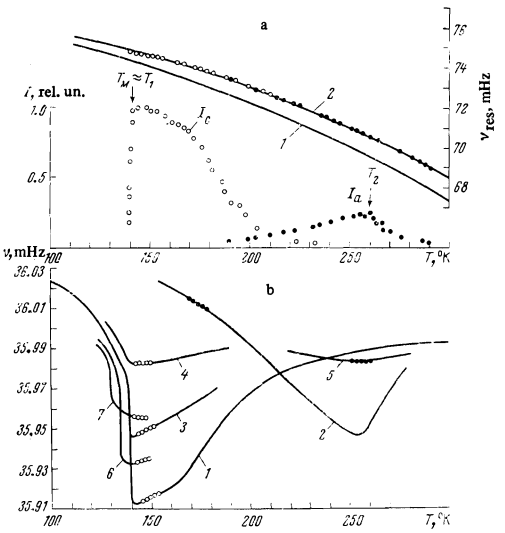

FIG. 4. a) Dependence of the resonant frequency ν_{res} and of the NMR signal intensity I on the temperature at various orientations of the crystals relative to h: ○—for h ∥ c (I_c), ●—for h ∥ a (I_a). Solid curves—NMR for $DyFeO_3$: 1—for domain-wall center, 2—for domain-wall periphery. b) Change, proportional to χ', of the generator frequency ν with changing temperature, at various orientations of the crystals relative to h: (○—for h ∥ c, ●—for h ∥ a) in the absence of a constant field H (curves 1 and 2) and in external fields H ∥ c (curve 3—for 0.2 kOe, 4—for 1 kOe) and H ∥ a (curve 5—for 1 kOe, 6—for 2 kOe, 7—for 4 kOe).

RESULTS OF NMR INVESTIGATIONS

Figure 4a shows the temperature dependences of the NMR frequency and of the amplitude intensities of the NMR signals I_c and I_a, respectively, for two cases of crystal orientation relative to the radio-frequency field, h ∥ c and h ∥ a.

Figure 4b illustrates the relative temperature variation of the real part of the high-frequency susceptibility, for the same two crystal orientations, h ∥ c (χ_c') and h ∥ a (χ_a') in the absence of an external constant field H (curves 1 and 2, respectively) and in external fields H (see the caption of Fig. 4b). Each curve in Fig. 4b consists of a continuous set of experimental points. At the point T_M = 140°K, a jump of I_c and χ_c is observed (the increase of χ_c' corresponds to an abrupt "dip" in the generator frequency). No NMR signal is observed at $T < T_M$. In the region of 260°K there is a second maximum for I_a and χ_a', while I_c and χ_c' have no singularities in this temperature region.

A comparison of Figs. 4a and 4b shows that the NMR intensities I_c and I_a and the susceptibilities χ_c' and χ_a' vary in like fashion.

The behavior of I_a and I_c in an external field is also determined by the values of χ_a' and χ_c'. It is seen from Fig. 4b that in the region 140—200°K, where m is close in direction to the a axis, an increase of the field H ∥ a leads to a gradual decrease of χ_c' and to a shift of the t transition at T_M to lower temperatures (curves 6 and 7). On the other hand, if the field is directed along the c axis, then the susceptibility decreases rapidly even in weak fields: in the field H = 200 Oe, the susceptibility χ_c' is decreased approximately to one-half (curve 3 in Fig. 4b), and a field of 1 kOe (curve 4) smooths out the jump of χ_c' near T_M almost completely. The NMR intensity I_c behaves similarly. It is seen from Fig. 5 that H ∥ a leads to a smooth decrease of I_c (curve 1), whereas in a field H ∥ c the NMR signal becomes comparable with the noise even in a field H = 200 Oe (curve 2). In the region of the high-temperature maxima of χ_a' and I_a, where m is close to the c axis, the character of the influence of the field H is reversed, namely, H ∥ c leads to a smooth decrease (curve 3 of Fig. 5), and the field H ∥ a leads to an abrupt decrease of I_a (curve 4 in Fig. 5) and χ_a' (curve 5 in Fig. 4b).

