

Studies of Potassium Ferrites. IV. Mössbauer Effect and Conductivity Studies of Mixed Fe-Ga and Fe-Al Compounds of Formula $K_{1+x}M_{11}O_{17}$: Electron Hopping and Oxidation at Room Temperature

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The ^{57}Fe Mössbauer spectra of a wide range of mixed Fe-Ga and Fe-Al analogs of $\text{K-}\beta$ -alumina have been obtained. Substitution with the nonmagnetic ions lowers the Néel temperature from 800 °K for the pure ferrite to less than 5°K for a 25% Fe-75% Ga sample. The spectra of the 50% substituted samples were paramagnetic at 295°K and consisted of a predominant octahedral Fe(III) doublet ($IS = 0.33$, $QS = 0.55 \text{ mm sec}^{-1}$), a partially averaged Fe(II)-Fe(III) resonance caused by electron hopping at about 10^7 Hz , and, for some preparation conditions, a minor tetrahedral Fe(III) doublet ($IS = 0.21$, $QS = 0.42 \text{ mm sec}^{-1}$). There is thus a delicate balance of Fe(III) site preferences. The spectra at 77°K showed partial magnetic splitting consistent with superparamagnetic regions in the lattice, which may arise because of decoupling between successive blocks in the structure. The results provide direct evidence that Fe(II)-Fe(III) electron hopping is responsible for the electronic conductivity, the activation energy of which was found to increase rapidly with dilution, from 6 kJ mole^{-1} for the pure ferrite to $41\text{--}65 \text{ kJ mole}^{-1}$ for the 25% Fe-Ga sample. For the 50% substituted samples the observed proportions of Fe(II) corresponded with the nonstoichiometric K^+ excess, showing that, at the high-temperature preparation conditions, compensation by oxygen interstitials or metal ion vacancies was not favored when Fe was present. Slow oxidation of the samples occurred in air at room temperature to produce a new doublet attributed to Fe(III) in tetrahedral sites close to the conduction planes. Two possible explanations are consistent with such results. Either Fe(II) is present on octahedral sites initially and forms Frenkel defects next to interstitial oxygens produced during oxidation, or alternatively, Fe(II) is present on both octahedral and bridging tetrahedral sites initially, which then accounts for the appearance of tetrahedral Fe(III) upon oxidation.

Introduction

Potassium ferrite, $\text{K}_{1+x}\text{Fe}_{11}\text{O}_{17}$, has the same structure as potassium β -alumina. However, the defects produced by the excess x nonstoichiometric potassium ions are of a different type for the two compounds. In the potassium ferrite, charge compensation occurs predominantly by reduction of Fe(III) to Fe(II) (1-4), rendering the material a good electronic conductor as well as a good ionic

conductor (5). On the other hand, X-ray (6) and recent neutron diffraction studies (7, 8) of Na- β -alumina showed the presence of charge-compensating interstitial oxygens. These were located in the conduction planes and induced the transfer of Al(III) ions from octahedral sites to the so-formed tetrahedral sites. The identification of this Frenkel defect reconciled the earlier evidence of Al(III) vacancies (9, 10) with the presence of oxygen interstitials.

We wished to explore the mode of compensation for solid solutions among the isostructural Fe, Al, and Ga analogs. We report in this paper Mössbauer and conductivity studies primarily aimed at determining the proportion of Fe(II) in the lattices. In addition, the Mössbauer spectra may provide information on the site preferences of Fe versus Al or Ga. The β -alumina structure contains spinel blocks consisting of four layers of oxygen and all the di- or trivalent metal ions, separated by layers of, in this case, potassium ions and oxygen ions. Within the stoichiometric unit cell of $K_2M_{22}O_{34}$ there are 12 spinel-type octahedral ($12k$) sites, and four tetrahedral (bridging) sites in layers on either side of the potassium layers, together with two octahedral ($2a$) sites and four tetrahedral sites further within the spinel blocks. All of the M sites are potentially available to Fe, Ga, or Al. Kuwabara and Takahashi (11) and Dudley and Steele (12) have shown that the K-ferrite/K-gallate system shows complete miscibility in all proportions. Cirilli and Brisi (13) have shown that the K-ferrite/K-alumina system is miscible, except over the central range of 40–55% Fe. Recently Akridge *et al.* (14) concluded from Mössbauer and uv-visible spectral studies of Na- β -alumina doped with 2 wt% Fe that both the Fe(II) and the Fe(III), which could be observed for different preparative conditions, occupied tetrahedral sites in the structure.

Experimental

Samples were prepared as for previous studies by grinding together AR-grade KNO_3 and Fe_2O_3 , Ga_2O_3 , or Al_2O_3 and firing at 1220°K in oxygen for 22 hr. Guinier X-ray photographs showed a mixture of mainly three-block (β'') with some two-block material (β) (15), having lattice parameters previously reported (12). Pellets were encapsulated in Pt foil and hot pressed, either in vacuum in graphite dies, or in 1 atm

oxygen in alumina dies after which the samples were mainly two-block, with some three-block material present. Vacuum-pressed samples were pressed at 1523 to 1643°K for 6 to 10 min at 3 to 5 MN m^{-2} . The oxygen-pressed samples were pressed at 1423 to 1593°K for 6–7 hr at 5 to 10 MN m^{-2} . After pressing it was estimated that the vacuum-pressed samples cooled to below 700°K in approximately 30 min, whereas the oxygen-pressed samples cooled over a longer period of time. All samples were prepared so as to give $x = 0.69$, and potassium analyses on the samples agreed with this nominal composition to within 0.02 in x . The 50% Fe–50% Al samples showed no evidence of two phases, implying that our preparative conditions were more favorable for complete solid solution than those of Cirilli and Brisi (13), who quote the solid solution limits as 40–55% Fe.

