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Mössbauer Study of Isomer Shift, Quadrupole Interaction, and Hyperfine Field in Several Oxides Containing Fe^{57}

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Mössbauer absorption by Fe^{57} was used to study isomer shift, quadrupole splitting, and hyperfine fields in several oxides containing iron. The established relations between isomer shifts and ionic states of Fe were further confirmed by measurements on $Fe^{2+}Ti_2O_5$, $Fe_2^{3+}TiO_5$ and several other mixed oxides. By utilizing this relation, in turn, to identify the ionic states when these are in doubt, it has been found that $(Fe,V)_2O_3$ incorporates the cation pair $Fe^{3+}-V^{3+}$, rather than $Fe^{2+}-V^{4+}$, and that "$SrFeO_3$" contains Fe^{4+} and Fe^{3+} in the ratio of 3:1. A well-defined quadrupole splitting was observed in $Fe_{1-x}O$ and in a number of the solid solutions (Fe,Mg)O, although their over-all symmetry is cubic. This is explained by the assumption of local asymmetry at the Fe nuclei caused either by vacancies or foreign ions. Hyperfine fields at the Fe^{3+} nuclei in $(Fe,Cr)_2O_3$, $(Fe,V)_2O_3$, and $(Fe,Al)_2O_3$ have values between 520 and 540 koe when extrapolated to 0°K, and the results are discussed in conjunction with their magnetic properties.

I. INTRODUCTION

THE discovery by Mössbauer[1] of recoil-free absorption by nuclei in solids provided a new method of investigation of the electronic and magnetic structures of solids. The most commonly used Mössbauer element is Fe^{57}, which offers convenient linewidth, half-life, and, above all, a wide range of compounds with particularly interesting magnetic properties. Several important iron compounds have already been studied by this new technique; among them are α-Fe_2O_3, by Kistner and Sunyar,[2] and FeF_2 by Wertheim.[3]

Mössbauer measurements on Fe ions in the paramagnetic state provide two parameters—the center shift ΔE, and the quadrupole splitting ϵ, as shown in Fig. 1 and defined by

$$\epsilon=\tfrac{1}{4}e^2qQ(1+\tfrac{1}{3}\eta^2)^{\frac{1}{2}},\quad eq=\partial^2V/\partial z^2,$$

where Q is the nuclear electric quadrupole moment for the excited state of Fe^{57} and η is the asymmetry parameter.

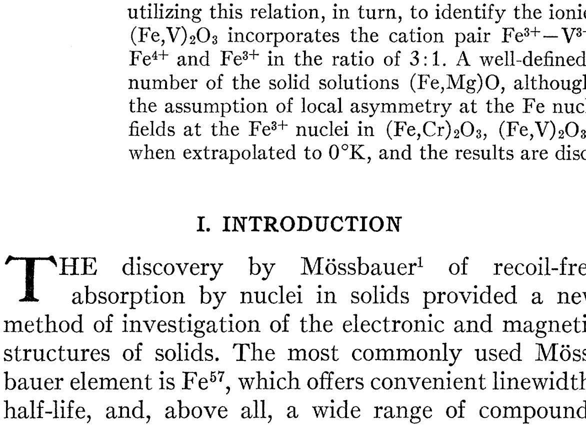

FIG. 1. Mössbauer absorption of $FeTi_2O_5$. The positive velocity indicates a motion of source toward absorber. The solid line is a synthesized curve for FeI:FeII=4:1 at the positions indicated by arrows (Γ=0.35 mm/sec).

The center shift was first observed by Kistner and Sunyar[2] in their study of α-Fe_2O_3 and it arises from two mechanisms. The first part is a second-order Doppler effect resulting from the thermal motion of the atoms and is temperature dependent. This part is usually small, when the source (usually stainless steel) and absorber (sample under examination) are at the same temperature and as a first approximation it may be neglected. The second part is "isomer shift"[4] which is due to the difference in the s-electron densities at the nuclei of source and absorber. This shift is proportional to $|\psi(0)_a|^2-|\psi(0)_s|^2$, where $|\psi(0)_a|^2$ and $|\psi(0)_s|^2$ are the total s-electron densities at the nucleus for absorber and source, respectively.[4-6]

The observed values of isomer shifts in several iron compounds can be divided into two groups—the one corresponding to the Fe^{3+} state is 0.3–0.6 mm/sec and the other corresponding to Fe^{2+} is 1.2–1.5 mm/sec, as illustrated in Table I. Walker, Wertheim, and Jaccarino[4] have utilized calculated ion wave functions to calibrate the isomer shift, thus allowing the identification of the Fe^{3+} electronic state as $3d^54s^x$ and the Fe^{2+} state as $3d^64s^x$. In the present study, the isomer shifts are used to identify the ionic state of Fe ions in several compounds, amongst which "$SrFeO_3$" is of particular interest as the majority of the ions have been considered to be Fe^{4+}.

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[2] O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters **4**, 412 (1960).

[3] G. K. Wertheim, Phys. Rev. **121**, 63 (1961).

[4] L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters **6**, 98 (1961).

[5] S. DeBenedetti, G. Lang, and R. Ingalls, Phys. Rev. Letters **6**, 60 (1961).

[6] I. Solomon, Compt. rend. **250**, 3828 (1960).

