INVESTIGATION OF IRON SUBLATTICES IN A MONOCRYSTAL OF THE ORTHOFERRITE $TmFeO_3$

A. G. KOCHAROV, A. A. LOSHMANOV, I. I. YAMZIN, and A. Ya. CHERVONENKIS

Institute of Crystallography, USSR Academy of Sciences

Submitted August 21, 1969

Zh. Eksp. Teor. Fiz. 58, 1511–1517 (May, 1970)

The methods of elastic magnetic scattering of neutrons ($\lambda = 1.07$ Å) and of torques were used to investigate the behavior of the antiferromagnetic structure formed by the moments of Fe^{3+} ions in the orthorhombic compound $TmFeO_3$ in the temperature interval from 78 to 720°K. The Néel temperature of the iron sublattices, determined from the temperature dependence of the integral magnetic reflection intensities, is 550 ± 5°K. The experimental temperature dependence of the integral intensities agrees with the Brillouin function for the ground spin state $S_{5/2}$ of the Fe^{3+} ion. The magnetic moment of the iron ions at 0°K is $4.68 \pm 0.08\ \mu_B$. It is shown that the anomaly of the torques in the temperature interval from 103 to 78°K is caused by reorientation of the weak-ferromagnetism vector from the [001] direction to the [100] direction; the reorientation is not complete at 78°K. Matters discussed include the reasons for the discrepancy between experimental and calculated form factors of the Fe^{3+} ion at large scattering angles, and the reasons for the shift of the temperature interval of reorientation between magnetic and neutronographic measurements.

IN recent years, the attention of investigators has been attracted by the orthoferrites of the rare-earth elements, with the general formula $MeFeO_3$ (where Me = Sm, Ho, Er, Tm, Y, etc.); these are promising materials in the microwave range.

The chemical structure of these orthoferrites belongs to the space group Pbnm; all these compounds display weak ferromagnetism. The weak ferromagnetism in these orthoferrites is due to a small deviation of the magnetic moments of the Fe^{3+} ions, which form an antiferromagnetic structure, from collinearity.

Neutronographic research[1] carried out on powder specimens has detected a different behavior of the iron and of the rare-earth sublattices. If the Néel temperature of the iron sublattices in the Ho and Er orthoferrites amounted to 700 and 620°K respectively, the ordering of the moments in the rare-earth sublattices set in at 6.5 and 4.3°K. The values of the magnetic moments of the iron ions were 4.60 and 4.62 μ_B. Furthermore, one is struck by the large diminution of the value of the moments on the Ho^{3+} and Er^{3+} ions (7.5 and 5.8 μ_B respectively) as compared with the values for the free ions. At temperatures below room temperature, there has been observed in these orthoferrites an abrupt change of intensity of the antiferromagnetic reflections; this is caused by a change of the orientation of the magnetic moments in the iron sublattices with respect to the axes of the orthorhombic cell. In this process, the moments, directed at room temperature along [100] (the a axis), were reoriented at low temperatures to the direction [001] (the c axis) in Ho orthoferrite, or to the direction [110] in Er orthoferrite. The limits of the temperature interval of reorientation, however, have not been determined.

In[2,3] an anomaly was detected in the torque curves in Tm orthoferrite in the 100°K region; this also was attributed to reorientation of the moments in the iron sublattices. Further investigations of torques[4] and of high-frequency losses[5] and neutronographic investigation[6] of the temperature behavior of the moments in the iron sublattices of Tm orthoferrite confirmed the presence of reorientation of the moments in the temperature interval 80 to 91°K; ordering of the moments in the rare-earth sublattices was not observed down to 1.6°K. The antiferromagnetic component of the "iron" moments changed from direction [100] (the a axis) at high temperatures to direction [001] (the c axis) at low temperatures. The ferromagnetic component underwent the reverse reorientation from [001] to [100]. However, insufficient angular resolution, resulting from the use of powder specimens[6], prevented the following of the course of the reorientation in this temperature interval.