Mössbauer measurements were made on samples ground either under hexane, or in air, and subsequently mixed with Apiezon grease. The thin absorber samples, for which the Mössbauer response approximates well to a linear function of concentration, contained 2–4 mg Fe cm^{-2} . Other samples contained 30 mg Fe cm^{-2} . A 15-mCi Co/Rh source was used with an NS900 multichannel analyzer coupled to an Exeter-type triangular waveform generator driving a rigidly mounted Harwell transducer. The spectra were folded to an accuracy of 0.3 channels on the low-velocity scans and an accuracy of 0.1 channels on the high-velocity scans, and were computed to the sum of Lorentzian peaks by least-squares refinement. The geometry was arranged so that cosine effects would be negligible. Selected samples showing spectral asymmetry were run at 45° to the γ -ray beam, with no observable change, showing the absence of orientation effects. The isomer shifts are quoted relative to Fe metal at 290°K as zero.

Low-temperature spectra of the paramagnetic materials were obtained using

vacuum cryostats, for which the blank absorptions were only 0.05%. Low-temperature spectra of the magnetic materials were obtained using a cryostat possessing a larger blank absorption, the peak of which is indicated in the appropriate figures.

Conductivity studies were performed in an oxygen-free argon atmosphere on the pressed pellets, and on electrochemically pumped samples using the van der Pauw geometry, as described previously (3). The conductivity observed immediately after the application of the constant current was assigned to the total conductivity, while that obtained from steady state conditions (after 1 to 2 hr) was ascribed to the electronic component of the conductivity, as previously discussed (5).

Results

Samples Having a Major Proportion of Fe

The room-temperature Mössbauer spectra of mixed Fe-Ga samples having 87.5 and 75% Fe substitution, and of composition

$K_{1.69}M_{11}O_{17}$, are shown in Fig. 1, together with the spectrum of the pure ferrite $K_{1.35}Fe_{11}O_{17}$ (4). The pure ferrite was pressed in oxygen, while the other two samples were pressed in vacuum.

In the pure ferrite each of the four crystallographically distinguishable Fe sites could be identified in the Mössbauer spectrum, as shown in Ref. (4). However, upon substitution, it is evident that the associated ionic disorder has resulted in a range of hyperfine fields such that the separate sites are no longer identifiable. In addition, the magnetic dilution has resulted in a progressive lowering of the Néel temperatures with substitution of Ga, evident as a diminution of the average hyperfine fields. The 50 and 25% Fe-Ga samples were completely paramagnetic at room temperature.

The spectra at 77°K are shown in Fig. 2, and include that of a vacuum-pressed 50% Fe-Ga sample, which is now just showing magnetic broadening. The spectra again show the effects of both a decreasing Néel temperature and an increasing range of hyperfine parameters with an increasing proportion of Ga in the lattice.

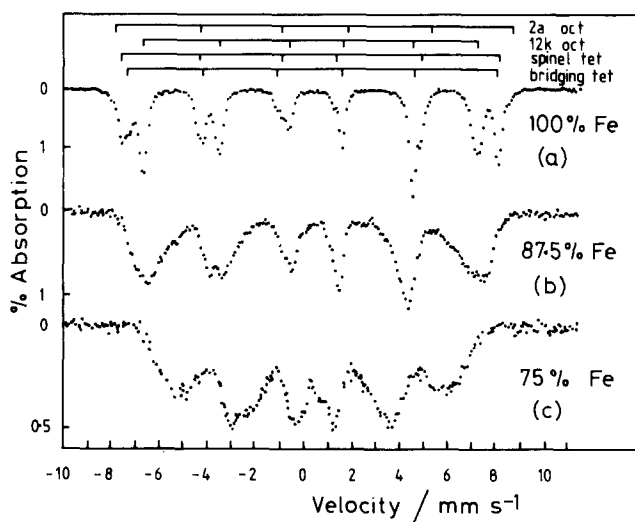


FIG. 1. Room-temperature Mössbauer spectra of (a) $K_{1.35}Fe_{11}O_{17}$, (b) $K_{1.69}Fe_{9.63}Ga_{1.37}O_{17}$, and (c) $K_{1.69}Fe_{8.25}Ga_{2.75}O_{17}$. The site assignments, as previously deduced (4), are shown.

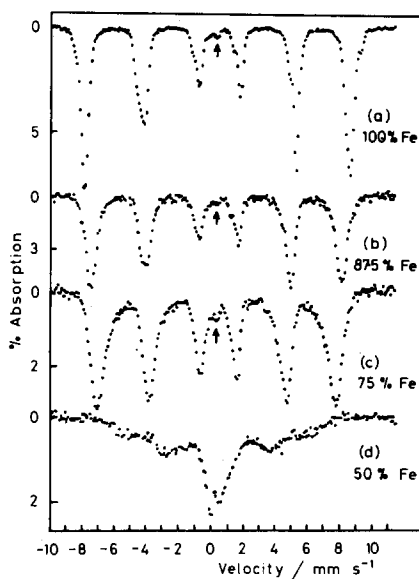


FIG. 2. Mössbauer spectra at 77°K of (a) $K_{1.35}Fe_{11}O_{17}$, (b) $K_{1.69}Fe_{9.63}Ga_{1.37}O_{17}$, (c) $K_{1.69}Fe_{8.25}Ga_{2.75}O_{17}$, and (d) $K_{1.69}Fe_{5.5}Ga_{5.5}O_{17}$. The arrow indicates a small peak from an impurity in the cryostat windows.

Samples Having 25% Fe–75% Ga

We shall next describe the samples having a high dilution of Fe by Ga, and return later to consider the more complex behavior of samples containing 50% Fe. During the initial stages of investigation it became evident that spectral changes occurred after samples had been exposed to air for extended periods, and that such changes could provide valuable clues to the interpretation of the multicomponent spectra. In order to reduce the effects of exposure to a minimum fresh samples having 25 and 50% Fe were prepared. They were quickly unloaded from the press and sealed in evacuated glass ampoules. The Mössbauer samples were prepared by quickly removing them from the ampoule, breaking the pellets in air, weighing, and grinding under hexane. When the hexane had almost completely evaporated, Apiezon grease was mixed with the slurry, which was then spread between Mylar

sheets. The samples were then loaded into a cryostat and kept in vacuum.

