High-Magnetic-Field Studies of Orthorhombic and Rhombohedral \( \text{Al}_{2-x}\text{Fe}_x\text{O}_3 \) 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 \( \text{Al}_{2-x}\text{Fe}_x\text{O}_3 \) (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 \( \text{GaFe}_2\text{O}_4 \). Rhombohedral \( \text{Al}_{2-x}\text{Fe}_x\text{O}_3 \) 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 \( \alpha\text{Fe}_2\text{O}_3 \).

We report high magnetic field Mössbauer and magnetization measurements on \( \text{Al}_{2-x}\text{Fe}_x\text{O}_3 \) compounds having orthorhombic and rhombohedral crystal structures. The orthorhombic form is of interest because it is isomorphic with piezoelectric, magnetoelectric and ferrimagnetic \( \text{GaFe}_2\text{O}_4 \).

The crystal structures of \( \text{AlFe}_2\text{O}_4 \) and \( \text{GaFe}_2\text{O}_4 \) have been recently reinvestigated.1,2 The orthorhombic phase is stable for an appreciable range of stoichiometric composition; i.e., \( \text{Al}_{2-x}\text{Fe}_x\text{O}_3 \) and \( \text{Ga}_{2-x}\text{Fe}_x\text{O}_3 \) have been prepared for values of about 0.6\( <x<1.0\) and 0.8\( <x<1.2\), respectively. Polycrystalline \( \text{Al}_{2-x}\text{Fe}_x\text{O}_3 \) 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 \( \text{Al}_2\text{O}_3 \). The unit cell dimensions of orthorhombic \( \text{AlFe}_2\text{O}_4 \) with \( x=1.0 \) correspond very closely to those given by Dayal et al.: \( a=8.60, b=9.25, \) 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 \( \text{Fe}^{3+} \) incorporated in the \( \alpha\text{Al}_2\text{O}_3 \) structure is explained by the thermal history.

![Graph](image-url)  
**Fig. 1.** Magnetization of \( \text{Al}_{2-x}\text{Fe}_x\text{O}_3 \) polycrystalline samples vs applied magnetic field.

![Graph](image-url)  
**Fig. 2.** Mössbauer absorption spectra at 4.2°K; orthorhombic \( \text{AlFe}_2\text{O}_4 \), (a) \( H=0 \), (b) \( H=75 \) kOe; rhombohedral \( \text{Al}_{2-x}\text{Fe}_x\text{O}_3 \), (c) \( H=0\), (d) \( H=75 \) kOe.
of the rhombohedral sample. This compound was grown as a single crystal from a molar mixture composed of 35% Na$_2$CO$_3$, 54% Al$_2$O$_3$, and 11% Fe$_2$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$^5$ 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$^3$ 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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