Studies of Potassium Ferrite, $K_{1+x}Fe_{11}O_{17}$. II. Mössbauer Effect and Spin Flopping

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The Mössbauer spectrum of the iron analog of K–β-alumina, $K_{1+x}Fe_{11}O_{17}$, where $x = 0.35$ to 0.86, has been obtained. Four magnetically split Fe^{3+} components can be resolved. At 295°K the magnetic flux densities at the nuclei are, for the $2a$ octahedral site 51.8 T, for the $12k$ octahedral site 43.8 T, and for the two tetrahedral sites, for which an assignment is suggested, 49.5 and 38.7 T. The random distribution of the excess potassium ions resulted in line broadening of the $12k$ octahedral, and bridging tetrahedral, spectra.

Spin flopping in the antiferromagnetic lattice at 4.2°K in an applied magnetic flux density of 2.5 T was inferred from the absence of any effect of the applied field on the spectrum. The consequently low values of the magnetocrystalline anisotropy constants are compared and contrasted with those of the similarly structured ferrimagnetic hexagonal ferrites, and the possible role of Fe^{2+} in reducing the anisotropy is discussed.

Introduction

Potassium ferrite and related compounds are of interest because their electrical and conduction properties complement those of the isomorphous K–β-alumina in a way which could provide the basis for an electrode–electrolyte pair in a solid state battery (*1, 2*). Part II of our study, which follows our report of the electrical conductivity of the ferrite (*3*), is concerned with the Mössbauer spectrum and magnetic properties of similarly prepared compounds.

The Mössbauer spectrum of potassium ferrite has not been published, although it has been briefly reported that four hyperfine patterns were evident (*4*). Gorter has studied the magnetic properties of the stoichiometric material $KFe_{11}O_{17}$ and has concluded that the material, because of the opposed ferri-magnetic lattices, should be regarded as antiferrimagnetic, although it could be more

generally described as antiferromagnetic. The Néel temperature was found to be 800°K (*5, 6*). The unusual temperature dependence of the magnetic susceptibility below the Néel temperature was taken to indicate a low anisotropy constant, although some doubt appeared to exist regarding the magnetic structure (*7*). We have obtained the Mössbauer spectra of potassium ferrites with potassium excesses x in $K_{1+x}Fe_{11}O_{17}$ ranging from 0.35 to 0.86 in order (i) to study the distribution of iron between the lattice sites and the type of compensating defect accompanying the excess potassium, and (ii) to investigate the magnetic properties of the lattice. Mössbauer spectro-scopy is particularly advantageous in the study of antiferromagnetic materials since it is unaffected by traces of ferro- and ferrimagnetic impurities which interfere with susceptibility measurements.

The basic lattice of the ferrite (*5, 8*) is isostructural with that of the alkali metal–β-

aluminas. There are four crystallographically identifiable Fe sites in the lattice of the stoichiometric material, which is formed by the interposition of potassium ions in oxygen-deficient layers occurring every fifth sheet of oxygens, which separate spinel blocks composed of four layers of oxygens and all the iron ions. Within the stoichiometric unit cell of $K_2Fe_{22}O_{34}$ the Fe^{3+} ions occupy 12 spinel-type octahedral ($12k$) sites and four spinel-type tetrahedral sites in layers on either side of the potassium layers, together with two octahedral ($2a$) sites and four tetrahedral sites further within the spinel block. Within each spinel block the spins of all the octahedral ions are parallel, while being antiparallel to all the tetrahedral ions. The ions are coupled antiparallel across the bridging oxygens so that the net moments of each spinel block oppose one another, giving a net antiferromagnetic (or in the manner of Gorter, anti-ferrimagnetic) behavior (5, 6).

Experimental

The Mössbauer samples were from different batches to those used previously (3). Analar grade K_2CO_3 and Fe_2O_3 were ground together, fired at 1170°K in oxygen, cooled, sealed, and pressed at 1473°K in oxygen to give only two block material, with unit cell parameters in agreement with the known values (8). A pellet initially of composition $K_{1.66}Fe_{11}O_{17}$ was coulometrically titrated to give $K_{1.35}Fe_{11}O_{17}$ and $K_{1.86}Fe_{11}O_{17}$ as shown by subsequent potassium analyses. However, the actual potassium excess within the lattice of the potassium-rich sample may be lower than indicated due to possible ex-solution of the potassium to the surfaces of the crystallites.