Figure 3a shows the paramagnetic spectrum obtained at 290°K from a 25% Fe–Ga sample which had been hot pressed in vacuum and protected from air as described above. A spectrum obtained using higher velocities did not reveal any magnetically split components, indicating a good solid solution of the Fe in the lattice. The figure shows the resolution of the spectrum into two doublets. The fit gave $\chi^2 = 216$ for 171 degree of freedom. The parameters of the two peaks of the major doublet were not constrained, and the areas were found to be the same to within two standard deviations. The intensities and half-widths, respectively, of the two smaller peaks were constrained to be equal. The parameters are given in Table I. The major doublet is consistent with Fe(III) in distorted octahedral sites (16, 17) and the minor doublet, accounting for $12 \pm 1\%$ of the total resonance area, has a higher isomer shift (IS) only consistent with Fe(II). The slightly larger half-width of 0.41 mm sec^{-1} , compared to that of the

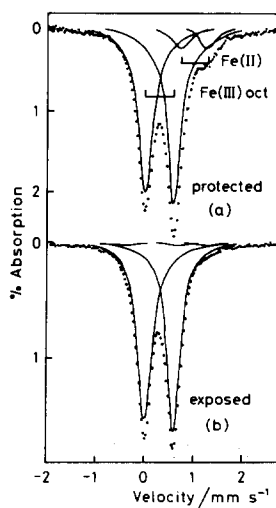


FIG. 3. Mössbauer spectra at 290°K of 25% Fe samples of composition $K_{1.69}Fe_{2.75}Ga_{8.25}O_{17}$. (a) protected from air and (b) exposed to air in a desiccator for about 1 year.

TABLE I
ISOMER SHIFTS (IS, mm sec⁻¹), QUADRUPOLE SPLITTINGS (QS, mm sec⁻¹), AND PERCENTAGE OF TOTAL RESONANCE AREA FOR SELECTED Fe-Ga FERRITES AT 290°K^a

		Fe(III) oct	Fe(III) tet' (small QS)	Fe(III) tet (large QS)	Fe(II)
25% Fe-75% Ga (protected)	IS	0.32 (1)			1.02 (4)
	QS	0.59 (1)			0.56 (4)
	%	88 (1)			12 (1)
50% Fe-50% Ga Type A (exposed)	IS	0.34 (1)	0.21 (8)	0.18 (7)	
	QS	0.55 (1)	0.42 (8)	0.86 (7)	
	%	90 (2)	5 (1)	5 (1)	
50% Fe-50% Ga Type B (exposed)	IS	0.34 (1)	0.21 (6)	0.18 (9)	
	QS	0.70 (1)	0.42 (6)	0.86 (9)	
	%	66 (10)	32 (10)	2 (1)	

^a Errors in the last figures are given in parentheses.

Fe(III) peaks of 0.36 mm sec⁻¹, reflects the increased sensitivity of the quadrupole splitting (QS) of Fe(II) to site distortion compared to Fe(III).

Part of the original sample was ground and left in air as a fine powder for 3 days before preparing the Mössbauer sample. The spectrum showed that the Fe(II) proportion had diminished by about one-half, and there was evidence of a new shoulder at about -0.3 mm sec⁻¹. This apparent oxidation of Fe(II) upon exposure to air was observed for all the 25 and 50% Fe samples. Eventually spectra such as those shown in Fig. 3b were obtained. This sample was hot pressed in oxygen and stored in pellet form for about 1 year in an air-filled desiccator. The change from vacuum to oxygen during pressing was not found to correlate with any observable spectral changes for the many samples studied. Computer analysis based on optimization of the χ^2 values did reveal about 1% Fe(II), visually evident as a slight shoulder at high velocity, together with the new peak, at about the 1% level, at about -0.35 mm sec⁻¹, which was more pronounced in the spectrum taken at 77°K. We shall comment on this peak later, which has been indicated in Fig. 3b.

Since the Guinier photographs did not show any detectable change over this period of storage, it was decided to investigate both the electronic and ionic conduction properties of this sample. Although extensive studies have been made of the ionic and electronic conductivity in the pure ferrite (3, 5) and ionic conductivity data are available for the pure gallate (18), only the ionic conductivity of mixed Fe-Ga samples has been studied in detail (11). At 653°K the electronic and ionic conductivities of our sample were 4.02×10^{-4} and 3.38×10^{-3} ohm⁻¹ cm⁻¹, and the activation energies were 65 and 20 kJ mole⁻¹, respectively.

The sample was coulometrically titrated to increase the potassium content by 0.29 in *x* to 1.98. The Mössbauer spectra at 290, 77, and 5°K are shown in Fig. 4. The presence of Fe(II) is now again evident. Computer fits (involving three Fe(II) doublets to represent the broadened spectrum at 77°K) gave the proportion of Fe(II) as 8, 10, and 10% at 295, 77, and 5°K, respectively. These values agree well with the value of 10.1% expected if all the titrated K⁺ were charge compensated by Fe(II). The constant Fe(II) proportion over the temperature range also indicates that electron hopping between

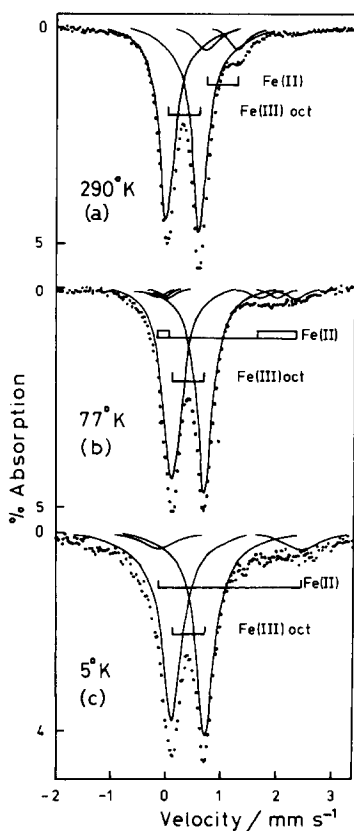


FIG. 4. Mössbauer spectra of sample, to which Fig. 3b relates, after electrochemically pumping in potassium.