In[4,5] it was shown that application of a magnetic field influences the position of the axis of easy magnetization and, as a result, the location and width of the temperature interval of reorientation. Heat treatment of the specimens in hydrogen had a similar effect.

The present paper presents the results of magnetic and neutronographic investigations of the behavior of the iron sublattices in a monocrystalline specimen of the orthoferrite $TmFeO_3$ over a wide range of temperature. Use of monocrystals made it possible to obtain more detailed information.

1. SPECIMENS AND METHOD

The $TmFeO_3$ monocrystals were grown by the method of crucibleless zone fusion in air or under controlled oxygen pressure[7], with use of oriented seeding. Monocrystals of length 50 mm and diameter 4 mm were obtained, oriented along the a, b, and c axes of the orthorhombic cell; from these the specimens to be investigated were cut. Torque measurements were made over a wide range of temperature on monocrystalline spheres of diameter 2 mm, in a constant field of 20 kOe.

The neutronographic investigation was made on cylindrical monocrystalline specimens of diameter 3.3. mm and height 11 mm, cut from the same "oxygen-free" monocrystalline bars as the specimens for magnetic measurements. In one specimen the a axis was oriented along the generators of the cylinder, in another the c axis. In the exposures, the specimens were so oriented that a cylinder generator was parallel to the vertical axis of the spectrometer. Observations were made at wavelength 1.07 Å of monochromatic neutrons. The monocrystal was placed in a cryostat or even with regulated temperature (accuracy of regulation ± 1°), which was placed on a goniometer head on the table of the diffractometer, for mapping of the reflections of the $\{0kl\}$ or $\{hk0\}$ band. The temperature was measured with a copper-constantan thermocouple in the low-temperature range and with a platinum, platinum-rhodium thermocouple in the high-temperature range.

2. RESULTS

A. High-temperature Region

In the high-temperature region, only neutronographic measurements were made.

At room temperature, along with reflections allowed by the space group Pbnm, there were observed superstructure reflections with indexes $k, l = 2n + 1$, indexed on the base of the collinear antiferromagnetic structure which is formed by the magnetic moments of the Fe^{3+} ions alone, and whose elementary cell coincides with the chemical.

The integral intensity according to rotation curves was measured for the superstructure reflections (011), (013), (031), (033), (015), (051), (017), and (055) in the temperature range from 293 to 570°K, and also for the nuclear reflections (022) from the specimen with a-orientation and for the nuclear reflections (110) and (220) from the specimen with c-orientation. The intensity of the nuclear reflections was measured at temperatures up to 720°K, and the values of the integral intensities were used thereafter for introduction of corrections for the Debye factor. In the calculations for room temperature, the value B = 0.71 was taken from[8].

The angular dependence of the integral intensity of the magnetic reflections at room temperature was normalized to that for the magnetic form factor of the Fe^{3+} ion[9], with allowance for the fact that $q^2 = 1$ for the reflections in question, since the magnetic moment of the Fe^{3+} ions at room temperature is directed along the a axis. The result of the normalization is shown in Fig. 1.

As is seen from Fig. 1, there is a significant deviation of the experimental values for the first two, strongest reflections. On increase of the scattering angle and resulting diminution of the intensity of the magnetic reflections, the discrepancy between the two curves rapidly vanishes. This effect is due to the presence of appreciable magnetic extinction in the first reflections. On the basis of such normalization, a correction was introduced for extinction for the first three reflections, on the assumption that the integral intensity for the subsequent reflections is unaltered. One should note the weaker angular dependence of the magnetic reflections at remote angles, as compared with the predicted form factor[9].

