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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 $Al_{1.6}Fe_{0.4}O_3$ 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 αFe_2O_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 $GaFeO_3$.

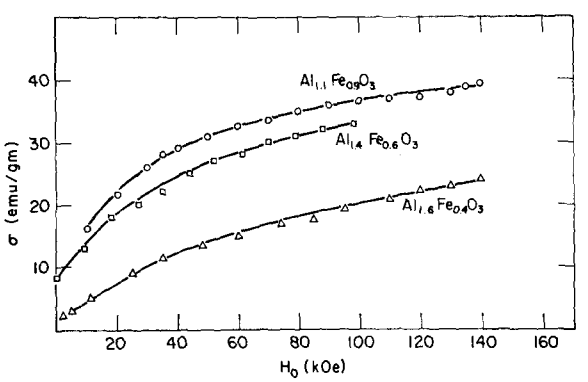

FIG. 1. Magnetization of $Al_{2-x}Fe_xO_3$ polycrystalline samples vs applied magnetic field.

The crystal structures of $AlFeO_3$ and $GaFeO_3$ have been recently reinvestigated.[1,2] 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 αAl_2O_3 structure is explained by the thermal history

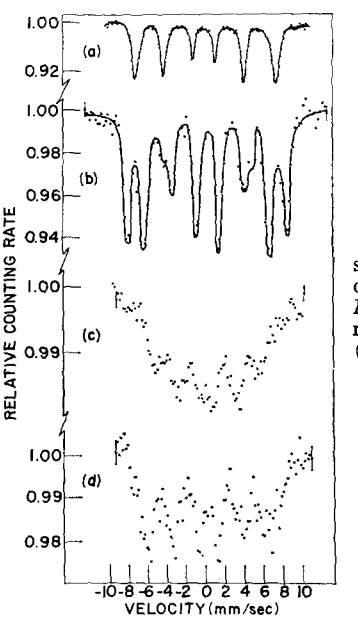

FIG. 2. Mössbauer absorption spectra at 4.2°K; orthorhombic $AlFeO_3$, (a) $H=0$, (b) $H=75$ kOe; rhombohedral $Al_{1.6}Fe_{0.4}O_3$, (c) $H=0$, (d) $H=75$ kOe.

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[1] R. R. Dayal, J. A. Gard, and F. P. Glasser, Acta. Cryst. **18**, 574 (1965).

[2] S. C. Abrahams, J. M. Reddy, and J. L. Bernstein, J. Chem. Phys. **42**, 3975 (1965).

of the rhombohedral sample. This compound was grown as a single crystal from a molar mixture composed of 35% Na_2CO_3, 54% Al_2O_3, and 11% Fe_2O_3, heated to 1400°C and slowly cooled at a rate of 2°C/h to 1100°C.

As in the case of $Ga_{2-x}Fe_xO_3$, the orthorhombic $Al_{2-x}Fe_xO_3$ crystals are piezoelectric. The orthorhombic $Al_{2-x}Fe_xO_3$ 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 $Ga_{2-x}Fe_xO_3$.

Magnetization measurements of orthorhombic $Al_{2-x}Fe_xO_3$ 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 αFe_2O_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.

ACKNOWLEDGMENT

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[3] R. B. Frankel, N. A. Blum, S. Foner, A. J. Freeman, and M. Schieber, Phys. Rev. Letters **15**, 958 (1965).