Fe(II) and Fe(III) is not occurring rapidly enough to influence the Mössbauer spectra.

The Fe(II) QS increased from 0.56 mm sec^{-1} at 290°K to between 1.5 and 2 mm sec^{-1} at 200°K , to approximately 2.6 mm sec^{-1} at 5°K . The sudden increase in the QS between 290 and 200°K was typical of many samples. Although similar room temperature values of the QS have been found in other defect oxides such as Fe_{1-x}O (19), one would have expected a larger QS for Fe(II) in the distorted β -alumina structure. Now Akridge *et al.* (14) have shown that Fe(II) in Na- β -alumina occupies tetrahedral sites, which results in a characteristic strong temperature dependence of the QS to yield small values at room temperature. However, the temperature dependence we

have observed over the range 100 – 200°K is quite different, and it is likely that the small observed QS at room temperature derives from an unusual Fe(II) crystal field splitting, giving an unusual temperature dependence. At 655°K the electronic and ionic conductivities were 1.03×10^{-3} and $1.86 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$, and the activation energies were 53 and 41 kJ mole^{-1} , respectively.

Samples Having 50% Fe Substitution

The Mössbauer spectra of the many samples studied having 50% Fe–Ga or 50% Fe–Al could be classified into two types: those which were similar to the 25% Fe samples already described (type A), and those which exhibited an additional doublet arising from tetrahedral Fe(III) (type B). Spectra of both types were observed for samples containing Ga, while only type B spectra were observed for samples containing Al. The presence of type A or type B spectra most likely reflects differences in the high-temperature conditions, which varied slightly from sample to sample. We were unable, however, to establish a correlation with any of the measured preparative conditions.

Figure 5 shows a selection of type A spectra. At 100°K (Fig. 5b), the spectra of the vacuum-pressed 50% Fe–Ga sample exhibits both the Fe(II) and octahedral Fe(III) doublets that the spectrum of the pumped 25% Fe sample showed at 77°K , as seen in Fig. 4b. Computer fitting, which was satisfactory with just two Fe(II) peaks, gave an Fe(II) area of $18 \pm 6\%$, which is consistent with the 12% corresponding to the K^+ excess. However, the Fe(II) peak expected at 290°K was almost absent, and the associated resonance intensity appears to have contributed to a broadening and intensification of the main higher-velocity peak. Reasonable fits could be obtained consistent with a doublet and a single broad resonance at about 0.6 mm sec^{-1} representing about 20% of the total area. Since the IS is between those

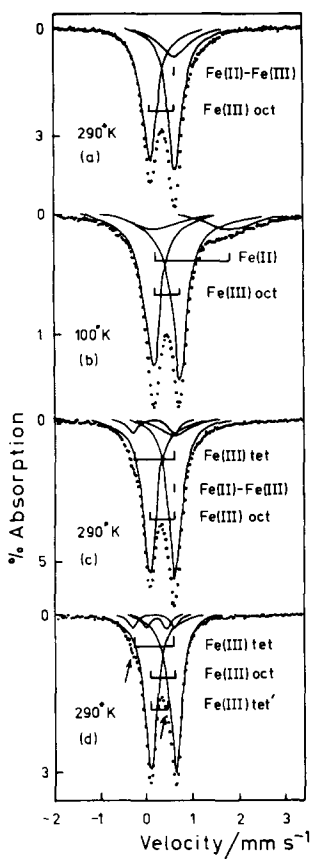


FIG. 5. Mössbauer spectra of type A for 50% Fe-Ga samples: (a, b) protected, (c) showing partial oxidation, and (d) showing complete oxidation (of another similar sample).

established for Fe(III) and Fe(II), we attribute this resonance to a mixed Fe(II)-Fe(III) peak caused by rapid electron hopping.

This conclusion is supported by the spectral changes observed upon oxidation. A portion of the above sample was ground and left in air for 3 days before running the spectrum, which is shown in Fig. 5c. A similar spectrum, shown in Fig. 5d, was obtained from an oxygen-pressed sample which had been left in air made up as a Mössbauer sample for several months. This spectrum now shows a loss of intensity in the region of the mixed Fe(II)-Fe(III) peak to give two major peaks of equal intensity. In addition,

the low-velocity shoulder found in the exposed 25% Fe sample is now quite apparent, and is indicated in Fig. 5d by the arrow at the left-hand side of the peaks. Close inspection of the large computer-drawn spectrum revealed another shoulder, indicated by the second arrow in Fig. 5d, and various computer fits confirmed the presence of a second small peak. Although the two small peaks were of similar intensities, the IS of 0.04 mm sec^{-1} obtained by assuming that they formed a doublet was too low for high-spin Fe(III) and Fe(II) in any coordination (16, 17). The QS did not change at 77°K . The possibility of low-spin octahedral Fe(II) or Fe(III), with which the data alone would be consistent, can be ruled out on chemical grounds. In other spectra it was noticed that each of the two small peaks could occur separately, indicating in fact that there are two low-intensity doublets and not just one. In Fig. 5d the two additional peaks required must overlap with the two major peaks, as indicated in the figure. Both of the ISs can only be in the tetrahedral Fe(III) range of 0.13 to 0.27 mm sec^{-1} (17), and the parameters are given in Table I.

