Giant Magnetostriction Due to Jahn-Teller Distortion in Fe_2TiO_4

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An anomalously large magnetostriction has been found in Fe_2TiO_4. The magnetostriction constants λ_{100} and λ_{111} are $(4.7\pm0.4)\times10^{-3}$ and $(1.3\pm0.4)\times10^{-3}$, respectively, at 77°K. The origin of the giant magnetostriction has been found to be due to the reduction of the elastic constant $c_{11}-c_{12}$ as the result of the presence of Jahn-Teller Fe^{2+} ions in the tetrahedral site.

This paper reports the first observation of the giant magnetostriction caused by the softening of the lattice in Fe_2TiO_4. Fe_2TiO_4, ulvöspinel, is an inverse spinel containing only Fe^{2+} ions and is cubic at room temperature. The crystal becomes weakly ferromagnetic below 142°K with a spontaneous magnetic moment of $0.2\mu_B$ at 4.2°K.[1] A neutron diffraction study[2] has shown that the magnetic structure is of the Néel type with the sublattice magnetic moments of $(4.2\pm0.2)\mu_B$ at 4.2°K on both sites. The weak ferromagnetic moment at 4.2°K appears by the canting of spins. The sublattice magnetization on the octahedral site decreases with increasing temperature faster than that on the tetrahedral site. The ferromagnetic moment due to the uncompensation of the sublattice moments therefore increases with increasing temperature. The resultant ferromagnetic moment makes an angle of about 45° with the spin direction at 77°K. The spins which align in the ⟨100⟩ direction perpendicular to [100] in the case of weak fields tend to orient to the field direction when more than 10 kOe of external field is applied parallel to [100]. The crystal was found to distort tetragonally at low temperatures[1] with the spins in the long axis and the tetragonal axis could be changed by the external field.[2] Therefore the tetragonal distortion on the order of $(c-a)/a=5\times10^{-3}$ has been suggested to be due to the anomalously large magnetostriction.[3]

The crystal distortion of a single crystal [(011) platelet] of almost pure ulvöspinel, $Fe_{2.05}Ti_{0.95}O_{4.00}$, has been studied as a function of temperature (77 to 300°K), magnetic field (up to 30 kOe), and field direction using the strain-gauge technique. The distortion of the lattice along the

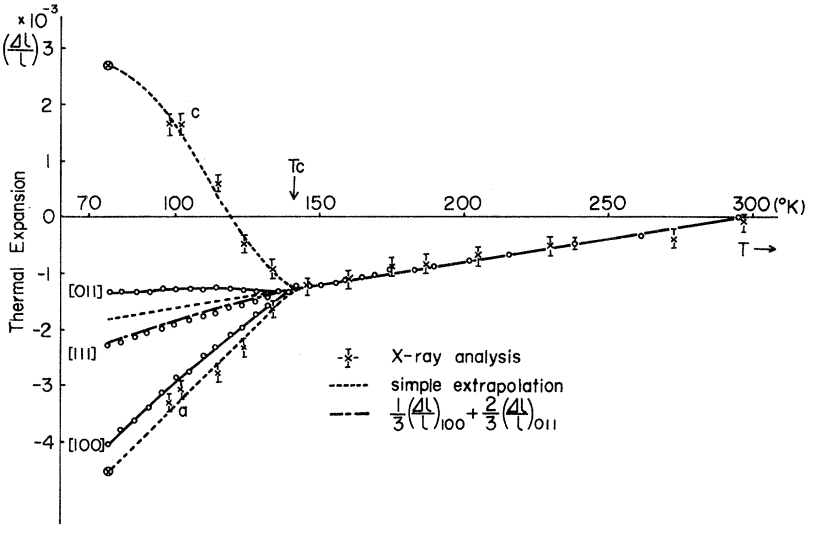

FIG. 1. Temperature variation of linear distortion along [100], [011], and [111] measured in zero field by the strain gauge technique. Variation of lattice constants with temperature determined by x-ray analysis is also shown on the same scale.

