JOURNAL OF SOLID STATE CHEMISTRY 6, 411–418 (1973)

Hyperfine Splitting of $^{57}Fe^{3+}$ Mössbauer Spectra in Diamagnetic Host Lattices

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Received June 15, 1972

The Mössbauer spectra of $^{57}Fe^{3+}$ substituted in 0.2 to 0.4 atom % of the octahedral sites in the host lattices $Na_{0.9}Mg_{0.45}Ti_{1.55}O_4$, TiO_2, Sc_2O_3, $LiScO_2$ and $MgAl_2O_4$ have been examined. Hyperfine splittings of the spectra were observed for all cases except Sc_2O_3. In all cases the electron spin resonance spectrum was found, or has been shown to be highly anisotropic as a result of the presence of strong axial or rhombic fields and consequent splitting of the $3d^5$ ground state energy levels. In several cases resolution of the ±5/2 and ±3/2 Mössbauer spectra was observed. Mössbauer spectra of the solid solutions $Na_{0.9}Mg_{0.45}Ti_{1.55}O_4$–$Na_{0.9}Fe_{0.9}Ti_{1.1}O_4$, $LiScO_2$–$LiFeO_2$ and TiO_2–$FeNbO_4$ have also been examined.

Introduction

The Mössbauer spectrum of Fe^{3+} in a diamagnetic or paramagnetic host lattice is typically a quadrupole-split absorption. However, when Fe^{3+} concentrations are low, and the time between successive flips of the $3d^5$ electronic spin states are comparable with, or longer than, nuclear precession times (0.5×10^{-8} sec), magnetic hyperfine structure (hfs) can be observed in the Mössbauer spectrum (*1–4*). In this case the *s*-electron density at the nucleus, and the effective field gradient there, is modified by the alignment of the $3d^5$ electron spin system with respect to the crystalline field, and frequently a six-line hfs spectrum is obtained which appears the same as that produced by a spin–spin alignment of the Fe outer electrons in ferromagnetic or antiferromagnetic materials such as Fe metal or Fe_2O_3. However, in the case of Fe^{3+} paramagnetic hfs, the ground state energy levels of the *S*-state $3d^5$ system can be split into three Kramer's doublets in the presence of a strong axial or rhombic field, and under conditions where all three pairs of energy levels, $M = \pm 5/2$, $\pm 3/2$, and $\pm 1/2$, are occupied, the interaction of each with the nuclear spin system of ^{57}Fe can, in principle, give rise to three superimposed hfs spectra. Resolution of the ±5/2 and ±3/2 spectra have been reported for several hosts (*1*, *5*, *6*) but the ±1/2 hfs is not usually resolved both because relaxation times within this doublet are shorter than those within the other two levels, and because in principle, the spectrum can consist of 11 rather weak peaks asymmetrically disposed (*1*, *2*, *5*). Ten of these peaks do however fall in doublets, and give an overall approximation to a six-line spectrum [Ref. (*2*), p. 187].

We have previously noted (*4*) a strong correlation between paramagnetic Mössbauer hfs and anisotropic electron spin resonance spectra, which also arise as a concomitant of the splitting of the Fe^{3+} ^6S ground state into Kramer's doublets. As these splittings result from crystalline fields strongly directed along specific crystal axes, we have examined the Mössbauer spectra of $^{57}Fe^{3+}$ in a number of host lattices containing such axes.

The present paper describes the results of this investigation, which included observations on the effects of temperature, Fe^{3+} concentration, and charge compensation.

Experimental Methods

Preparation of Compounds. The compounds examined were made by powder reactions at 1000°C for those containing sodium or lithium, and at 1200 to 1400°C for the remainder. Starting materials included sodium oxalate, lithium carbonate, Fe_2O_3, MgO, TiO_2 (anatase form), magnesium and aluminum sulfates and ammonium dichromate were all of analytical or Fisher Certified grade. Sc_2O_3, 99.5%, obtained through the courtesy of the Bureau of Mines, South Australia, was further purified by dissolution in hydrochloric acid, removal of iron by thiocyanate–methyl ethyl ketone treatment, and recovery as oxalate. $MgAl_2O_4$ was made from the sulfates, finely ground and heated at 1000°C before addition of ^{57}Fe, and finally heated at 1200°C. Nb_2O_5 used in the preparation of TiO_2–$FeNbO_4$ solid solutions was of 99.9% purity.