A survey of quadrupole splitting in several iron compounds was made by DeBenedetti *et al.*[5] They observed that the Fe^{3+} state exhibits a small splitting—$\epsilon \lesssim 0.1$ mm/sec—as may be expected from the *S* state of its $3d^5$ electronic configuration. Fe^{2+} ions, on the other hand, exhibit a large splitting of the order of $\epsilon \sim 1.5$ mm/sec, when the ions are located in noncubic surroundings. This conclusion appeared to be valid for the group of compounds they investigated (Table I). However, more recent results on oxides have revealed a much wider variety of quadrupole interactions. For example, Fe^{3+} in yttrium-iron garnet shows a splitting of 0.39–0.47 mm/sec,[7] while the rather small value of 0.3–0.5 mm/sec[8] is found for Fe^{2+} in $FeTiO_3$.

When the magnetic moments are ordered, ferromagnetically or antiferromagnetically, the Mössbauer absorption spectrum consists of "6 fingers" because of the hyperfine field. The temperature dependence[9] of the hyperfine field in metallic Fe has established that in a given compound this field is proportional to the atomic moment. In several oxides already investigated,[2,7,10,11] the hyperfine fields of Fe^{3+} have values in the narrow range 500–550 koe at 78°K with the single exception of 460 koe for Fe^{3+} in the tetrahedral site of YIG.[11] This seems to indicate that the hyperfine field of Fe^{3+} is mainly a property of the ion itself. A number of oxide solid solutions with α-Fe_2O_3 were therefore studied to gather further information.

II. EXPERIMENTAL

The Mössbauer spectra from the 14.4-kev gamma ray of Fe^{57} were measured by using a type-321 stainless steel source, moved sinusoidally, and a velocity sorting system, as described previously.[12] This source, combined with the stainless steel absorber, gives a half-width at half maximum of 0.28 mm/sec. This linewidth, Γ, is the customary value for a stainless steel source although it is approximately double the theoretical width. The line positions measured on standard samples such as Fe metal, α-Fe_2O_3, and $KFeF_3$ agree satisfactorily with the published data.

Powder samples were prepared with reagent grade materials containing natural Fe. In most cases the constituent materials were fired at a suitable temperature either in air or in alumina thimbles contained in silica tubes evacuated to a pressure of between 10^{-2} and 10^{-3} mm of mercury if there was any possibility of oxidation. X-ray diffraction powder photographs of the products were taken with the appropriate radiation on a Norelco diffraction unit and in many cases chemical analysis for iron content was performed. Details of preparation and the x-ray and analysis data are summarized in the following sections.

Table I. Center shift, ΔE, and quadrupole splitting, ϵ, of several iron compounds determined at room temperature by Mössbauer absorption (in mm/sec). The center shift is referred to the stainless steel source.

Ionic state	Compound	ΔE	ϵ	Reference
Fe^{3+}	Fe_2O_3	0.47	0.12	Kistner and Sunyar[a]
	$FeCl_3$	0.45	0	DeBenedetti *et al.*[b]
	$Fe_2(SO_4)_3$	0.55	0	DeBenedetti *et al.*[b]
	$Y_3Fe_2(FeO_4)_3$ (Oct.)	0.55	0.47	Alff and Wertheim[c]
	(Tet.)	0.35	0.39	Bauminger *et al.*[d]
	Fe_2TiO_5	0.48	0.35	Present paper
Fe^{2+}	$FeCl_2 \cdot 4H_2O$	1.35	1.50	DeBenedetti *et al.*[b]
	$FeSO_4 \cdot 7H_2O$	1.40	1.60	DeBenedetti *et al.*[b]
	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	1.40	0.88	DeBenedetti *et al.*[b]
	FeF_2	1.40	1.34	Wertheim[e]
	$KFeF_3$	1.39	0	Walker *et al.*[f]
	$FeTiO_3$	1.20	0.31	Ruby and Shirane[g]
	$FeTi_2O_5$	1.15	1.50	Present paper

[a] See reference 2.
[b] See reference 5.
[c] See reference 7.
[d] See reference 11.
[e] See reference 3.
[f] See reference 4.
[g] See reference 8.

For the Mössbauer experiments the samples were prepared such that the amount of Fe^{57} was less than 0.5 mg/cm². The data presented in this paper give the Mössbauer absorption as a percentage of the nonresonant absorption. The background due to 120-kev gamma rays, which amounts to $\frac{1}{4}$ to $\frac{1}{2}$ of the total counts, was determined with a $\frac{1}{16}$-in. Al sheet and was subtracted from the data. For a standard run, each point represents total counts numbering $(1\text{–}4)\times 10^4$.

In several compounds investigated in this paper the observed absorption spectrum is a result of superposition of two or more absorption curves, either because of quadrupole splitting from equivalent Fe ions or because of the existence of nonequivalent Fe ions with dissimilar spectra. The observed curves could be closely matched by superposing curves calculated from the empirical formula

$$y=\frac{y_0}{1+0.75(x/\Gamma)^2+0.25(x/\Gamma)^4},$$

where y_0 corresponds to the height of an individual peak, x is the distance from the middle of the peak and Γ is the half-width at half maximum. The x^4 term was added to give a better fit with the observed curves of stainless steel and $KFeF_3$ in the range $x/\Gamma > 1$. This function may not have the proper characteristics for large values of x/Γ, but it is a good approximation when $x/\Gamma < 3$. The same Γ value is used for all of the components of a given sample. The values of y_0 are adjusted to give the best fit with the observed curve and the ratio of y_0's, of course, corresponds to the relative numbers of Fe ions.