three different crystallographic directions [100], [011], and [111] measured in zero field is shown in Fig. 1 as a function of temperature. In the figure, the variation of the lattice constants with temperature determined by powder x-ray analysis is also plotted on the same scale. The distortion was found to occur below the Curie temperature T_c. The figure indicates that the contraction in the [100] direction of the (011) platelet was almost the same as the short a-axis contraction, suggesting that the greater part of the crystal was single domain with the a axis parallel to [100]. The linear distortion of the lattice $(\delta l/l)_\beta$ in a direction characterized by a directional cosine β is given by $(\delta l/l)_\beta = \sum_{ij} e_{ij}\beta_i\beta_j$, where e_{ij} are the equilibrium strains. The domain distribution as well as the intrinsic distortion in the domain were determined by combining the results of x-ray and strain-gauge measurements. The values at 77°K are $\bar{e}_{xx}{}^0 = (4.7 \pm 0.4) \times 10^{-3}$, $\bar{e}_{yy}{}^0 = (-2.4 \pm 0.3) \times 10^{-3}$, $e_{xy} = e_{xz} = (-0.1 \pm 0.1) \times 10^{-3}$, and $e_{yz} = (-0.8 \pm 0.4) \times 10^{-3}$. The $\bar{e}_{ii}{}^0$ are strains in the domain relative to a virtual cubic state with the same volume ($\sum_i \bar{e}_{ii}{}^0 = 0$). The distortion was found to be monoclinic, but the deviation from the tetragonal symmetry is small.

When the magnetic field was applied in the [100] direction below T_c the crystal was elongated in this direction as shown in Fig. 2. The variation of the lattice along [100] occurred very slowly at 77°K; it took more than 3 min to attain equilibrium after the magnetic field was changed. Such a time effect was not observed at 102°K. The equilibrium value of the distortion did not show hysteresis when the field was higher than 13 kOe. The variation of the lattice was very small if the field was applied in any other direction. The neutron diffraction study of Ref. 1 has shown that the crystal becomes a single domain in the [100] field higher than 10 kOe.[2] Therefore the distortion in the [100] field could be determined directly from $(\delta l/l)_\beta$ along [100], [010], [011], and [111]. The results at 77°K are $\bar{e}_{xx} = (3.5 \pm 0.3) \times 10^{-3}$, $\bar{e}_{yy} = (-1.8 \pm 0.3) \times 10^{-3}$, $e_{xy} = e_{xz} = (-1.0 \pm 0.3) \times 10^{-3}$, and $e_{yz} = (0.7 \pm 0.7) \times 10^{-3}$. The deviation from tetragonal symmetry was increased in the [100] field.

The crystal distortion $(\delta l/l)_\beta$ has been analyzed in terms of the linear magnetostriction which can be expressed by

$$(\delta l/l)_\beta = \tfrac{3}{2}\lambda_{100}(\textstyle\sum_i \alpha_i{}^2\beta_i{}^2 - \tfrac{1}{3}) + 3\lambda_{111}(\sum_{ij} \alpha_i\alpha_j\beta_i\beta_j),$$

where α is the direction cosine of the spins.

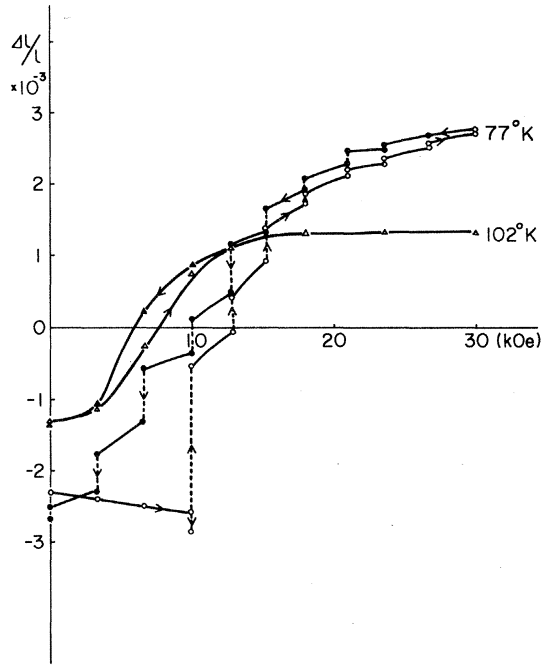

FIG. 2. Field dependence of linear distortion along [100] in a magnetic field parallel to [100] measured at 77 and 102°K. Vertical dashed lines with arrows indicate time effect.

Since the spins in a domain align in the [100] direction in zero field, the magnetostriction constant λ_{100} is equal to $\bar{e}_{xx}{}^0$ which is $(4.7 \pm 0.4) \times 10^{-3}$ at 77°K. The fact that the linear distortion along [100] at 30 kOe is only 75% of $\bar{e}_{xx}{}^0$ suggests that the spins deviate from [100] even in a magnetic field of 30 kOe. The deviation angle was estimated to be 24.5° at 77°K. Using this angle and the off-diagonal strain e_{xy}, λ_{111} was determined to be $(1.3 \pm 0.4) \times 10^{-3}$.