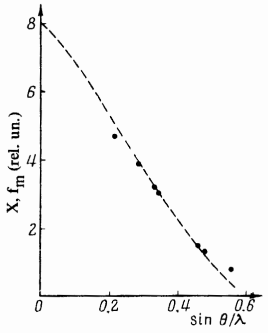

FIG. 1

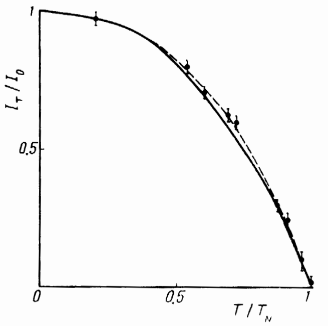

FIG. 2

FIG. 1. Angular dependence of the integral intensity of magnetic reflection, $X = \sqrt{I_{0kl} \sin \theta_{0kl}}$ (points), and magnetic form factor f_m of the Fe^{3+} ion [4] (dashed curve). An experimental point with coordinates $\sin(\theta/\lambda) = 0.1115$, $X = 4.70$ is absent on the figure.

FIG. 2. Dependence of the reduced integral intensity (experimental points and dashed curve) on reduced temperature, and square B_S^2 of the Brillouin function for spin state $S_{5/2}$ (solid curve).

The values of the integral intensities of the magnetic reflections, corrected for extinction, Debye factor, and form factor, were used to determine the temperature dependence of these intensities, which is shown in Fig. 2 together with the square of the Brillouin function, B_S^2, calculated for the ground state $S_{5/2}$ of the Fe^{3+} ion. The Néel temperature of the iron sublattices used to determine these curves was obtained by extrapolation of the corrected values of the integral intensities of the magnetic reflections to the value zero; it was 550 ± 5°K. One should note the discrepancy between the curves in Fig. 2 in the middle range of temperature—small, but exceeding the limits of experimental error.

The values of the integral intensities, corrected for the Brillouin factor, were converted to absolute units on the basis of the integral intensity of the reflection (004) from an extinctionless monocrystal of NaCl of dimensions 10 × 2 × 0.5 mm. The absence of extinction in the NaCl monocrystal was verified by sequential mappings on transmission and reflection with sequential thinning of the crystal by etching in water. The correction for the Debye factor for NaCl at room temperature was taken from[10].

From the absolute values obtained for the intensity of the integral magnetic reflections, values of the magnetic moments of the Fe^{3+} ions, μ_{Fe}, were calculated. The spread of the values of μ_{Fe} calculated from all the measured reflections was less than ± 2% and lay within the limits of total experimental error, taking into account the errors of measurement of the intensities from the orthoferrite and the NaCl and the errors in the determination of the Néel temperature and of the Debye factors. The mean value of μ_{Fe} according to all the measured reflections was 4.68 ± 0.08 μ_B. It should be mentioned that the value of the magnetic moment calculated for the reflection (055), on the assumption that it satisfies the Fe^{3+} form factor from[9], lies appreciably lower and amounts to about 1 μ_B, whereas the value of the moment obtained from the experimental value agrees, within the limits of error, with the value of μ_{Fe} obtained from the other reflections. This suggests an actual discrepancy between the form-factor dependence of our magnetic reflections and the form factor of[9] at remote angles of reflection.

B. Low-temperature Measurements

a) Magnetic measurements. Figure 3 shows the angular dependence of the torque for a $TmFeO_3$ monocrystal in the (001) plane, taken at various temperatures. It is seen from the figure that in a certain temperature interval the torques reveal an anomalous character, similar to that found earlier[2,3]: with increase of temperature, the magnetization along the orthorhombic axis a decreases along with a decrease of the anisotropy energy. The temperature dependence of the magnetization along the a axis, constructed from these data (Fig. 4, a), shows that the reorientation of the magnetization vector (the weak ferromagnetic component) from the a to the c axis, and consequently of the direction of the antiferromagnetic moments from the c to the a axis, begins near 80°K and is completed at 105°K. But as follows from Fig. 4, the orientation along the a axis is incomplete even at 78°K. For the crystal grown under oxygen pressure (the "oxygen" bar), the analogous temperature range was shifted about 5°K toward lower temperatures (Fig. 4, b).

b) Neutronographic measurements. The integral intensity of the magnetic reflection (011) was measured in the temperature range 130 to 78°K. In addition, check measurements of the intensity of the magnetic reflection (013) were made at temperatures 105 and 78°K.