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[8] S. L. Ruby and G. Shirane, Phys. Rev. **123**, 1239 (1961).

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III. ISOMER SHIFT AND QUADRUPOLE SPLITTING

Fe_2TiO_5

This compound is the mineral pseudo-brookite, which has orthorhombic symmetry and contains Fe^{3+} in the paramagnetic state.[13] It was prepared from Fe_2O_3 and TiO_2 at 1300°C in air and had the lattice parameters $a=3.72$ A, $b=9.78$ A, $c=9.98$ A, in good agreement with published data.[13,14] The x-ray pattern also revealed a trace of Fe_2O_3.

According to Wyckoff,[14] Fe ions are located in $8f$ sites and Ti ions in $4c$ sites of the space group *Cmcm*. The Ti ions are surrounded by fairly regular octahedra of oxygen ions at distances between 1.90 and 1.99 A, but the Fe ions are in much more strongly distorted octahedra. Four of the oxygen ions are disposed almost tetrahedrally at distances between 1.83 and 1.97 A, while the remaining two are situated at a distance of 2.31 A.

The Mössbauer pattern shows a quite distinct quadrupole splitting of 0.35 mm/sec, with a center shift of 0.48 mm/sec, the latter value being typical for the Fe^{3+} ion. As far as is known, this is the first example in which a quadrupole effect has been observed for Fe^{3+} in the paramagnetic state. The magnitude of the split is similar to that obtained for Fe^{3+} in the tetrahedral sites of YIG[11] and it is possible that there is some significance in the oxygen ion distribution around the Fe^{3+} ion in pseudo-brookite as described above.

$FeTi_2O_5$

By analogy with pseudo-brookite, this compound was selected as an example of an oxide containing Fe^{2+} in the paramagnetic state and having surroundings with low symmetry. It was prepared by firing a mixture of Fe, Fe_2O_3, and TiO_2 at 1000°C in an evacuated silica tube. Chemical analysis gave the Fe^{2+} content as 21.9% (theoretical is 24.1%). The x-ray pattern was single phase, apart from a trace of rutile, with orthorhombic lattice parameters $a=3.74$ A, $b=9.81$ A, and $c=10.10$ A, in reasonably good agreement with Akimoto *et al.*[13] These authors have assigned the pseudo-brookite structure to $FeTi_2O_5$, but the distribution of the Fe and Ti ions and their parameters have not been determined in this case. Two reasonable alternatives exist for the location of the cations; either Ti ions occupy the $8f$ sites and Fe the $4c$ sites or else 4 Ti ions and 4 Fe ions share the $8f$ sites and the remaining Ti ions are found on the $4c$ sites. By analogy with spinels, the latter arrangement may be considered "inverse," and in view of the complete range of solid solution between Fe_2TiO_5 and $FeTi_2O_5$,[13] is rather more plausible.

The results of Mössbauer measurements are shown in Fig. 1 and Table I. The observed quadrupole splitting, $\epsilon=1.50$ mm/sec, is quite large compared with the splitting found in other oxides (~ 0.3 mm/sec) but is similar to the values reported for non-oxides by DeBenedetti, Lang, and Ingalls.[5] This might be a mere consequence of the fact that to date this compound is the only oxide studied in which Fe^{2+} has surroundings of low symmetry.

A noticeable asymmetry is observed in both absorption peaks, and this could correspond to the superposition of a second quadrupole splitting of rather smaller magnitude but with identical center shift resulting from the existence of Fe^{2+} on two kinds of sites. The solid line in Fig. 1 is synthesized by assuming the ratio of FeI:FeII=4:1, $\Gamma=0.35$ mm/sec, and ϵ (FeII) $=1.00$ mm/sec. In view of the possible structural alternatives described above, it is very reasonable to assume that most of the Fe ions are situated on the $8f$ sites in strongly distorted oxygen octahedra and therefore show the greater quadrupole split. The remaining Fe ions are in $4c$ positions in the more regular octahedra and show the smaller quadrupole effect.

In an attempt to make the distribution of the cations more random and therefore test the hypothesis, a specimen was fired at 1250°C and quenched in water, but the results were inconclusive, as the spectrum showed little, if any, change.

$SrFe^{4+}O_3$

The existence of a Fe^{4+} state in this compound, which in reality is always deficient in oxygen and has a limiting composition $SrFeO_x$ ($x\sim 2.9$), has been reported by several authors[15–18] and the magnetic properties[17,18] of the $(Sr,La)FeO_3$ and $Sr(Ti,Fe)O_3$ systems have been investigated in some detail, the compound $SrFeO_{2.86}$ having a Néel point at about 50°K.

The material was obtained by first heating a mixture of $SrCO_3$ and Fe_2O_3 at 1000°C in argon. This product was ground and refired at 1400°C in oxygen. Chemical analysis for oxidizing power gave an Fe^{4+}:Fe^{3+} ratio of 0.68:0.32. The x-ray pattern showed a single cubic phase with considerable line-broadening possibly corresponding to a tetragonal distortion as reported by Watanabe,[16] although no actual line splitting could be detected in the present case. The lattice parameter was 3.869 A, identical to the figure obtained by Yakel[15] for a material $SrFeO_{2.93}$.

