FERRIMAGNETIC STRUCTURE OF MAGNETOELECTRIC $Ga_{2-x}Fe_xO_3$

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(Received 28 October 1965)

In this Letter we report microscopic magnetic studies of $Ga_{2-x}Fe_xO_3$ via high-field Mössbauer measurements and macroscopic magnetic-moment measurements. Studies on both single-crystal and polycrystalline samples show that this material is ferrimagnetic, with magnetic moments directed close to or along the c-axis, instead of a canted antiferromagnetic structure as previously assumed[1] or inferred.[2] A similar ferrimagnetic structure has been determined for the isomorphic compound $Al_{2-x}Fe_xO_3$ which is also piezoelectric. A consistent analysis was possible only when high magnetic fields were applied in order to align the net magnetization, thereby eliminating one of the major difficulties with earlier analyses, viz., the large anisotropy of this material which could easily be misinterpreted as an indication of a canted antiferromagnetic structure. Two distinguishable hyperfine fields are observed corresponding to inequivalent sites with approximately 5 μ_B per Fe^{3+} ion, thus eliminating possible questions concerning low-moment states. The qualitative features of the measurements vary uniformly for $0.8 \leq x \leq 1.2$, indicating no unusual stoichiometry-dependent characteristics. These measurements also eliminate some earlier suggested models for the magnetoelectric effect, but remain consistent with the symmetry requirements for the observation of a magnetoelectric effect in this material. Our results firmly establish the model used by Bertaut et al.[3] to interpret their unpublished zero-field neutron diffraction measurements with powders.

The piezoelectric material $Ga_{2-x}Fe_xO_3$ ($x \approx 1$), first prepared by Remeika,[4] has aroused great interest because in addition to its spontaneous magnetic moment observed by Remeika and studied in detail by Nowlin and Jones,[5] very large magnetoelectric effects were reported by Rado.[1] The detailed crystal structure has been determined by Abrahams, Reddy, and Bernstein[2] who find four cation sites, two octahedral and two tetrahedral, with Ga^{3+} occupation of one tetrahedral site and Ga^{3+} and Fe^{3+} distribution over the other three sites. From the available data a magnetic structure consisting of a canted spin system (with large canting angles) was inferred.[2] While Rado used a theoretical model which assumed the material to be a canted antiferromagnetic structure, i.e., a weak ferromagnet, in order to explain the nondiagonal character of the magnetoelectric susceptibility, he pointed out[1] the importance of knowing the actual magnetic structure before a complete understanding of the magnetoelectric properties of $Ga_{2-x}Fe_xO_3$ could be achieved.

We have examined the magnetic structure of $Ga_{2-x}Fe_xO_3$ for $x = 0.8$, 1.0, and 1.2 with intense external longitudinal magnetic fields using Mössbauer techniques and a vibrating sample magnetometer modified for axial fields in superconducting magnets.[6] Both Fe^{57}-enriched polycrystalline samples and a mosiac of x-ray oriented single crystals were investigated with a constant-acceleration Mössbauer spectrometer at temperatures from 320 to 4.2°K.

In some experiments the absorbers consisted of crushed crystals grown from a melt with a 20% enrichment of Fe^{57} and embedded in Lu-

cite. The melt consisted of (mole%) 6.2 Bi_2O_3, 29.0 $Ga_{2-x}Fe_xO_3$, 20.5 PbO, and 44.3 B_2O_3. Each sample was analyzed chemically and by x rays. The Curie temperature determined from zero-field Mössbauer spectra was found to vary with composition in qualitative agreement with previous magnetization measurements[5]; $T_C = 305°K$ for $x = 1.20$ and $T_C = 205°K$ for $x = 0.80$. The spectra indicate a ferrimagnetic ordering with an unequal distribution of spins of nearly equal magnitude on the spin-up and spin-down sublattices. Taken together with the magnetization measurements, we find the spins to lie close to or along the c axis (the easy axis of magnetization) in zero external field. The qualitative features of the Mössbauer spectra were independent of composition both above and below the Curie temperatures, indicating the same magnetic ordering over the entire range of composition studied, $0.8 \leq x \leq 1.2$.