Figure 3 shows the shift of the AFM → WFM transition under the influence of a field H ∥ a. In the presence of the field, the transition was observed by us both with the aid of magnetic measurements (see the preceding section) and by measuring the NMR intensity I_c and the susceptibility χ_c'. The temperature interval of the transition in the latter case was estimated from the steepest section of the dependence of χ_c' on T, from curves similar to curves 6 and 7 of Fig. 4b. As seen from Fig. 3, the re-

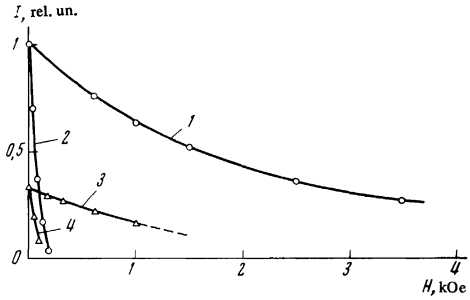

FIG. 5. Dependence of the NMR signal intensity I on the magnitude and direction of **H** at various temperatures (○–for h ∥ c, Δ–for h ∥ a): curves 1–for **H** ∥ a, 153 K; 2–for **H** ∥ c, 153 K; 3–for **H** ∥ c, 240 K; 4–for **H** ∥ a, 240 K.

sults obtained by different methods on the influence of **H** ∥ a on the transition temperature are in good agreement.

DISCUSSION OF RESULTS

To interpret the NMR data, it is important to ascertain whether the NMR signal is produced by nuclei located in domains or whether it is connected with nuclei in the domain walls. The following facts indicate that the NMR enhancement is due to the interaction of h with **m** in the domains. First, the NMR signal is maximal when the angle φ between h and **m** in the domains is close to $\pi/2$ and lies in the ac plane. In the case of the "intrawall" signal, it is natural to expect the signal to be maximal at $\varphi = 0$ (h is directed along the "easy" axis), where then the wall displacement is maximal. Second, application of an external constant field **H** ∥ h (curves 2 and 4 in Fig. 5) leads to a faster decrease of the signal intensity than in the case **H** ⊥ h, when **H** is almost parallel to the easy-magnetization axis (curves 1 and 3 in Fig. 5). The decrease of the NMR intensity in the case **H** ⊥ h is typical of nuclei in domains, the gain of which varies like $H_n/(H_a + H)$ (H_n is the local field at the nucleus, H_a is the anisotropy field). Third, the NMR frequencies fit well the temperature dependence of the "domain" NMR frequency[2)] obtained in [8] for pure $DyFeO_3$. The NMR frequency for nuclei at the centers of domain walls (curve 1 in Fig. 4a) decreases more steeply with temperature.

As shown in [3,4], maxima of the gain η in the domains are observed for the $ErFeO_3$ and $TmFeO_3$ crystals following reorientation of the c-a type at the points T_1 (start of reorientation) and T_2 (end of reorientation, $T_2 > T_1$). In our case we also observed two maxima for the intensities I_c and I_a and the corresponding susceptibilities χ_c' and χ_a'.

The maxima of I and χ' are analogous in their physical nature to the susceptibility singularities observed at T_1 and T_2 in the crystals $TmFeO_3$ and $ErFeO_3$ in a wide range of frequencies, starting with 60 Hz [7] and all the way to 5400 MHz [8]. A theoretical treatment of the high-frequency properties of orthoferrites is presented in [9,10]. That these phenomena are related is indicated by the complete identity of the behavior of the NMR intensity and χ'. The gain η in the domains, like χ', is determined by a quantity $d\theta/dh$, which characterizes the small deviation of **m** from the equilibrium direction θ_0 under the influence of a weak radio-frequency field h. In those cases when h ∥ c or h ∥ a, recognizing that h is small, we can assume accordingly $\varphi \approx \theta_0$ or $\varphi \approx \pi/2 - \theta_0$. The expression given in [4] for $d\theta/dh$ then reduces to

$$\frac{d\theta}{dh_c} \approx \sin\theta_0 \Big/ \frac{1}{m}\left(\frac{\partial^2 F_a}{\partial\theta^2}\right)_{\theta=\theta_0}, \quad \frac{d\theta}{dh_a} \approx \cos\theta_0 \Big/ \frac{1}{m}\left(\frac{\partial^2 F_a}{\partial\theta^2}\right)_{\theta=\theta_0} \qquad (1)$$

where $F_a = K_1 \sin^2\theta + K_2 \sin^4\theta$ is the anisotropy energy in the ac plane (the angle θ is measured from the c axis). The quantity $(1/m)(\partial^2 F_a/\partial\theta^2) = H_a$ is the anisotropy field that characterizes the "rigidity" of the coupling of **m** with the direction θ_0. At the points T_1 and T_2, where $-K_1 = 2K_2$ and $K_1 = 0$, respectively, a local loss of "rigidity" of the spin system takes place, since H_a vanishes (in a real crystal, H_a has a certain finite value at T_1 and T_2). The spin system is not acted upon in this case by the restoring forces at small deviations of **m** from θ_0, and this leads to an increase of the amplitude of the oscillation of the spins in the field h, and consequently to the appearance of maxima of χ' and η. The indicated loss of "rigidity" causes, in particular, the frequencies of the antiferromagnetic resonance to vanish in theory at the points T_1 and T_2 [9,10].