The Mössbauer spectrum of this compound is shown in Fig. 2. The solid curve shown on the same figure was calculated by superposing two peaks centered at 0.10 mm/sec and 0.55 mm/sec with a relative intensity of 3:1. The linewidths of both lines were adjusted to

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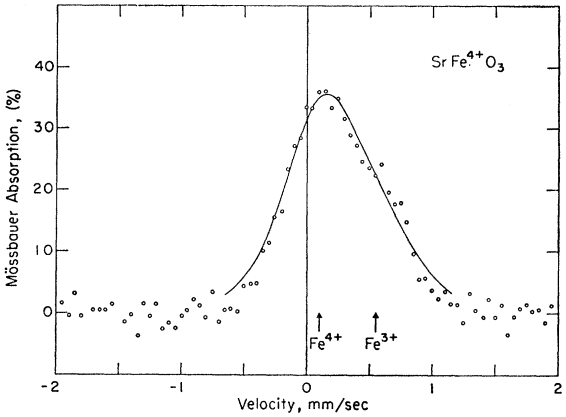

FIG. 2. Mössbauer absorption of $SrFeO_3$. The solid curve is synthesized by assuming $Fe^{4+}:Fe^{3+}=3:1$ at the positions indicated by arrows ($\Gamma=0.35$ mm/sec).

0.35 mm/sec to fit the data. The second absorption peak at 0.55 mm/sec can be identified as Fe^{3+} from its center shift. The first peak should therefore correspond to Fe^{4+}. The intensity ratio of 3:1 required for the best fit is somewhat larger than the ratio of Fe^4 to Fe^{3+} determined by chemical analysis.

This observed center shift for Fe^{4+} is in the right direction compared with those of Fe^{2+} and Fe^{3+}. However, if we assume the state $3d^4$ for Fe^{4+}, the estimate by Walker *et al.*[4] places the center shift well on the negative side. One possible cause for the discrepancy may be the nature of the environment of the Fe^{4+} ions in this compound. The paramagnetic susceptibility measurements by Clevenger[18] gave an effective moment of $8.05\mu_B$ compared with the calculated value of $5.17\mu_B$. The suggestion was advanced that this might be a result of the preferential alignment of Fe^{3+}, caused by some electron exchange mechanism between Fe^{3+} and Fe^{4+}. Though there is no concrete evidence for this model at present, magnetic measurements on the present sample of $SrFeO_3$ reveal that there is some field dependence of moment (also found by Waugh[17]) such that the familiar expression $\sigma=\sigma_0+\chi H$ holds, where σ_0 is a weak, spontaneous moment, in this case around 0.4 emu/g over the range 80°K to room temperature. Without making allowance for this parasitic moment, a moment of $8.2\mu_B$ is obtained at 10,000 oe, but if deducted a value of $4.8\mu_B$ is found, which is much more consistent with the assumption of a simple paramagnetic $3d^4$ state. Of course, the presence of a weak moment may in itself be the result of some sort of electron exchange, but the possibility of a trace of ferromagnetic impurity must not be overruled.

Thus, owing to the nonstoichiometric nature of the substance, the value of the observed isomer shift may not be typical of the $3d^4$ state and should be accepted with some reservation.

FeO

The nonstoichiometric properties of this compound have been investigated in detail.[19–21] The compound has a rock-salt type structure but always has a cation deficiency to an extent determined by the conditions of preparation. This implies that some of the iron is in the Fe^{3+} state. A preliminary study by Wertheim of this compound by Mössbauer measurements[10] revealed two peaks which were assigned to Fe^{3+} and Fe^{2+}, respectively, since the cubic symmetry of FeO was assumed to eliminate quadrupole splitting as a possible interpretation. Our re-examination of several FeO compositions reveals that in addition to the existence of Fe^{3+}, Fe^{2+} ions exhibit a quadrupole splitting even when the over-all symmetry of the crystal is cubic.

Two compositions in the Wüstite field established by Darken and Gurry[20] were initially selected, $Fe_{0.94}O$ and $Fe_{0.91}O$. These were prepared by firing Fe and Fe_2O_3 in the form of compacted disks in evacuated silica tubes at 1000°C, followed by rapid quenching in water. Chemical analysis figures for ferrous and total iron content gave the actual compositions as $Fe_{0.941}O$ and $Fe_{0.915}O$. The lattice parameters, 4.306 A and 4.295 A, respectively, were in good agreement with those of Jette and Foote[19] and Foster and Welch.[21] However, there was considerable line broadening on the x-ray pattern and the high-angle lines were not resolved into doublets. This, together with the Mössabauer results, gave rise to some suspicion that the structure might have a small intrinsic distortion. However, by firing the starting materials in the form of a loose powder at 800°C, followed by quenching, a specimen of $Fe_{0.919}O$ was subsequently prepared with a cubic pattern having reasonably sharp lines and well-resolved doublets, and a lattice parameter of 4.297 A. The line broadening may thus be a result of internal lattice strains caused by the rather severe crushing and grinding process required in the former case.