Introduction of ^{57}Fe. ^{57}Fe as a weighed quantity of metal was dissolved in 2 *N* nitric acid in a small standard flask. Precise volumes of this solution were then added to weighed quantities of prefired and finely ground compounds or compositions. After careful evaporation to dryness the preparations were heated to 400–600°C to decompose residual nitrates, finely ground and then heated either at 1000°C or 1200–1400°C. All preparations were reground and fired at least twice.

Mössbauer Spectra. The Mössbauer spectra were recorded on an instrument with a constant acceleration drive and multichannel analyzer storage of spectra as described previously (7). Temperatures were either taken as those of the coolant, i.e., liquid nitrogen, or measured with a calibrated thermocouple attached to the back of the specimen. Chemical shifts for ^{57}Fe are measured with respect to the center of the sodium nitroprusside doublet as zero and calibrated by a standard iron foil. In most cases the spectra were analyzed by a least squares computer program but for those cases which gave very poor spectra only visual estimates of the parameters were made.

Results

The oxide host lattices studied are listed in Table I. For low concentrations of Fe^{3+}, in otherwise iron-free host lattices, Fe enriched to 95% in ^{57}Fe was used to obtain sufficient intensity in the spectra. In such cases, 0.2 to 0.5% of the metal ions in the host lattice were substituted by Fe^{3+} ions. Except for Sc_2O_3, Mössbauer hyperfine structure was observed for Fe^{3+} in each of the host lattices shown in Table I. The results for each system are discussed in turn, and some general conclusions are made at the end of the paper. The Mössbauer data for all of the systems are summarized in Table II. In all cases, Fe^{3+} was in octahedral coordination.

$Na_{0.9}Fe_{0.9}Ti_{1.1}O_4$–$Na_{0.9}Mg_{0.45}Ti_{1.55}O_4$. The compound $Na_xFe_xTi_{2-x}O_4$, $0.9 > x > 0.75$ has an orthorhombic structure which is a rearrangement of that of calcium ferrite (*8*), with lattice parameters $a = 9.248$, $b = 2.973$, and $c = 11.344$ Å. The very short *b* axis length corresponds to an octahedral edge length, the structure repeating by edge sharing in the *b* direction, and by a combination of edge and corner sharing in the *a* and *c* directions. Sodium ions are contained in double channels between the strings of edge-shared octahedra directed along the *b* axis and occupy only 90% of the available crystallographic sites. We have recently found that $Na_{0.9}Mg_{0.45}Ti_{1.55}O_4$

TABLE I

OXIDE HOST LATTICES EXAMINED FOR Fe^{3+} MÖSSBAUER HYPERFINE SPECTRA

Compound or system	Crystal symmetry and structure type	Structural Ref.
$Na_{0.9}Fe_{0.9}Ti_{1.1}O_4$–$Na_{0.9}Mg_{0.45}Ti_{1.55}O_4$	Orthorhombic $Na_xFe_xTi_{2-x}O_4$	(*8*)
TiO_2	Tetragonal, rutile	(*9, 10*)
$FeNbO_4$–TiO_2	Tetragonal, rutile	(*11*)
Sc_2O_3	Cubic, C-rare earth	(*12*)
$LiScO_2$, $LiScO_2$–$LiFeO_2$	Tetragonal, distorted NaCl	(*13*)
$MgAl_2O_4$	Cubic, spinel	(*14*)