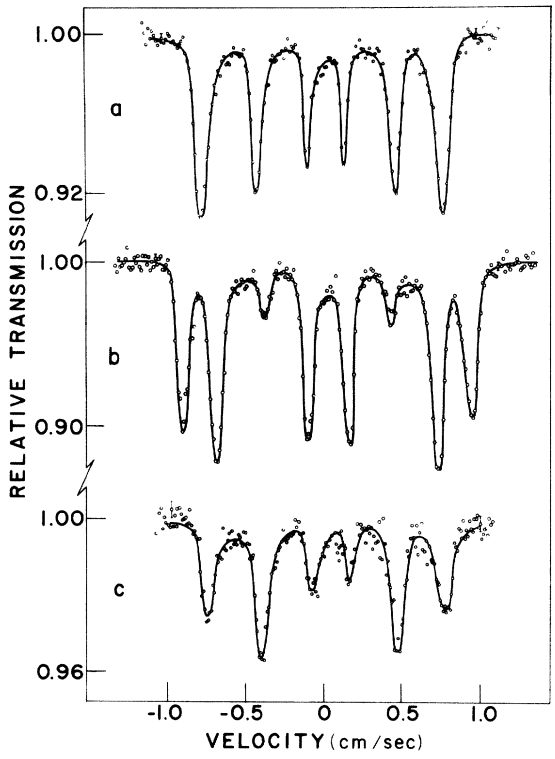

FIG. 1 (a) Mössbauer spectrum of polycrystalline $Ga_{0.80}Fe_{1.20}O_3$ at $H = 0$ kOe, $T = 4.2°K$ using the 14-keV γ ray from a Co^{57} in Cu source. (b) Spectrum of $Ga_{0.80}Fe_{1.20}O_3$ at $H = 75$ kOe, $T = 4.2°K$, near saturation. (c) Spectrum of a mosiac of oriented single crystals at $H = 0$ kOe, $T = 77°K$. The b axis ($c < a < b$) is perpendicular to the plane of the mosaic and is parallel to the γ-ray transmission direction.

Below the Curie temperature[7] a six-line spectrum appeared[3] [Fig. 1(a)], but the width and shape of the lines indicated at least two different hyperfine fields. Application of an external magnetic field H_0 altered the spectrum dramatically. As H_0 increased, the $\Delta m = 0$ lines disappeared and the outer $\Delta m = \pm 1$ lines split into doublets of unequal intensity. The measured hyperfine fields for the two components at $T = 4.2°K$ and $H_0 = 75$ kOe [Fig. 1(b)] were 560 ± 5 kOe and 420 ± 5 kOe, from which zero-external-field hyperfine fields of 485 ± 5 kOe and 495 ± 5 kOe, respectively, were calculated, in agreement with a fit to the spectrum obtained at zero external field. At 4.2°K saturation (i.e., complete disappearance of the $\Delta m = 0$ lines) occurred for $H_0 = 90 \pm 10$ kOe; as T increased, the applied field necessary for saturation decreased (e.g., $H_0^{sat} \approx 50$ kOe at $T = 77°K$).

The mosiac of single crystals was oriented so that the b axis ($c < a < b$) was perpendicular to the plane of the mosaic and collinear with the direction of γ-ray transmission and H_0. The spectrum at 77°K and $H = 0$ [Fig. 1(c)] showed an enhancement of the $\Delta m = 0$ lines. Application of H_0 resulted in the disappearance of the $\Delta m = 0$ lines and a spectrum similar to that in Fig. 1(b).