The results for the three compositions are quite similar and are shown in Fig. 3 and Table II. First, there can be little doubt that the two observed peaks must be interpreted as a quadrupole splitting of Fe^{2+}, because their center gives a value of 1.2 mm/sec, the expected center shift for Fe^{2+}. The asymmetry of the curve near 0.35 mm/sec indicates an additional absorption due to Fe^{3+}. The solid curve in Fig. 3 is obtained by the superposition of the two Fe^{2+} peaks and one Fe^{3+} peak (at 0.35 mm/sec) in the ratio of 4:4:1, with $\Gamma=0.30$ mm/sec. Theoretical ratio for $Fe_{0.915}O$ is 4:4:1.7. This discrepancy should not be taken too seriously since the estimate of the Fe^{3+} content from the Mössbauer data is quite crude.

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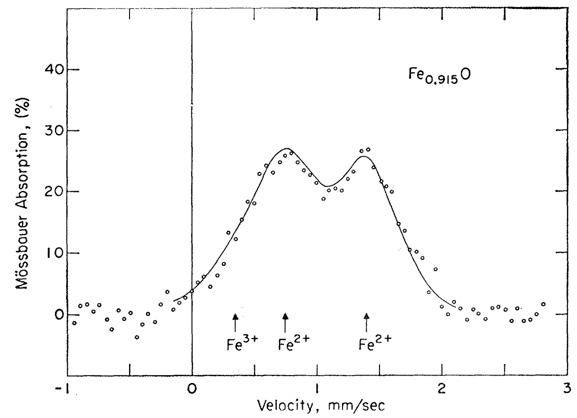

FIG. 3. Mössbauer absorption of $Fe_{0.915}O$. The solid curve is a superposition of 8 Fe^{2+} and 1 Fe^{3+} in the ratio of 4:4:1, with $\Gamma=0.30$ mm/sec.

The observed quadrupole splitting, $\epsilon=0.3$ mm/sec, is smaller than the value observed in $FeTi_2O_5$, but it is quite close to the value observed in $FeTiO_3$. This quadrupole splitting was an unexpected result because of the cubic symmetry of FeO. One possible explanation is that the symmetry of the crystal is not really cubic although the distortion is too small to be detected by x-ray techniques. The second, and more likely, explanation is that the cation vacancies remove *local* cubic symmetry at the Fe nucleus. In the composition $Fe_{0.915}$, 66% of the Fe ions have at least one vacancy somewhere among the twelve nearest neighboring metal positions, if the vacancies are distributed at random. Though the available data do not exclude the existence of Fe^{2+} with a single peak at 1.15 mm/sec, it may be concluded that at least two-thirds of the total Fe^{2+} shows the quadrupole splitting.

This model is in accordance with the observations that the quadrupole splitting is somewhat more clearly defined in $Fe_{0.919}O$ and $Fe_{0.915}O$ than in $Fe_{0.941}O$, which possesses less vacancies. This conclusion should be taken with some reservation because of the additional possibility of local lattice distortion caused by the quenching process in the course of the sample preparation.

TABLE II. Center shift, ΔE, and quadrupole splitting, ϵ, for several cubic iron compounds at room temperature. An estimated error is ±0.05 mm/sec.

Compound	Lattice parameter *a* (A)	ΔE (mm/sec)	ϵ (mm/sec)
$Fe_{0.941}O$	4.306	1.15	0.30
$Fe_{0.919}O$	4.297	1.15	0.34
$Fe_{0.915}O$	4.295	1.15	0.32
$(Fe_{0.75}Mg_{0.25})O$	4.298	1.15	0.32
$(Fe_{0.58}Mg_{0.42})O$	4.277	1.17	0.36
$(Fe_{0.20}Mg_{0.80})O$	4.239	1.20	0.34
$(Fe_{0.10}Mg_{0.90})O$	4.225	1.15	0.34

The quadrupole effect observed in FeO led us to the examination of the (Fe,Mg)O system, in which the compositions could be made virtually stoichiometric. As for FeO itself, it is of interest to examine the behavior of Fe^{3+} and Fe^{2+} ions below the Néel temperature at 198°K, especially in view of the model recently proposed by Roth.[22] Measurements are now under way and will be reported separately.

(Fe,Mg)O

The (Fe,Mg)O samples were prepared by heating Fe, Fe_2O_3, and MgO in evacuated silica tubes at temperatures between 700° and 1000°C, followed by rapid quenching. The compositions were determined by chemical analysis for ferrous and total iron content and are listed in Table II. X-ray patterns revealed a single cubic phase in each case, with lattice parameters as recorded in Table II. The parameters show a linear variation with composition and agree closely with the figures given by Jay and Andrews[23] and Petterson.[24] The $(Fe_{0.75}Mg_{0.25})O$ and $(Fe_{0.58}Mg_{0.42})O$ specimens were found to contain a trace of free iron by chemical tests, for which no correction has been made.

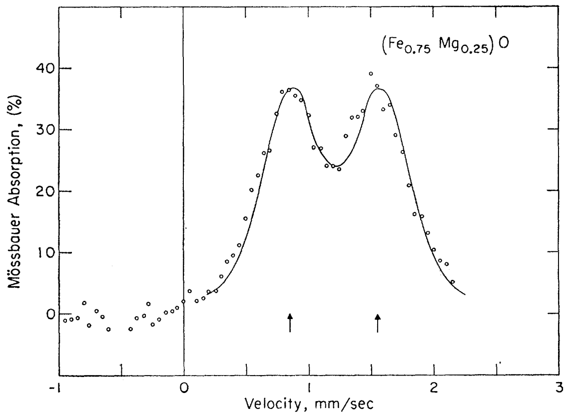

FIG. 4. Mössbauer absorption of $(Fe_{0.75}Mg_{0.25})O$. The solid curve is synthesized by assuming two peaks as indicated and $\Gamma=0.28$ mm/sec.