The results of the measurements are given in Fig. 5, where the temperature dependence of the integral intensity of the reflection (011) is presented. As is seen from the graph, in the temperature interval from 103 to 78°K there occurs a reorientation of the antiferromagnetic moments, leading to a diminution of the integral intensity. The integral-intensity ratio I(103°K)/I(78°K) is 1.44. The analogous ratio for the reflection (013) is 3.85.

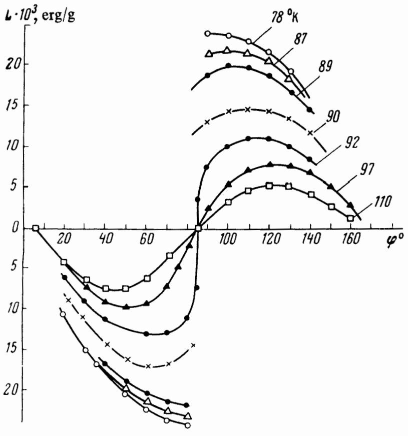

FIG. 3. Torque curve of a $TmFeO_3$ monocrystal grown in air; plane (001), field 20 kOe.

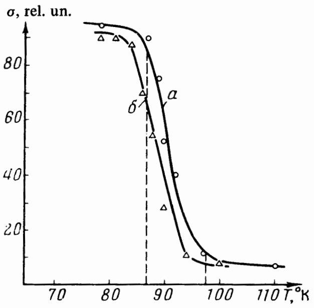

FIG. 4

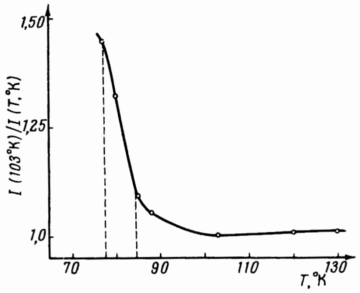

FIG. 5

FIG. 4. Temperature dependence of the magnetization of a $TmFeO_3$ monocrystal along the orthorhombic a axis: a, monocrystal grown in air; b, monocrystal grown under oxygen pressure 10 atm. The dashed lines bound the region of most abrupt change of the quantity being measured.

FIG. 5. Temperature dependence of the ratio of integral intensities of the magnetic reflection (011) of a $TmFeO_3$ monocrystal grown in air.

The observed effect is caused by a turning of the moments in the iron sublattices from a direction parallel to the a axis to a direction parallel to the c axis of the orthorhombic cell; the noncollinearity is preserved, since the weak ferromagnetic moment is preserved.

The integral-intensity ratio of the reflections (011) and (013) for ideal orientation of the moments along the a and c axes is 1.54 and 5.84, respectively. The smaller experimental values of the ratios and their temperature dependence (Fig. 5) show that the reorientation process is not complete at 78°K; the direction of the moments makes an angle ~ 10° with the c axis.

3. DISCUSSION OF RESULTS

Comparison of the results obtained with the data of a neutronographic investigation of the isostructural Ho and Er orthoferrites[1] reveals a nearly linear decrease of the Néel temperature with increase of the number of 4f-electrons on the rare-earth ion (700, 620, and 550°K, respectively, for the Ho, Er, and Tm orthoferrites). But the value of the magnetic moment of the Fe^{3+} ion, within the limits of error, remains constant (4.60, 4.62, and 4.68 μ_B, respectively, with error ± 2%); all three values are less than the value 5 μ_B characteristic of the ground spin state $S_{5/2}$ of the Fe^{3+} ion. Along with this should be noted the different orientation of the antiferromagnetic moments of the Fe^{3+} ions with respect to the crystallographic axes in these orthoferrites at low temperatures.

Such a difference of the magnetic sublattices of the iron ions in Ho, Er, and Tm orthoferrites can be explained by the presence of indirect exchange via the O^{2-} ion, as also in α-Fe_2O_3. In this connection one must take into account that in the whole exchange interaction, besides the bonds with angle 180°, of the type Fe—O—Fe, the bonds with angle 90° make an appreciable contribution[11]. Since these orthoferrites exhibit a contraction of the lattices on going from Ho to Tm and a different deviation from the ideal atomic configuration for space group Pbnm, it is natural to expect a change of nature of the exchange in the sublattice of iron ions, and a related change of the Néel temperature.