According to (1), the direction of the maximum susceptibility for the region $T \approx T_1$ ($\sin\theta_0 \approx 1$) is the c axis, and for the region $T \approx T_2$ ($\cos\theta_0 \approx 1$) it is the a axis, as is observed in the experiment. Inside the reorientation region $T_1 < T < T_2$, the quantities I_a, I_c, χ_a', and χ_c' are determined by the temperature dependences of H_a and θ_0.

In the region of the low-temperature maximum of I_c and χ_c', the situation is made more complicated by the presence of the point $T_M = 140°K$, below which the crystal goes over into the AFM state as a result of a reorientation of the c–b type. It was of interest to ascertain whether a jump of I_c and χ_c' is observed at T_M if the temperature region of the c–a reorientation is located at a considerable distance from the T_M point. To this end we measured χ_c' and searched for an NMR signal in crystals with larger cobalt content ($DyFe_{0,994}Co_{0,006}O_3$), for which, according to the magnetic-measurement data, $T_M \approx 130°K$ and T_1 exceeds room temperature. No anomaly of χ_c' was observed in this crystal at the point T_M, and there was no NMR signal. We conclude therefore that the abrupt jumps of I_c and χ_c at T_M are due to the fact that owing to the transition to the WFM phase the crystal turns out to be in a state with low value of H_a, because of the proximity of T_M and T_1, although magnetic measurements have shown that **m** begins to deviate noticeably from the a axis only at $T > 170°K$ (Fig. 2). The temperature T_2 corresponding to the maximum of I_a and χ_a' (260°K) is also shifted somewhat relative to the temperature at which, according to the magnetic-measurement data, the angle θ_0 becomes equal to zero (~ 300°K). The reasons for this discrepancy in the determination of T_1 and T_2 by different methods are not yet clear.

It is seen from Fig. 3 that the transition from the AFM phase to the WFM phase shifts practically linearly in temperature with increasing field **H** ∥ a. The value of this shift is ~2.5 deg/kOe. The shift of T_M in a field **H** ∥ a, shown in Fig. 3, should be treated as a temperature dependence of a certain critical (or threshold) field H_{cr} that induces the AFM → WFM transition. The field H_{cr} is directed in our case perpendicular to the AFM vector **l**. An induced AFM → WFM transition of this type was observed in hematite in a field **H** ⊥ **l** below the Morin point [11], although the analogy between these transitions may not be complete.

Unlike the smooth spin-reorientation transition in the ac plane, the AFM → WFM transition takes place prac-

tically jumpwise. Judging from the curves 6 and 7 in Fig. 4b, the presence of a field does not lead to a significant smearing of the transition, and only decreases the jump of the susceptibility χ_c'. It is known that in the case of spin reorientation, when the first anisotropy constant reverses sign, the character of the transition is determined by the sign of the second anisotropy constant. A negative sign of the constant K_2', corresponding to b—c reorientation, with a sign-variable first anisotropy constant explains the jumplike character of this transition. No temperature hysteresis was observed in b—c reorientation.

A positive sign of the constant K_2 in the ac plane causes the orientation of the c—a type to proceed via two second-order phase transitions at T_1 and T_2. The length of the a—c reorientation interval is apparently due to the large value of $K_2 > 0$, which is comparable with K_1 in magnitude over a wide temperature interval, inasmuch as the relation $\sin^2\theta_0 = -K_1/2K_2$ should be satisfied at $T_1 < T < T_2$[2]. The large values of K_1 and K_2 may be due to the presence of Co^{2+} ions, which have a degenerate orbital ground state. As noted above, the presence of univalent fluorine in the ion flux can contribute to the appearance of the divalent cobalt ions.