All of these materials exhibit well-defined quadrupole splitting with an almost constant ϵ of 0.35 mm/sec. Figure 4 shows the data for $(Fe_{0.75}Mg_{0.25})O$ together with the synthesized curve with $\Gamma=0.28$ mm/sec. The lower limit of Fe concentration at which the quadrupole effect disappears has not yet been determined.

These results, combined with the observations on FeO, indicate that a local disorder, caused either by vacancies or by different species of ions, is responsible for the quadrupole effect. A quadrupole effect in cubic

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crystals was previously observed by Kawamura *et al.*[25] in NaBr-NaCl mixed crystals by means of the nuclear resonance absorption of Na. One important feature of the present case is the fact that the splittings observed are almost independent of composition. This is in accordance with the suggestion by DeBenedetti *et al.*[5] that the field gradient at the Fe^{2+} nucleus is caused mainly by the ion itself. However, further study of the dependence of the quadrupole effect on composition as well as temperature is needed to shed more light on this problem.

IV. INTERNAL FIELDS IN α-Fe_2O_3 TYPE COMPOUNDS

The $(Fe,Cr)_2O_3$ and $(Fe,V)_2O_3$ systems have been the subject of a detailed magnetic and neutron diffraction investigation[26] and a few specimens were selected in an attempt to correlate the Mössbauer data with some of the magnetic and structural features.

Solid solutions of $(Fe,R)_2O_3$, (R=Al,Cr,V), were prepared by ignition of the respective oxide mixtures. In the case of the aluminum compound a wet method was used to give a more reactive starting mixture which was fired in oxygen at 1400°C. The final iron content was determined by analysis. The chromium compounds were obtained by heating the sesquioxides in air at 1300°C and the vanadium materials by firing the sesquioxides in evacuated silica tubes at 1000°C. The iron content was checked analytically in each case and was in close accordance with the nominal composition. The x-ray patterns were single phase, and lattice constants are listed in Table III. They agree very closely with published data.[27–31]

As the R_2O_3 content increases, the Néel temperatures decrease fairly rapidly and for the Cr_2O_3 and V_2O_3 series are below room temperature when the Fe_2O_3 content drops below about 30%. The transition temperatures are recorded in Table III.

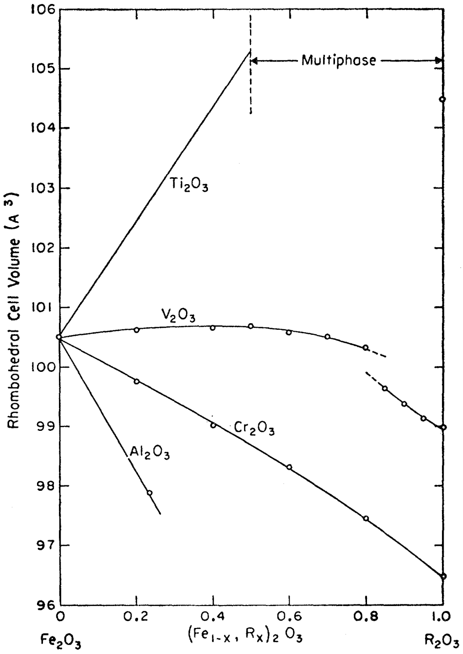

FIG. 5. Variation of unit cell volume with composition in the systems, $Fe_2O_3-R_2O_3$ (R=Ti, V, Cr, or Al).

The results of Mössbauer measurements for five solid solutions are summarized in Table III, together with the results for α-Fe_2O_3. From the center shift ΔE, there appears to be no doubt that the Fe ions are in the trivalent state in all of the compositions studied. This is to be expected for Al and Cr substitution but is somewhat surprising as far as the $(Fe,V)_2O_3$ system is concerned. Although the problem of clarifying the valency states in mixed oxides containing two or more $3d$ ions is generally difficult if not impossible, there is some slender chemical evidence which favors the combination $Fe^{2+}-V^{4+}$. The variation of unit cell volume with composition resembles the behavior of the $Fe_2O_3-Ti_2O_3$ system[32] rather than that of the $Fe_2O_3-Cr_2O_3$ system (Fig. 5) to the extent that there is a maximum at the mid-point. In both the latter cases the valency states are reasonably well-established; viz. $Fe^{2+}-Ti^{4+}$ and $Fe^{3+}-Cr^{3+}$. Moreover, this variation is consistent with the idea of substitution of an ion of a certain size (i.e., $Fe^{2+}+V^{4+}$ for $2Fe^{3+}$) up to the composition $FeVO_3$ followed by the substitution of an ion of a different size (i.e., $2V^{3+}$ for $Fe^{2+}+V^{4+}$) over the remainder of the system rather than a straightforward substitution of V^{3+} for Fe^{3+}, although the existence of a small miscibility gap complicates matters. The assumption of the $Fe^{2+}-V^{4+}$ state would also be in accordance with the value of about $2.6\mu_B$ for the average magnetic moment per mole of $(Fe_{0.5}V_{0.5})_2O_3$ calculated from neutron diffraction data. Finally, the ion-pair $Fe^{2+}-V^{4+}$ is certainly the stable combination in solution

TABLE III. Hyperfine field, H_i, in solid solutions based on α-Fe_2O_3. H_0 is the extrapolated value at 0°K.