In the previous section, we mentioned the discrepancy of the form-factor values for the Fe^{3+} ions in the orthoferrite and in the spinel[9] at large scattering angles. This discrepancy can be explained by assuming a certain "unfreezing" of the orbital moment of the iron ions in the orthoferrite lattice. In such a case, the form factor can be expressed as the sum of a spin form factor f_S and an orbital f_L. Since the orbital contribution is small, but the value of f_L decreases with scattering angle more slowly than does the value of f_S[12], the contribution from f_L should in principle show up at remote scattering angles.

The shift of the temperature interval of reorientation in the case of the "oxygen" specimen can be explained by oxidation of the Fe^{2+} ions in the growth process. An analogous explanation can be given for a certain discrepancy between the values of the temperature interval obtained in this paper and in papers[5,6], since the crystals investigated in[5,6] were obtained from solution in a melt of lead salts and consequently could contain Fe^{4+} ions. According to[13], the presence in orthoferrite crystals of Fe^{2+} and Fe^{4+} ions appreciably influences the position and width of the temperature range of reorientation.

Besides the displacement of the temperature interval, which may be caused by the conditions under which the specimens were obtained, we observed a displacement of the region of most rapid change of the quantity being measured (the region in Figs. 4 and 5 bounded by the dashed lines), between the magnetic and the neutronographic measurements. In the case of the neutronographic measurements, the change near 100°K has a smoother character, and the region of abrupt change is shifted to lower temperatures.

The observed discrepancy may be due to the presence of an external field at the time of the magnetic measurements, or to temperature hysteresis, since the magnetic measurements were made on heating and the neutronographic on cooling of the specimen. Neutronographic check measurements on heating the specimen, within the limits of experimental error, revealed no hysteresis. In[5], however, there is an indication of a displacement of the temperature interval of reorientation under the influence of an external field.

---

[1] W. C. Koehler, E. O. Wollan, and M. K. Wilkinson, Phys. Rev. **118**, 58 (1960).

[2] C. Kuroda, T. Migadai, A. Naemura, N. Niizeki, and H. Takata, Phys. Rev. **122**, 446 (1961).

[3] K. P. Belov, A. M. Kadomtseva, T. M. Ledneva, T. L. Ovchinnikova, and V. A. Timofeeva, ZhETF Pis. Red. **2**, 253 (1965) [JETP Lett. **2**, 161 (1965)].

[4] E. M. Gyorgy, J. P. Remeika, and F. B. Hagedorn, J. Appl. Phys. **39**, 1369 (1968).

[5] R. C. LeCraw, R. Wolfe, E. M. Gyorgy, F. B. Hagedorn, J. C. Hensel, and J. P. Remeika, J. Appl. Phys. **39**, 1019 (1968).

[6] J. A. Leake, G. Shirane, and J. Remeika, Solid State Commun. **6**, 15 (1968).

[7] S. A. Medvedev, A. M. Balbashov, and A. Ya. Chervonenkis, Monokristally tugoplavkikh i redkikh metallov (Monocrystals of High-melting and Rare Metals), Metallurgiya, 1969, p. 15.

[8] G. Will, and O. Eberspächer, Z. anorg, allgem. Chem. **356**, 163 (1968).

[9] L. M. Corliss, J. M. Hastings, and F. G. Brockman, Phys. Rev. **90**, 1012 (1953).

[10] W. J. L. Buyers and T. Smith, J. Phys. Chem. Solids **25**, 483 (1964).

[11] E. J. Samuelsen, Physica **34**, 241 (1967).

[12] G. E. Bacon, Neutron Diffraction (Russ. transl.) IIL, Moscow, 1957, p. 215. [Oxford Univ. Press].

[13] E. M. Gyorgy, J. P. Remeika, and D. L. Wood, J. Appl. Phys. **39**, 3499 (1968).

Translated by W. F. Brown, Jr.
180