Measurements were made on ground samples exposed to the atmosphere for a minimum period after preparation, mixed with apiezon grease, and containing 30 mg of Fe cm^{-2}. A $^{57}Co/Rh$ source was used with an NS 900 multichannel analyzer coupled to an Exeter-type triangular waveform generator (9) driving a Goodman transducer. The spectra were folded with an accuracy of better than 0.1 channel and computed to the sum of Lorentzian peaks by least-squares refinement.

Results and Discussion

Spectral Assignments

Mössbauer spectra of $K_{1.35}Fe_{11}O_{17}$ are shown in Fig. 1 at 295, 77, and 4.2°K, and at 4.2°K with an applied magnetic flux density of 2.5 Tesla. The spectrum at 295°K can be resolved into four six-line hyperfine patterns assigned to the four sites, as shown. The computed areas were consistent with the site occupancies deduced from the unit cell. There were no obvious visual differences between this sample and the other two investigated, for which x was 0.66 and 0.86.

We investigated the possibility of Fe^{2+} being detected in the spectra, since Kennedy and Sammells (2) interpreted their Mössbauer spectra of paramagnetic Fe-doped Na–β-alumina in terms of a mixture of Fe^{3+} and Fe^{2+} ions. Moreover, electrical conductivity and electrochemical measurements on potassium ferrite indicate that the excess potassium is charge compensated by the creation of Fe^{2+} in this lattice as well (1, 3, 10). It is also well known that Fe^{2+} can occur in the spinel blocks of various types of hexagonal ferrites (7) and Fe^{2+} was detected by Mössbauer spectroscopy
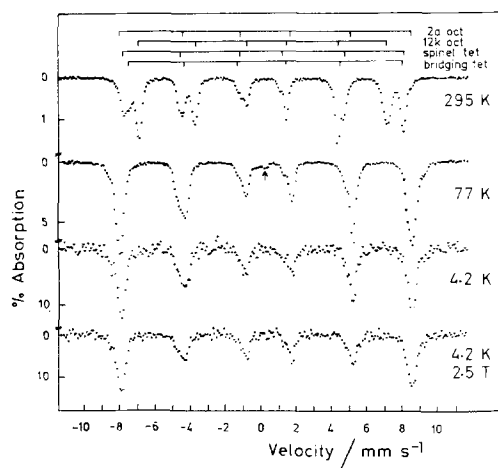

FIG. 1. Mössbauer spectra of $K_{1.35}Fe_{11}O_{17}$ at 295, 77, and 4.2°K, and at 4.2°K with a magnetic flux density of 2.5 Tesla applied perpendicular to the γ-ray direction. The site assignments at 295°K are indicated. The velocity is with respect to iron metal at 295°K as zero. The arrow indicates a small peak from an impurity in the cryostat windows.

in the W ferrite $BaFe_2^{2+}Fe_{16}^{3+}O_{27}$ (11). However, the small proportion of the total iron as Fe^{2+} in the three compounds, which was 3.2, 6.0, and 7.8%, rendered it at the limits of detection, particularly if the spectral peaks were broad, as is often found in disordered Fe^{2+} compounds (12), or if electron hopping was occurring between Fe^{2+} and Fe^{3+}, as found in Fe_3O_4 (13, 14). Hence, no conclusion could be reached from the Mössbauer spectra regarding the question of Fe^{2+} in the lattice. The isomer shifts of the four components were in the known range for Fe^{3+} ions in octahedral (0.31–0.41 mm sec^{-1}) and tetrahedral sites (0.13–0.27 mm sec^{-1}), respectively (15).