Spectra of type B are shown in Fig. 6 and are for a sample pressed in oxygen. The doublet labeled Fe(III) tet' clearly occurs at the same velocities as the small doublet of the same label in Fig. 5d, supporting this assignment. Fits to the data of Fig. 6c using four unconstrained peaks were consistent with the areas expected from the three doublets at the velocities shown. Only approximate computer fits could be obtained for the type B spectra, even for thin absorbers, due to the many overlapping peaks involved. The approximate parameters are given in Table I. For Fig. 6c, the tet' doublet represented about $32 \pm 10\%$ of the total area, while the Fe(III) tet doublet represented about $2 \pm 1\%$ of the total area.

Figure 6a shows the spectrum of the protected sample. As many as 28 different sets of starting parameters and constraints were

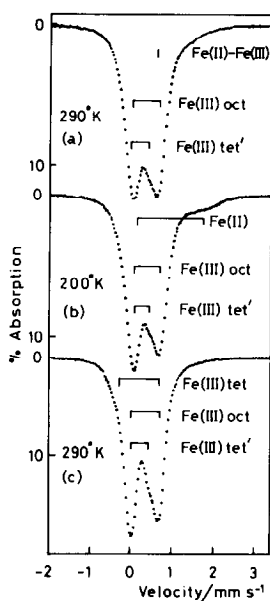


FIG. 6. Mössbauer spectra of type B for 50% Fe-Ga samples: (a), b) protected, (c) exposed to air.

tried in order to obtain a credible fit to the data. Although many fits gave acceptable sums of residuals, the peaks could not be accurately assigned and grouped, but an approximate interpretation of the fits did reveal a peak at about 0.6 mm sec^{-1} . This peak is assigned to a mixed Fe(II)-Fe(III) resonance, of apparent non-Lorentzian shape, which would explain the difficulty in fitting. Confirmation of the presence of Fe(II) is seen in the spectrum obtained at 200°K (Fig. 6b).

Discussion

Fe(III) Site Occupancies

The existence of the pure compounds of Fe, Al, and Ga having the β -alumina structure shows that each of these ions can occupy each of the available sites in the structure. The Mössbauer spectra have shown that samples of 50% Fe-Ga and 25% Fe-Ga (type A) can be prepared having very small proportions of Fe(III) in tetrahedral sites,

with most if not all of the Fe in octahedral sites. Thus Fe can show a strong preference for the octahedral sites under some preparative conditions. However, under other conditions (type B samples) both octahedral and tetrahedral sites are occupied, reflecting the delicate balance of site preferences. For 2 wt% Fe in Na- β -alumina, the balance between the site energies has been shown by Mössbauer and uv-visible spectral studies (14) to favor tetrahedral occupancy. The Mössbauer parameters obtained (14) are in good agreement with those found for tetrahedral Fe(III) (small QS) in type B spectra.

Akridge *et al.* (14) did not assign the tetrahedral Fe(III) to one or the other of the two possible types of tetrahedral site in the lattice. However, we have observed two tetrahedral Fe(III) doublets. We suggest that the doublet with the small QS represents Fe(III) in the spinel-type sites within the spinel blocks in the β -alumina structure, while the doublet with the unusually large QS arises from a site adjacent to the conduction plane, such as the bridging tetrahedral site or a Frenkel defect site, both of which might be expected to be quite distorted. These possibilities will be discussed later.

Fe(II) and Electron Hopping

The paramagnetic Mössbauer spectra of the 50 and 25% Fe samples clearly identified Fe(II) in the lattices. Hitherto the presence of Fe(II) in the pure ferrite had been inferred from the appreciable values of the electronic conductivity, since the magnetically split Mössbauer spectra of the pure ferrite were too complex to enable Fe(II) identification (4). Charge compensation of the excess K^+ ions in $\text{K}_{1+x}\text{Fe}_{11}\text{O}_{17}$ was shown from coulometric titration studies to be predominantly by Fe(II) rather than by incorporation of interstitial oxygens (4). In the 50% Fe samples the observed proportion of iron as Fe(II) of $18 \pm 6\%$ is consistent with the expected value of 12% if all the excess K^+ were compensated in this way. For the 25%

sample, however, the value obtained of $12 \pm 1\%$ is only half of the expected value of 24% for complete Fe(II) compensation, and indicates that another method of compensation, such as with oxygen interstitials, is also operative at these low proportions of iron.

Evidence of rapid electron hopping between Fe(II) and Fe(III) at a rate in the vicinity of 10^7 Hz at 290°K was obtained from the Mössbauer spectra of the 50% substituted Al and Ga compounds. Fe(II)–Fe(III) hopping has not been reported to occur between tetrahedral–octahedral pairs. In the β -alumina structure, either of the two tetrahedral sites is certainly much further away from any neighboring Fe sites than are the octahedral sites, and the presence of hopping implies that some or all of the Fe(II) are on octahedral sites in order to permit electron hopping. Only tetrahedral Fe(II) was found in doped Na- β -alumina by Akridge *et al.* (14), which must reflect a different site preference.

Electron hopping, or what can be described as small polaron motion, has been described by Holstein (20) and applied to Fe₃O₄ by Haubenreisser (21). For pairs of equivalent sites bounded by the same anion sublattice, more rapid hopping would be expected for shorter Fe(II)–Fe(III) distances. In a series such as Fe_{1-x}O, Fe₃O₄, and the β -aluminas the octahedral Fe–Fe distances decrease from between 3.047 to 3.026 Å for Fe_{1-x}O, decreasing with x , to 2.968 Å for Fe₃O₄, to values lower than these in the β -aluminas. For this structure there are two appropriate distances. The 12*k*–12*k* octahedral distances are given by $a/2$. However the 12*k*–2*a* octahedral distances depend on the distortion of the oxygen framework, and require single-crystal data for precise determination. These distances can be calculated from such data for Na- β -alumina (10) to be 2.797 and 2.734 Å, respectively. The 12*k*–12*k* distances are comparable for K- β -alumina (2.798 Å) (12), and increase in

going to K- β -gallate (2.917 Å) (12) and to K- β -ferrite (2.958 to 2.970 Å, depending on x and worker) (12).