Compound	Rhomobohedrat lattice parameters a (A)	α	T_N (°K)	ΔE (mm/sec)	ϵ	H_i (10^3oe)	H_0
Fe_2O_3	5.426	55° 17′	950	0.47	+0.20	520	535
$(Fe_{0.77}Al_{0.23})_2O_3$	5.372	55° 22′	810	0.47	+0.20	495	520
$(Fe_{0.5}Cr_{0.5})_2O_3$	5.384	55° 26′	470	0.47	+0.18	435	540
$(Fe_{0.2}Cr_{0.8})_2O_3$	4.981	55° 15′	155	0.50	(0.10)	···	···
$(Fe_{0.5}V_{0.5})_2O_3$	5.436	55° 05′	450	0.51	+0.22	430	540
$(Fe_{0.3}V_{0.7})_2O_3$	5.450	54° 44′	200	0.60	(0.10)	···	···

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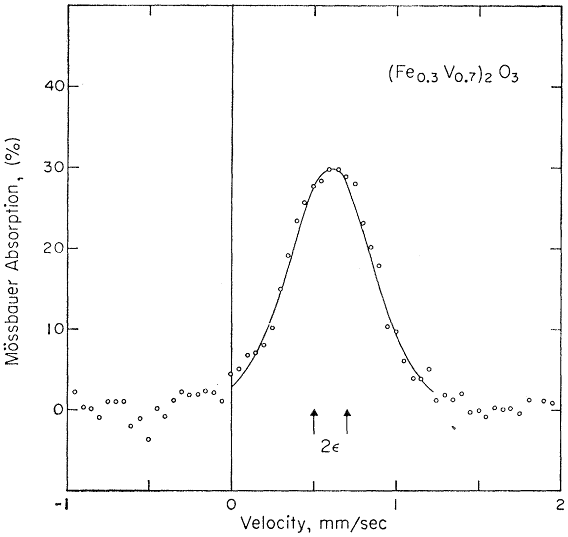

FIG. 6. Mössbauer absorption of $(Fe_{0.3}V_{0.7})_2O_3$. The solid curve represents a superposition of quadrupole doublet as indicated by arrow. ($\Gamma=0.25$ mm/sec.)

and a similar relationship frequently holds in the solid state.

The nonlinearity of the plot of lattice parameters against composition in spite of the simple substitution V^{3+} for Fe^{3+} can probably be attributed to the influence of direct interactions between V^{3+} pairs when the concentration of V^{3+} becomes fairly high, as suggested by Goodenough.[33]

A quadrupole effect in α-Fe_2O_3 was first observed by Kistner and Sunyar,[2] who estimated $\epsilon=-0.12$ mm/sec. Recently, Buchanan and Wertheim[34] have reexamined the effect, taking into account correctly the direction of the internal field with respect to the principal axis of the field gradient. Their result gives $\epsilon=+0.22$ mm/sec. Our estimates of the splittings for the compositions in the antiferromagnetic state, in which the spins are in the (111) plane as in α-Fe_2O_3, were made by using the table given by Parker[35] and are listed in Table III. For $(Fe_{0.3}V_{0.7})_2O_3$ and $(Fe_{0.2}Cr_{0.8})_2O_3$, which are paramagnetic at room temperature, the observed curve was in each case interpreted as the superposition of a closely spaced doublet. Figure 6 shows the synthesized curve for $(Fe_{0.3}V_{0.7})_2O_3$ with $\Gamma=0.25$ mm/sec and $\epsilon=0.1$ mm/sec. It should be mentioned, however, that an equally good fit can be obtained by assuming $\Gamma=0.30$ mm/sec and $\epsilon=0$ mm/sec.

The hyperfine fields for $(Fe_{0.77}Al_{0.23})_2O_3$, $(Fe_{0.5}Cr_{0.5})_2O_3$, and $(Fe_{0.5}V_{0.5})_2O_3$ are listed in Table III. The extrapolated fields at 0°K, H_0, obtained from the appropriate Brillouin functions, are also listed in the same table. Within this structurally similar family, it appears that the hyperfine fields, H_0, do not differ by much irrespective of the surroundings of the Fe ion.

This result is rather significant when taken in conjunction with the neutron diffraction observations.[26] These indicate that, although both $(Fe_{0.5}Cr_{0.5})_2O_3$ and $(Fe_{0.5}V_{0.5})_2O_3$ possess the α-Fe_2O_3 type of magnetic structure, the observed intensities at room temperature fall short of those expected on the basis of their average magnetic moments determined from the appropriate Brillouin function. The intensity deficiency is about 45% in each case, which corresponds to a decrease of 25% in the observed moment.