The magnetic flux densities found in $K_{1.35}Fe_{11}O_{17}$ at 295°K for the four types of Fe^{3+} are given in Table I. The structure of the hexagonal ferrite $BaFe_{12}O_{19}$ only differs from that of $K_{1+x}Fe_{11}O_{17}$ in the structure of the bridging layers between the spinel blocks (7), and although it is ferrimagnetic it has a similar Néel temperature (740°K) compared to potassium ferrite. The data for $BaFe_{12}O_{19}$ for the sites common to both structures has therefore been included in the table.

As would be expected from the position of the 2a sites in the middle of the spinel block in both of these compounds, the magnetic flux densities are in good agreement with each other. However, only in potassium ferrite is the 2a site independently resolved. The magnetic flux densities of both spinel tetra-

hedral sites are similar to that of the single tetrahedral site in $BaFe_{12}O_{19}$. The bridging tetrahedral site only occurs in potassium ferrite. The halfwidths of these peaks were noticeably broader than those of the spinel tetrahedral spectrum, which is well explained by the influence of the range of local environments created by the nearby randomly distributed excess potassium in the layers. This fact suggested the tentative assignment adopted for the two equally populated tetrahedral sites.

The halfwidths of the peaks from the 12k octahedral sites were also broadened by interactions with the nearby excess potassium ions. The magnetic flux density at 295°K was slightly larger than the corresponding value for $BaFe_{12}O_{19}$, but still showed a slow approach to the saturation value characteristic of these layer-like ferrites (16, 17). At 77°K and even more so at 4.2°K the hyperfine field from the 12k sites approached those of the two tetrahedral sites, which were all above 50 T at 4.2°K. The value for the 2a sites had risen to 54.8 T at 4.2°K.

Spin Flopping

Application of an external magnetic flux density of either 2.5 or 5.0 T perpendicular to the direction of the γ rays had no noticeable effect on the intensities, positions, or halfwidths of any of the peaks at 4.2°K for any of the three samples. This can be seen, for the case of a 2.5 T flux density, from the spectrum shown in the figure for $K_{1.35}Fe_{11}O_{17}$. Such behavior indicates that the material is antiferromagnetic, and furthermore, that spin flopping (7, 19) has occurred.

The absence of any changes in the intensities of peaks 2 and 5 in the spectrum shows that the magnetic dipoles have not been aligned along the direction of the applied field as would have been the case if the material were ferro- or ferrimagnetic. For most antiferromagnetic lattices the application of a 2.5 T flux density would result in line-broadening due to the vector addition of the applied and randomly oriented internal fields. FeF_2, for instance, exhibits this behavior (20). However, in the case of potassium ferrite, the magnetocrystalline anisotropy must be sufficiently low

TABLE I

MAGNETIC FLUX DENSITIES AT THE NUCLEUS AT 295°K, IN TESLA[a]

Site	$K_{1.35}Fe_{11}O_{17}$	$BaFe_{12}O_{19}$ (from 16–18)
2a octahedral	51.8 ± 0.6	52
12k octahedral	43.8 ± 0.3	42
Spinel-type tetrahedral	49.5	49
Bridging tetrahedral	48.7	Not found in this structure

[a] The assignment of the two tetrahedral ion spectra to the two types of tetrahedral sites is tentative.

to permit the applied field to reorient the spin directions into the most stable configuration. This is basically perpendicular to the applied

Gorter found from susceptibility measurements on nominally stoichiometric crystals to be of the order of 10^{-4} I cm^{-3} (6). The unam-

ssigned, at low temperatures, to the $2a$ site, in the center of the spinel block (23, 24). In contrast, the Fe^{2+} in $BaFe^{2+}_{0.6}Ti^{4+}_{0.6}Fe^{3+}_{10.8}O_{19}$ did not contribute to the anisotropy, and was assigned to the $12k$ sites next to the Ba^{2+} layers, thereby compensating the charge on Ti^{4+} which was situated in these layers (23).

From the above evidence there appears to be only slight energy differences between the $2a$ and $12k$ sites even in the presence of excess charge in the layers (either La^{3+} or Ti^{4+}) and it would seem likely that at normal temperatures the Fe^{2+}–Fe^{3+} hopping process in potassium ferrite would include both types of site.

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