The magnetostriction constants λ_{100} and λ_{111} are connected with the elastic constants c_{ij} through the relations $\lambda_{100} = -\frac{2}{3}B_1/(c_{11} - c_{12})$ and $\lambda_{111} = -\frac{1}{3}B_2/c_{44}$, where B_1 and B_2 are the magnetoelastic constants. The magnetostriction observed in Fe_2TiO_4 is almost on the same order of magnitude as that found in CoO ($\lambda_{100} = -8 \times 10^{-3}$ at 0°K)[4] and in Tb ($\lambda_{100} = 6.2 \times 10^{-3}$ at 80°K)[5] and an order of magnitude greater than that in cubic ferrites containing Co^{2+} ions.[4] The magnetostriction for such materials has been interpreted to be due either to Co^{2+} ions or to rare-earth atoms that have an orbital magnetic moment.[4,6] However the Mössbauer study by Ôno, Chandler, and Ito[7] has suggested that the ground state of the ferrous ions in Fe_2TiO_4 is the orbital singlet. The magnetoelastic constants can not therefore

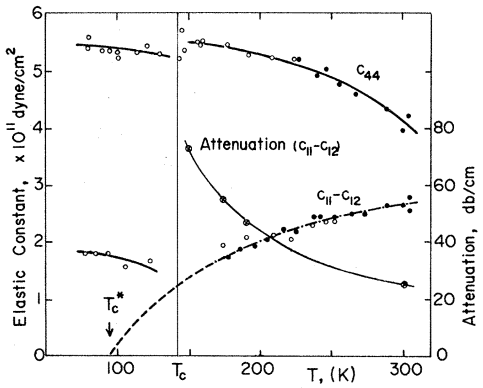

FIG. 3. Temperature dependence of elastic constants $c_{11}-c_{12}$ and c_{44} determined by the ultrasonic pulse echo technique with carrier frequency of 10 MHz. Closed and open circles indicate the data taken by using Canada balsam and Nodaq stopcock grease as bonds, respectively. The dashed line for $c_{11}-c_{12}$ vs T is a theoretical fit by the least-squares method. Attenuation of the v_{110} shear mode which couples with $c_{11}-c_{12}$ is also shown.

be large enough to explain the giant magnetostriction.

Temperature dependence of elastic constants $c_{11}-c_{12}$ and c_{44} determined by means of the ultrasonic-pulse echo technique for the same specimen[8] are shown in Fig. 3. The constant $c_{11}-c_{12}$ at room temperature is almost an order of magnitude smaller than that of magnetite (Fe_3O_4) and it decreases anomalously with decreasing temperature in the paramagnetic region and attains minimum around T_c. c_{44} is also about half as large as that of magnetite. The magnetostriction is really enhanced by reduction in $c_{11}-c_{12}$. B_1 and B_2 were evaluated to be -520 ± 50 cm^{-1} and -810 ± 230 cm^{-1} per molecule at 77°K. This is on the same order of magnitude as those of Co^{2+} in spinel ($B_1\sim300$ cm^{-1}).[4] The figure also shows a striking increase in the attenuation in the shear mode as the temperature approaches T_c.

The origin of such a softening of the lattice is related to the presence of Jahn-Teller Fe^{2+} ions in the tetrahedral site.[9] It has been reported[10,11] that the presence of small quantities of Jahn-Teller ions in yttrium iron garnet leads to a large low temperature acoustic loss and to a reduction in sound velocity. This phenomenon was interpreted as a relaxation process between three possible directions in the Jahn-Teller distortion.

A theoretical discussion of the Jahn-Teller effect on the elastic properties has been given recently by Kataoka and Kanamori.[12] They predicted that $c_{11}-c_{12}$ decreases with decreasing temperature with a dependence of $1-T_c^*/T$ above the critical temperature T_c^* of the Jahn-Teller transformation, and becomes minimum at T_c^*. As shown by a dashed line in Fig. 3, the observed data for $c_{11}-c_{12}$ were fitted well by the theoretical equation $c_{11}-c_{12}=3.94(1-96.4/T)\times10^{11}$ dyne/cm^2 lending support to our interpretation. This suggests that the cooperative Jahn-Teller distortion would have occurred at 96°K in this crystal in the absence of magnetic ordering. The existence of the large acoustic loss even at 300°K suggests that the distortion is fluctuating with a relaxation time slower than 10^{-7} sec. This would be a characteristic of the Jahn-Teller distortion induced by tetrahedral-site Fe^{2+} ions as has been suggested by Goodenough.[9]

The cooperative Jahn-Teller distortion temperature is affected by the long-range magnetic ordering through the magnetoelastic coupling, if the magnetic ordering temperature is close to T_c^*. Allen[13] has discussed this coupling and explained the first-order phase transition in UO_2 as well as the anomalous decrease of c_{44} at this temperature. He has also suggested that the distortion and spontaneous polarization of the sublattice moment would appear simultaneously and that the transition is second order if the magnetoelastic coupling ϵ is not sufficiently large compared with the magnetic interaction zJ ($\frac{2}{7}\geq\epsilon/zJ\geq0$ in his notation). The argument is fundamentally the same for Fe_2TiO_4 and this situation seems to be realized in this crystal.