The room-temperature Mössbauer spectra of Fe_{1-x}O does not show evidence of electron hopping (19), while that of Fe₃O₄ has been interpreted as indicating electron hopping (22, 23), although there is currently some controversy over this conclusion (24). Notwithstanding such recent indications of metallic properties in Fe₃O₄, the comparisons do show that the mixed ferrites have Fe–Fe distances appropriate for delocalizing interactions. Such clear evidence of the effect of electron hopping as has here been provided in a paramagnetic spectrum has for many years not been available. Recently Lotgering and van Diepen observed the effect in the paramagnetic spectrum of Zn²⁺[Zn_{(1-x)/2}²⁺Ti_{(1+x)/2}⁴⁺Fe_{1-x}³⁺Fe_x²⁺]₄O₄ (25), which shows spectral characteristics very similar to those of the 50% Fe–Ga ferrites. Thus although some doubt has been cast on the interpretation of the spectrum of Fe₃O₄ (24), the spectrum of the above mixed spinel and that of the mixed ferrite provide support for the presence of electron hopping in such oxides.

Turning to the values for the activation energy for electronic conductivity in mixed Fe(II)–Fe(III) oxides, we find values of 19, 6, and 6 kJ mole⁻¹ for Fe_{1-x}O (26), Fe₃O₄ (27), and K_{1.6}Fe₁₁O₁₇ (3), respectively. The value found for K_{1+x}Fe_{2.75}Ga_{8.25}O₁₇ varied from 65 kJ mole⁻¹ for a sample with a low Fe(II) content, to 41 kJ mole⁻¹ for the pumped sample. These values show a marked increase from the figure of 6 kJ mole⁻¹ for the pure ferrite, and reflect the influence of cation disorder in rendering the Fe sites inequivalent. In addition, the conduction pathways will be forced to be tortuous by the presence of a high concentration of nonparticipating ions. Such a strong influence of the Fe(II) concentration has also been found in other mixed systems such as the mixed spinel Ni_{1-x}Fe_x(II)Fe₂O₄,

for which the activation energy for electronic conductivity increased from 5 to 46 kJ mole⁻¹ when x decreased from 0.4 to 0 (28). The latter value may well even represent conduction by another mechanism. Electronic conductivity in mixed oxides containing Fe(II) is further discussed in Part I (3).

Judging from the above, the activation energy for electronic conduction in the 50% Fe–Ga sample would be expected to be somewhere between 6 and 41 kJ mole⁻¹. Although electron hopping is fast enough to possibly influence the Mössbauer spectrum of Fe₃O₄, which has an activation energy of 6 kJ mole⁻¹, one would not expect an averaged Mössbauer spectrum if the activation energy were much higher than this. However, the results for the 50% Fe–Ga sample do show that the Fe(II) spectrum is averaged with some, but not all, of the Fe(III) in the sample. We interpret this as indicating rapid localized hopping between partially isolated Fe(II)–Fe(III) pairs or groups. The conductivity on the other hand is determined by the more difficult transfers between the groups. A similar general explanation was proposed for the mixed spinel (25). However, in the mixed ferrites the $12k$ – $2a$ distances are likely to be shorter than the $12k$ – $12k$ distances, as discussed above, and localized hopping between the central $2a$ ion and the six adjacent $12k$ ions may be more favorable than between adjacent $12k$ ions. However, long-range motion of charge requires hops between $12k$ sites. Thus the Mössbauer spectra may be averaged by rapid $2a$ – $12k$ hopping while the conductivity is determined by the slower $12k$ – $12k$ hopping.

Let us consider the ionic conductivity. The activation energies for K⁺ in compositions of approximately K_{1.6}M₁₁O₁₇ are 25, 37, and 26 kJ mole⁻¹ for the pure Fe (5), Ga (18), and Al (29) analogs, and 34 kJ mole⁻¹ in a mixed 80% Fe–20% Ga sample (11). The values obtained for K_{1+x}Fe_{2.75}Ga_{8.25}O₁₇ ranged from 20 to 53 kJ mole⁻¹ for the low and high K contents, respectively. Both the

spinel-block metal ion and the K content are thus seen to influence the ionic conductivity.

Magnetic Properties

Dilution of the Fe in the lattice was accompanied by a lowering of the Néel temperature and, in the more dilute samples (see Fig. 2d), the presence of a range of effective ordering temperatures characteristic of the presence of superparamagnetic regions in the lattices. Such an effect (30) is often found in magnetically dilute materials, and arises from a range of domain sizes, and is more pronounced if partial segregation of the two types of cations has occurred during cooling of the sample.

If we look at the magnetic structure of the pure ferrite (31), magnetic coupling between blocks occurs via the tetrahedral ions above and below each bridging oxygen ion. The coupling is antiferromagnetic, resulting in the net moments of each block being coupled antiferromagnetically. Now in the substituted ferrites most, if not all, of the Fe ions were shown to be in the octahedral sites. The usual coupling between the blocks requires one Fe above and one Fe below a bridging oxygen. The number of such pairs of tetrahedral Fe will drop off very rapidly as the proportion of tetrahedral Fe diminishes. Even if we assume the tetrahedral Fe(III), indicated in the Mössbauer spectrum of the 50% Fe–Ga samples of type B (Fig. 6), were located in the bridging rather than the spinel tetrahedral sites, the proportion of Fe(III) in the bridging tetrahedral sites would only be approximately one-third of 50%, or 17%. This gives the proportion of Fe(III) pairs about a bridging oxygen as 0.17², or 0.03. The interblock coupling from this source is therefore very small in such a sample. Nevertheless the Mössbauer spectra of all of the 50% substituted samples showed partial magnetic broadening at 77°K. We interpret these results, in the light of the above, as indicating the existence of magnetic ordering within each spinel-type

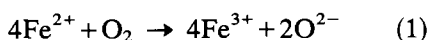
layer, but not necessarily between successive layers. Two magnetic ordering temperatures might be expected: that of the effective Néel temperature for intralayer ordering, and that for inter- plus intralayer ordering. A similar situation exists in the layered halides, such as Rb_2FeF_4 (32).

