High-Magnetic-Field Studies of Orthorhombic and Rhombohedral Al_{2-x}Fe_xO_3 Compounds

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Mössbauer and magnetic susceptibility experiments at temperatures down to 4.2°K and in external fields up to 140 kOe show orthorhombic Al_{2-x}Fe_xO_3 (0.6<x<1.0) to be a collinear highly anisotropic ferrimagnet; the material is also piezoelectric and has magnetic properties similar to those of the isomorphous compound GaFeO_3. Rhombohedral Al_{2-x}Fe_xO_3 is paramagnetic above 80°K, and at 4.2°K exhibits a Mössbauer spectrum characteristic of a nonunique hyperfine field; the application of an external magnetic field produces a spectrum with an enhanced \( \Delta m = 0 \) line which suggests a canted spin structure similar to that in the high-temperature phase \( (T > 260°K) \) of \( \alpha FeO_3 \).

We report high magnetic field Mössbauer and magnetization measurements on Al_{2-x}Fe_xO_3 compounds having orthorhombic and rhombohedral crystal structures. The orthorhombic form is of interest because it is isomorphic with piezoelectric, magnetoelectric and ferrimagnetic GaFeO_3.

The crystal structures of AlFeO_3 and GaFeO_3 have been recently reinvestigated. The orthorhombic phase is stable for an appreciable range of stoichiometric composition; i.e., Al_{2-x}Fe_xO_3 and Ga_{2-x}Fe_xO_3 have been prepared for values of about 0.6<x<1.0 and 0.8<x<1.2, respectively. Polycrystalline Al_{2-x}Fe_xO_3 samples were prepared by heating the oxides at 1390°C for 48 h in oxygen. For values of x>1.0 we were unable to prepare an orthorhombic phase. Samples with x<0.6 formed an orthorhombic phase, but mixed with small amounts of Al_2O_3. The unit cell dimensions of orthorhombic AlFeO_3 with x=1.0 correspond very closely to those given by Dayal et al.\(^1\): \( a = 8.60, b = 9.25, \) and \( c = 4.97 \) Å. The orthorhombic compound with x=0.6 has a much smaller unit cell, the low-index lines yield the values: \( a = 7.55, b = 8.20, \) and \( c = 4.69 \) Å. The rather large amount of Fe\(^{3+}\) incorporated in the Al_2O_3 structure is explained by the thermal history.

![Fig. 1. Magnetization of Al_{2-x}Fe_xO_3 polycrystalline samples vs applied magnetic field.](image1)

![Fig. 2. Mössbauer absorption spectra at 4.2°K; orthorhombic AlFeO_3, (a) \( H = 0 \), (b) \( H = 75 \) kOe; rhombohedral Al_{2-x}Fe_xO_3, (c) \( H = 0 \), (d) \( H = 75 \) kOe.](image2)
of the rhombohedral sample. This compound was grown as a single crystal from a molar mixture composed of 35% $\text{Na}_2\text{CO}_3$, 54% $\text{Al}_2\text{O}_3$, and 11% $\text{Fe}_2\text{O}_3$, heated to 1400°C and slowly cooled at a rate of 2°C/h to 1100°C. As in the case of Ga$_{2-x}$Fe$_x$O$_3$, the orthorhombic Al$_{2-x}$Fe$_x$O$_3$ crystals are piezoelectric. The orthorhombic Al$_{2-x}$Fe$_x$O$_3$ Mössbauer spectra at 4.2°K show an ordered spin system composed of at least two magnetically nonequivalent sites with oppositely directed spins. An external field causes the middle hyperfine lines ($\Delta m = 0$) to vanish, while the outer lines ($\Delta m = \pm 1$) split into two well-resolved components similar to those reported previously$^3$ for Ga$_{2-x}$Fe$_x$O$_3$.

Magnetization measurements of orthorhombic Al$_{2-x}$Fe$_x$O$_3$ with $x = 0.6$ and 1.0 polycrystalline material are not saturated at 4.2°K and 140 kOe. It should be mentioned that magnetic saturation has not been achieved on polycrystalline GaFeO$_3$ materials at 78°K and 140 kOe. The lack of saturation is due to the extremely high magnetic anisotropy of these compounds. This was shown earlier$^4$ by Mössbauer and magnetic moment measurements on GaFeO$_3$ single crystals. Saturation was just achieved at about 80 kOe along principal axes at 78°K. The magnetization curves are shown in Fig. 1.

Rhombohedral Al$_{1.6}$Fe$_{0.4}$O$_3$ is paramagnetic above 80°K with a quadrupole split Mössbauer doublet, and at 4.2°K shows a poorly defined magnetic hyperfine spectrum suggesting a distribution of hyperfine fields or short-range magnetic order. Upon the application of an external magnetic field the spectrum is somewhat sharpened and the intensity of the $\Delta m = 0$ lines increases with the applied external field. This is shown in Fig. 2, where the spectra are qualitatively similar to those of a canted spin system such as $\alpha$Fe$_2$O$_3$ above the Morin transition. The field-dependence of the magnetic moment at 4.2°K up to 140 kOe is shown in Fig. 1.

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