The giant magnetostriction has also been observed in the solid solution between Fe_2TiO_4 and Fe_3O_4.[14] The magnetostriction of this series increases with increasing Fe^{2+} ions in the tetrahedral site.[8] This provides us with more evidence that Fe^{2+} ions in tetrahedral sites are responsible for the giant magnetostriction. It is finally remarked that the magnetic properties such as the magnetic anisotropy and the magnetization process in Fe_2TiO_4 are mainly determined by the giant magnetostriction.[2]

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[1]Y. Ishikawa, Phys. Lett. 24A, 725 (1967).

[2]Y. Ishikawa, S. Sato, and Y. Syono, to be published.
[3]Y. Ishikawa, Y. Syono, and S. Sato, in Proceedings of the International Conference on Ferrites, 6-9 July 1970, Kyoto, Japan (to be published).
[4]J. Kanamori, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol I, p. 189.
[5]A. E. Clark, B. F. Desavage, and R. M. Bozorth, Phys. Rev. 138, A216 (1965).
[6]E. Callen and H. B. Callen, Phys. Rev. 139, A455 (1965).
[7]K. Ôno, L. Chandler, and A. Ito, J. Phys. Soc. Jap. 25, 174 (1968).
[8]Y. Syono, Y. Fukai, and Y. Ishikawa, to be published.
[9]J. B. Goodenough, J. Phys. Chem. Solids 25, 151 (1964).
[10]E. M. Gyorgy, M. D. Sturge, D. B. Fraser, and R. C. LeCraw, Phys. Rev. Lett. 15, 19 (1965).
[11]M. D. Sturge, J. T. Krause, E. M. Gyorgy, R. C. LeCraw, and F. R. Merritt, Phys. Rev. 155, 218 (1967).
[12]M. Kataoka and J. Kanamori, private communication.
[13]S. J. Allen, Phys. Rev. 167, 492 (1967).
[14]Y. Syono, Jap. J. Geophys. 4, 71 (1965).

Anomaly in the Angular Distributions for (He^3, t) Reactions*

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A systematic angular shift is noted between distorted-wave calculations and measured angular distributions for (He^3, t) reactions on even-even targets. The shift is apparent for final states whose isospin is one unit lower than that of the target state.

A recent article[1] presented evidence that (He^3, t) angular distributions for $J^\pi = 0^+$ anti-analog states could not be fitted well with $L = 0$ distorted-wave (DW) calculations but that $L = 1$ calculations were in good agreement with the data. We present evidence here that the inability to fit (He^3, t) angular distributions for certain low-lying states may be a general deficiency in the current distorted-wave treatment of the reaction mechanism. A persistent angular shift is noted between DW calculations and the measured angular distributions to $T_<$ final states from even-even targets. The shift cannot be removed by realistic adjustment of the parameters of the standard DW calculations.

The purpose of the present note is to summarize this feature which is evident in a number of experiments performed with the He^3 beam of the Argonne tandem Van de Graaff accelerator. They encompass the reactions $Ca^{48}(He^3, t)Sc^{48}$,[2] $Sr^{88}(He^3, t)Y^{88}$,[3] $Zr^{90}(He^3, t)Nb^{90}$,[4] and $Zr^{96}(He^3, t)Nb^{96}$.[5] Bombarding energies were 23 MeV for the Ca^{48} and Sr^{88} targets and 21 MeV for the Zr targets. The tritons from the reactions on Ca^{48}, Sr^{88}, and Zr^{96} were detected on photographic plates placed in the focal plane of an Enge split-pole spectrograph; a position-sensitive detector was used for the reactions on Zr^{90}.

Experimental angular distributions for $J^\pi = 4^+$ and 6^+ states are compared with DW calculations in Fig. 1. Since the 6^+ state in Y^{88} is apparently unresolved from a 7^+ state, the angular distribution for a 5^- state has been shown instead. An angular shift of 2-7° between the curve and the data is seen in every case. Although not shown, the shift is also present for 2^+ and 8^+ states.

The states of Sc^{48} are believed to be members of the $(f_{7/2})^2$ multiplet, the even-parity states of Y^{88} and Nb^{90} belong to the $(g_{9/2})^2$ multiplet, the 5^- state arises from the $(p_{1/2}g_{9/2})^{-1}$ configuration, and the states of Nb^{96} are members of the $(g_{9/2}d_{5/2})^{-1}$ multiplet. The data thus span cases in which a neutron is replaced by a proton in the same orbit, in which the neutron and proton orbits have different spins but the same parity, and in which the two orbits differ in both spin