One possible explanation is that owing to the substitution of other ions in the Fe_2O_3 lattice, a certain fraction of the Fe^{3+} moments is tilted at random away from the magnetic axis in the (111) plane. Whether a particular moment is tilted and its direction will depend upon the cation distribution amongst its nearest neighbors. The moment calculated from neutron diffraction data is the average value of the component along the magnetic axis and is therefore reduced in size. However, the Mössbauer measurements reflect only the magnitude and not the component of the Fe^{3+} moment.

Alternatively, a second model may be considered in which the Fe^{3+} moments are aligned to the extent expected from a Brillouin function, but the substituted cations, Cr or V, are oriented more or less at random. The neutron diffraction results are in reasonable agreement with this model and the Mössbauer results are not affected as long as the Fe^{3+} moment is constant in a given sample.

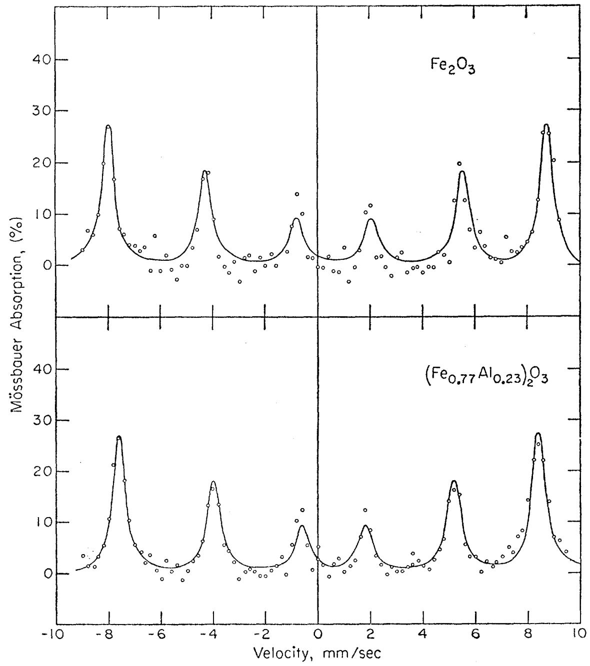

FIG. 7. Mössbauer absorption of α-Fe_2O_3 and $(Fe_{0.77}Al_{0.23})_2O_3$. The solid lines are synthesized with $\Gamma=0.30$ mm/sec and a peak ratio of 3:2:1.

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There is also, of course, the possibility that the apparently constant hyperfine fields are a result of compensating effects between the crystal structure and the actual Fe moment in the compositions investigated.

The $(Fe_{0.77}Al_{0.23})_2O_3$ composition was investigated with the specific purpose of examining whether line broadening occurred as a result of local fluctuations in the hyperfine field due to different numbers of nearest Fe neighbors. This effect was observed in the FeAl system[36] and is largest in the case of the two outermost peaks. The Al ion was selected because of its nonmagnetic nature. Figure 7 shows the observed and calculated absorption peaks for $(Fe_{0.8}Al_{0.2})_2O_3$ as well as Fe_2O_3. Both curves were calculated with $\Gamma=0.30$ mm/sec and a peak ratio of 3:2:1. The function $y=(1+x^2/\Gamma^2)^{-1}$ was utilized in order to ensure proper behavior at large x. Noticeable line broadening was not observed.

This result is in accordance with the model that the hyperfine field observed by the Mössbauer measurements is proportional to the moment at a given temperature, and not to the component of the moment along the magnetic axis. The latter may be affected by local fluctuations caused by the number of Fe neighbors but the moment itself retains the proper value for Fe^{3+}. In the metallic Fe—Al system, on the other hand, the moment is dependent upon the distribution amongst the nearest metal neighbors.

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Optical Spectrum of the Semiconductor Surface States from Frustrated Total Internal Reflections

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Through the use of multiple internal reflection and a modulation of the charge in the surface via the field effect, sufficient sensitivity is obtained to observe absorption of infrared radiation resulting from transitions involving the semiconductor surface states. This offers the possibility of obtaining the optical spectra and thus some rather direct information about the surface states. The principal other mechanism which contributes to the signal in this experiment is the free-carrier absorption arising from a modulation of the free-carrier density in the semiconductor space-charge region. The results of some observations on a silicon surface are discussed.

INTRODUCTION AND TECHNIQUE

INTERNAL reflection of radiation from a semiconductor surface is less than total because of absorption at the surface. A measure of this absorption can be used to monitor the free-carrier density in the semiconductor space-charge region[1] and to obtain the spectra of foreign molecules chemisorbed on the surface.[2] The purpose of this paper is to present evidence that absorption resulting from optical transitions involving the surface states can also be detected, hence the spectrum of the semiconductor surface states can be obtained from an analysis of internally reflected radiation. The importance of being able to obtain some very direct information regarding the surface states, as might be done from the optical spectrum, can be appreciated when it is recalled that in analyzing the results obtained from field effect and conductivity measurements, which have been so widely used to date, the number of parameters are increased and adjusted until agreement with experiment is obtained.

Because of the low density of the surface states,[3] manyfold increase of sensitivity must be obtained over conventional infrared spectroscopy in order to observe them. Figure 1(a) is a schematic diagram of the technique used in the present experiment where the required gain in sensitivity comes from two sources. Firstly, the use of multiple internal reflections serves to give a direct increase in signal strength.[2] Secondly, by modulating the population in the surface states through the use of an external alternating electric field, instead of chopping the infrared, it is possible to amplify only the change in the infrared intensity resulting from a change

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