Because of the layer-like shape of the magnetic domains in the first stage of ordering, superparamagnetic behavior might be anticipated in which the resultant magnetic moment of the layer domains may be rotating at a rate fast enough to give a paramagnetic type of susceptibility as measured in a conventional magnetic balance. However, if the rate were less than 10^7 Hz the ^{57}Fe nuclei would experience a static field during the time of nuclear excitation, and a normal magnetically split Mössbauer spectrum would be obtained. At rotation rates comparable to 10^7 Hz a spectrum such as that shown in Fig. 2d would be expected.

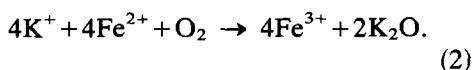
For the 25% Fe-Ga sample, the absence of magnetic splitting in the Mössbauer spectrum even at 5°K is rather surprising. However, this could be explained by the presence of either layered domains which are superparamagnetic or ordered clusters of Fe ions in the layers which are superparamagnetic.

Oxidation Effects

The ease of oxidation of the ferrites has not been commented on previously and is a factor which needs to be considered to ensure reliability and reproducibility of experimental results. The oxidation process could be formulated as either



or



The first reaction implies incorporation of O^{2-} into the ferrite lattice. The second reaction involves removal of K^+ from the lattice.

If ferrite pellets are left in air a white film often forms on the surface, indicating removal of K^+ to form, in air, K_2CO_3 . However, pellets left in a dessicator to oxidize do not show any change in appearance, suggestive of a type (1) reaction.

Gross breakdown of the ferrite structure into simple oxides is supported neither by the unchanged Guinier photographs following oxidation, nor by the absence of any magnetically split Mössbauer pattern which would have arisen from Fe_3O_4 , Fe_2O_3 , or KFeO_2 . One must conclude that the tetrahedral Fe(III) produced by oxidation represents a site in the ferrite structure. However, many of the samples had undetectable proportions of Fe(III) in tetrahedral sites before oxidation, and since the normal tetrahedral sites in the lattice would then all be filled with either Al or Ga, appearance of tetrahedral Fe(III) would necessitate exchange of Fe(III) on an octahedral site with Al or Ga on a tetrahedral site, which would be a very slow process at room temperature. The possibility that the appearance of the tetrahedral Fe(III) spectrum could be due to such a site exchange process independent of the oxidation process can be ruled out, since the tetrahedral Fe(III) spectrum was absent in samples sealed for many months, but appeared within 3 days of grinding in air. Grinding alone could not have influenced the samples in this way since the unoxidized sealed samples were also ground (under hexane) prior to obtaining the Mössbauer spectra. We therefore associate the appearance of the tetrahedral Fe(III) spectrum with the disappearance of the Fe(II) spectrum. We have assessed the results on the basis of three models, depending upon whether Fe(II) resides on octahedral sites (model I), on a mixture of octahedral and tetrahedral sites (model II), or on tetrahedral sites (model III).

In model I, oxidation of octahedral Fe(II) would normally produce octahedral Fe(III). The appearance of the tetrahedral Fe(III)

sites with the large QS upon oxidation could be explained by the creation of Frenkel defects. Roth, from X-ray evidence from β -alumina (6), suggested that these could be formed by the displacement of Al(III) from an octahedral site into a tetrahedral site constituted by the presence of interstitial oxygen. The displacement is illustrated in Fig. 7. Further investigations of β -alumina (7, 8) have supported this model. In the 50% Fe mixed ferrites we have shown that charge compensation of the excess K^+ has occurred by means of Fe(II), and therefore that oxygen interstitials would not be expected in the initial samples. However, penetration by oxygen into the conduction planes during oxidation of the Fe(II) in the samples could lead to the formation of Frenkel defects, and the newly created tetrahedral Fe(III) may be responsible for the new doublet in the Mössbauer spectra.

Let us make a quantitative comparison between the proportion of Frenkel defects expected and that obtained. Each O^{2-} enter-

ing the conduction plane will have oxidized two Fe(II) ions somewhere in the lattice, but not necessarily adjacent to the O^{2-} ion. Now since each excess O^{2-} ion is close to two octahedral metal ions, one above and one below, the pure ferrite would be expected to possess Frenkel defects in a proportion equal to Fe(II) initially. In a mixed solid, however, the number of Fe(III) in Frenkel defects will be reduced by the fraction of Fe(III) in the $12k$ octahedral sites, given that the O^{2-} ions do not discriminate between the two types of cation. For the 50% Fe-Ga samples which showed no initial tetrahedral Fe(III) (type A), Fe(III) will occupy $5.5/7 = 79\%$ of the 7 octahedral sites per 11 sites per formula, where we have not distinguished between the six $12k$ and the one $2a$ octahedral sites per formula. The 12% iron as Fe(II) expected from the potassium excess x of 0.69 should thus produce $0.12 \times 79 = 9.5\%$ iron in Frenkel defects in the oxidized sample. However, only $5 \pm 1\%$ of tetrahedral Fe(III) was obtained (Fig. 5d).