We note that a 90° rotation of the spins, connected with the a—c reorientation, does not noticeably affect the temperature dependence of the NMR frequency. This indicates that the anisotropy contribution to the local field at the nuclei in this crystal is small. The NMR signal splitting observed in $TuFeO_3$ and $ErFeO_3$[3,4], was not observed in the region of the a—c reorientation. The distortions that lower the symmetry of the unit cell to monoclinic in the interval $T_1 < T < T_2$ are apparently small, because of the large temperature region over which the reorientation takes place, in comparison with the orthoferrites of thulium and erbium, in which this region occupies only ~10°K.

CONCLUSION

The crystal with composition $DyFe_{0,998}Co_{0,002}O_3$ is an object unique in the abundance of the phase transitions observed in the interval 77—300°K. The small amount of cobalt, which apparently enters into the structure in the form of divalent ions, strongly alters the energy of the magnetic anisotropy, causing the appearance of a reorientation of the type a—c that extends over more than 100° and a shift of the T_M point to 140°K as against $T_M \approx 40$°K for nonsubstituted $DyFeO_3$. The large temperature region of reorientation of the spins in the a—c plane is due to the large value of $K_2 > 0$ in this plane, which is comparable with K_1 in a wide temperature interval. The transition at T_M takes place jumpwise, this being due to the negative sign of the second anisotropy constant K_2' in spin reorientation to the b axis of the rhombic c crystal. Application of an external field $\mathbf{H} \parallel$ a in the AFM phase can induce an AFM → WFM transition at $T < T_M$. In this case the transition hardly spreads out in fields up to 10 kOe. Since the anisotropy field depends strongly on the temperature near the region of spin reorientation, an abrupt jump of the susceptibility and of the NMR gain, which determines the intensity of the NMR absorption, is observed in the investigated single crystal, where T_M and T_1 are close to each other.

In the crystal $DyFe_{0,994}Co_{0,006}O_3$, in which T_1 is far from T_M, no such phenomenon was observed.

The NMR absorption intensity, just as the high-temperature susceptibility χ', is determined by the temperature dependence of the angle θ_0 and of the anisotropy field H_a. The points T_1 and T_2 correspond to the maxima of the NMR intensity and of χ'. The singularities of the NMR intensity and χ' at the points T_1 and T_2 can readily be accounted for from the point of view of the theory developed to explain the high-frequency properties of orthoferrites in the reorientation region[9,10]. The absence of NMR frequency splitting in the region $T_1 < T < T_2$ is evidence of negligible distortion of the rhombic lattice in the ac reorientation process.

[1)] Moscow State University.

[2)] Introduction of a small number of cobalt ions into $DyFeO_3$ cannot greatly change the local field at the Fe^{57} nuclei.

[1] R. L. White, J. Appl. Phys. **40**, 1061, 1969.
[2] K. P. Belov and A. M. Kadomtseva, Usp. Fiz. Nauk **103**, 577 (1971) [Sov. Phys.-Uspekhi **14**, 154 (1971)].
[3] V. D. Doroshev, A. S. Karnachev, N. M. Kovtun, E. E. Solov'ev, A. Ya. Chervonenkis, and A. A. Shemyakov, Phys. Stat. Sol. (b) **51**, K31 (1972).
[4] N. M. Kovtun, A. S. Karnachev, E. E. Solov'ev, A. Ya. Chervonenkis, and A. A. Shemyakov, Fiz. Tverd. Tela **14**, 2150 (1972) [Sov. Phys.-Solid State **14**, 1856 (1973)].
[5] L. Holmes, L. G. Van Uitert, and R. Heaker, J. Appl. Phys. **42**, 657, 1971.
[6] A. V. Zalesskiĭ, A. M. Savvinov, I. S. Zheludev, and A. N. Ivashchenko, Fiz. Tverd. Tela **15**, 903 (1973) [Sov. Phys.-Solid State **15**, 623 (1973)].
[7] R. Wolfe, R. D. Pierce, S. E. Maszko, and J. P. Remeika, Appl. Phys. Lett. **11**, 245, 1967.
[8] R. C. Le Craw, R. Wolfe, E. M. Gyorgy, F. B. Hagedorn, J. C. Hensel, and J. P. Remeika, J. Appl. Phys. **39**, 1019, 1968.
[9] J. R. Shane, Phys. Rev. Lett. **20**, 728, 1968.
[10] F. B. Hagedorn and E. M. Gyorgy, Phys. Rev. **174**, 540, 1968.
[11] J. Kaczér and T. Shalnikova, Proc. Int. Conf. on Magnetism, Nottingham, 1964, p. 589.

Translated by J. G. Adashko
185