The intensity ratios of the lines in a Mössbauer spectrum arising from hyperfine fields give information concerning the directions of the fields relative to the axis of γ-ray propagation as well as the relative populations of sites with different hyperfine fields. The six hyperfine lines for a given field have intensities in the ratio $3:R:1:1:R:3$, where R denotes the intensity of the $\Delta m = 0$ line and is a function of the angle θ between the γ-ray propagation direction and the hyperfine-field (nuclear moment) direction; $R = 4\sin^2\theta/(1+\cos^2\theta)$. For a random distribution of hyperfine-field directions, $R = 2$. Since the hyperfine fields are essentially collinear with the corresponding atomic moments, these directions are also determined. In fact, the hyperfine field in Fe^{3+} has a negative direction with respect to the atomic-moment direction. Analysis of the high-magnetic-field Mössbauer line intensities and positions for a polycrystalline absorber shows that $Ga_{2-x}Fe_xO_3$ has a collinear ferrimagnetic structure where the ferrimagnetism is due to the unequal distribution of spins of nearly equal magnitude on the sublattices. From the

magnitude of the hyperfine fields, the moments are about 5 μ_B for each iron atom; and from the relative population of the spin-up and spin-down sublattices, determined from the relative strengths of outer $\Delta m = \pm 1$ lines in the high-field spectrum, the net moment per Fe^{3+} in $Ga_{0.80}Fe_{1.20}O_3$ is about 1 μ_B, in agreement with our magnetization data and those of Nowlin and Jones.[4] The high-field spectra of a canted spin antiferromagnet would have shown enhanced $\Delta m = 0$ lines and a small shift to lower field with no splitting of the outer $\Delta m = \pm 1$ lines.[8] From the single-crystal mosaic we find enhanced $\Delta m = 0$ lines, and thus that the spins lie in the *ac* plane in zero external field.

Magnetic-moment measurements were made on multicrystalline samples from the batch used to prepare the mosaic as well as on a single-crystal needle of $Fe_{0.86}Ga_{1.14}O_3$ originally examined by Nowlin and Jones.[4] The magnetic moment was nearly saturated at 4.2°K for $H_0 = 75$ kOe applied along the *a*, *b*, or *c* axis, in agreement with the Mössbauer results. The magnetic moment along the *c* axis is almost saturated by an applied field of 3 kOe, but an appreciable ($\simeq 30\%$) nonlinear increase occurs before complete saturation. The ease of magnetizing decreases from the *c* to the *a* to the *b* axis. The magnetic data are consistent with a ferrimagnet having a large anisotropy.[9]

Neutron-diffraction measurements on single crystals of $Ga_{2-x}Fe_xO_3$ would be of interest in assigning exact values to the moments and in detecting any possible small spin component perpendicular to the *c* axis. As mentioned previously, neutron-diffraction measurements on powders have not shown additional scattering expected from a canted-spin moment. Neglecting uncertainties in such powder measurements (which arise because of the small moment), these results are consistent with a ferrimagnetic ordering.

We have also made preliminary measurements on the isomorphous compound $Al_{2-x}Fe_xO_3$. For $x \approx 1$, this material is piezoelectric. Mössbauer measurements in intense magnetic fields show a ferrimagnetic ordering, qualitatively the same as $Ga_{2-x}Fe_xO_3$ but having a smaller spontaneous ferrimagnetic moment. Further Mössbauer and magnetic-moment measurements are now in progress, as are experiments to determine the existence of an expected magnetoelectric effect in this material.

We wish to acknowledge the valuable assistance of E. J. McNiff, Jr., for his help with the magnetic-moment measurements and are indebted to Professor R. V. Jones for providing the single-crystal materials. We thank S. C. Abrahams and G. T. Rado for discussions.

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*Work supported by the U. S. Air Force Office of Scientific Research.

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[9]Also of interest is the very recent observation of a linear, isotropic magnetoelectric at magnetic fields above those required for saturation reported by G. T. Rado, in Proceedings of the Eleventh International Conference on Magnetism and Magnetic Materials, San Francisco, California, 16-19 November 1965 (unpublished).