Consider now the type B sample with $32 \pm 10\%$ tetrahedral Fe(III) initially for which Fe(III) occupies $53 \pm 16\%$ of the total number of octahedral sites in the lattice. The expected percentage of iron in the Frenkel sites, given 12% as Fe(II) originally, is $0.12 \times 53 = 6.4\%$. The observed value was $2 \pm 1\%$. Again, for the 25% sample, the proportion of octahedral sites occupied by Fe was 39%, and from the value of x of 0.69 one would expect $0.12 \times 39 = 4.7\%$ of the iron to be in Frenkel sites, compared to the observed value of about 2% (Fig. 3b). Mössbauer studies of surface species would lead one to expect only a slightly lower f factor (governing the spectral response) for surface ions than for bulk ions (17). Although this may be a factor contributing to the low observed proportions of the proposed ions in Frenkel sites, the results may also suggest that not all of the potential Frenkel sites form at room temperature, or that Frenkel defects form preferentially with Ga or Al rather than with

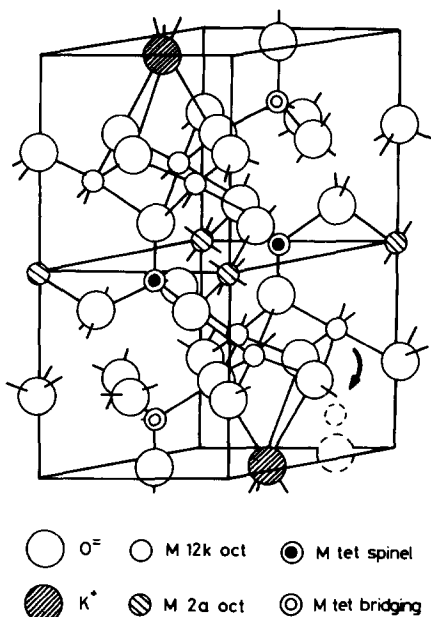


FIG. 7. The Frenkel defect in the β -alumina structure, formed as indicated by the arrow.

Fe. Such an explanation in terms of octahedral Fe(II) forming tetrahedral Fe(III) in a Frenkel defect according to model I is consistent with the results for all of the samples studied, namely, the 25% Fe-Ga, 50% Fe-Ga (type A), 50% Fe-Ga (type B), and 50% Fe-Al (type B) samples.

In model II, Fe(II) is assumed to be distributed between octahedral and tetrahedral sites. Some Fe(II) must reside on octahedral sites to allow electron hopping, as previously discussed. On the other hand, Akridge *et al.* (14) have established that Fe(II) occupies tetrahedral sites in doped Na- β -alumina. In model II oxidation of tetrahedral Fe(II) produces the new tetrahedral Fe(III) doublet. The large QS of this doublet implies an assignment to the distorted bridging tetrahedral sites. In this model only part of the original proportion of Fe(II) will appear as tetrahedral Fe(III) upon oxidation, thus providing an explanation for the smaller observed proportion of tetrahedral Fe(III) than might have been expected on the basis of model I. The figure would suggest, in terms of model II, that 30–50% of the total Fe(II) resided on bridging tetrahedral sites initially. Such results are in keeping with the fact that Mg(II) has been located on the bridging tetrahedral sites in β -alumina (8).

For the 50% Fe samples at 290°K, electron hopping has caused an apparent collapse of the resolvable Fe(II) components, and the high-velocity peak from any tetrahedral Fe(II) should be evident as a shoulder on the main peak (at a velocity of approximately 1.2 mm sec^{-1} as estimated from the data of Akridge *et al.* (14)), but certainly at a velocity equal to or higher than the expected IS of 1.0 mm sec^{-1} . Inspection of Figs. 5a and 6a only reveals slight shoulders in this region, indicating that certainly the majority of the Fe(II) is on octahedral sites. The shoulder could, of course, alternatively arise from the broad averaged Fe(II)–Fe(III) peak, as suggested in Fig. 5a. Any tetrahedral Fe(II) shoulders at 290°K should be of comparable

proportions to the new tetrahedral Fe(III) peaks in Figs. 5d and 6d, which, upon visual inspection, is a possibility which cannot be excluded. Unfortunately the presence of the non-Lorentzian, averaged Fe(II)–Fe(III) resonance at 290°K prevents accurate computer fitting to test such a relationship.

This IS of $1.02 \pm 0.04 \text{ mm sec}^{-1}$ at 290°K of the Fe(II) doublet has been obtained from the spectrum of the 25% Fe sample (Fig. 3a). The ISs for Fe(II) in tetrahedral sites in FeAl_2O_4 , FeV_2O_4 , and FeCr_2O_4 (33) are 0.98, 0.81, and 0.81 mm sec^{-1} , respectively, and that for Fe(II) in Na- β -alumina is 0.97 mm sec^{-1} (14). The two available measurements for the IS of octahedral Fe(II) in spinels give values of 1.23 and 1.19 mm sec^{-1} for GeFe_2O_4 and $\text{Fe/GeCo}_2\text{O}_4$, respectively (34). On the basis of these values our figure of 1.02 mm sec^{-1} would appear to be slightly on the low side for octahedral Fe(II), but nevertheless this assignment could not be ruled out due to the limited number of examples available and the spread of values among them.

In model III we have considered the possibility of all the Fe(II) residing on tetrahedral sites. For the 50% Fe samples this clearly cannot be the case since the spectral collapse of Fe(II) between low temperature and 290°K could not be accounted for unless electron hopping were occurring. For the 25% Fe samples, as well as for the 50% Fe samples, the new doublet produced by oxidation is obviously much smaller in proportion than the initial Fe(II) doublet, indicating that model III does not apply.

In summary, the evidence is consistent with either model I or II, but not with model III. We can conclude that at least approximately half of the Fe(II) in the initial samples occupies octahedral sites, probably both the $12k$ and $2a$ sites, as discussed in the section on electron hopping. If all of the Fe(II) is on octahedral sites then the data would be consistent with the creation of Frenkel defects upon oxidation. If the remainder of

the Fe(II) were on tetrahedral sites, most likely the bridging tetrahedral sites, then it is not necessary to invoke the formation of Frenkel defects upon oxidation to explain the results.

The study has shown the perhaps unexpected high-temperature stability of Fe(II) in the mixed ferrites, with favorable consequences for the electronic conductivity of such samples. The range of sites which both Fe(III) and Fe(II) can occupy attests to the great substitutional versatility of the β -alumina structure, which inevitably emphasizes the need to carefully consider the preparative conditions and thermal histories of these materials.

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