TABLE II

MÖSSBAUER DATA FOR $^{57}Fe^{3+}$ IN DIAMAGNETIC AND PARAMAGNETIC HOST LATTICES

Oxide system	Temp (K)	Isomer shift (mm/sec)	Quadrupole splitting (mm/sec)	Magnetic field (kG)
$Na_{0.9}Fe_{0.9}Ti_{1.1}O_4$/ $Na_{0.9}Mg_{0.45}Ti_{1.55}O_4$				
1:0	80	0.76	0.58	—
	295	0.64	0.57	—
0.5:0.5	80	0.75	0.56	—
	295	0.64	0.56	—
0.1:0.9	80	0.70	0.61	—
	295	0.63	0.59	—
0.4% ^{57}Fe	80	0.72	—	500[a]
	295	Very broad spectrum		
TiO_2				
0.2% ^{57}Fe	80	0.7[b]	0.45	—
		0.72	—	530
0.4% ^{57}Fe	80	0.60[b]	0.45	—
		0.84	—	530
$FeNbO_4/TiO_2$				
0.8:0.2	80	0.78	0.50	—
	295	0.67	0.50	—
0.5:0.5	80	0.78	0.47	—
	295	0.67	0.46	—
0.1:0.9	80	0.77	0.42	—
	295	0.66	0.46	—
0.4% ^{57}Fe NbO_4	80	0.78[b]	0.42	—
		0.72	—	510
	295	0.59[b]	—	—
^{57}Fe in Sc_2O_3				
	80	0.76	0.87	—
	295	0.61	0.85	—
$Li^{57}FeO_2$ in $LiScO_2$				
	80	0.58	0.3	530[a]
	295	Very broad spectrum		
^{57}Fe in $MgAl_2O_4$				
	80	0.53	—	510[a]
	295	0.55	—	~510

[a] Field due to the ±5/2 state.

[b] Resonance absorption in the central region of the spectrum.

is isostructural with $Na_xFe_xTi_{2-x}O_4$, with Mg^{2+} and Ti^{4+} randomized over the same set of octahedral sites as are Fe^{3+} and Ti^{4+}, and in the present work have established that the Fe^{3+} and Mg^{2+} compounds form a continuous solid solution series.

The structure is highly anisotropic, and for low concentrations of Fe^{3+} in the Mg end member, this leads as expected to a splitting of the ground state levels of the $3d^5$ system, as evidenced by a strong electron spin resonance signal found at $g' = 4.3$ rather than at $g' = 2.00$ (*4*, *9–11*).

For 0.4 atom % of $^{57}Fe^{3+}$ in $Na_{0.9}Mg_{0.45}Ti_{1.55}O_4$, magnetic hfs was also observed in the Mössbauer spectrum at 80 K, Fig. 1a, Table I. Although the spectrum was not well resolved it

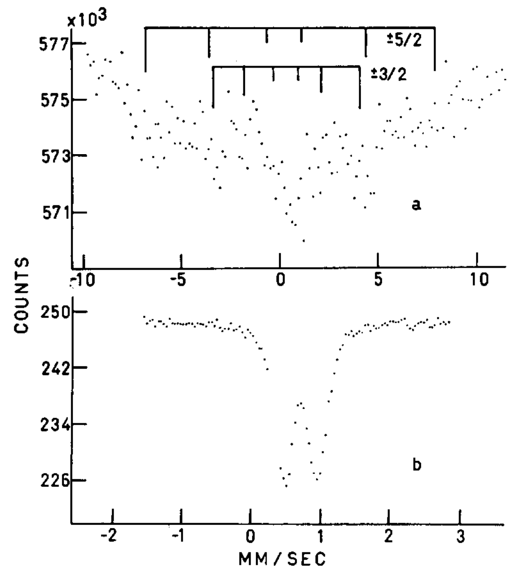

FIG. 1. Mössbauer spectrum at 80 K of (a) 0.4% ^{57}Fe in $Na_{0.9}Mg_{0.5}Ti_{1.55}O_4$; (b) 0.5 $Na_{0.9}Fe_{0.9}Ti_{1.1}O_4 \cdot 0.5$ $Na_{0.9}Mg_{0.45}Ti_{1.55}O_4$.

appears consistent with partial resolution of the ±5/2 and ±3/2 spectra; the ±1/2 spectrum being collapsed due to its more rapid relaxation rate and thus causing the build up in the center of the spectrum. As the Fe concentration was increased, the hfs spectrum collapsed, and was replaced by a single quadrupole-split absorption, Fig. 1b. This behavior is very similar to that observed in the series $NaScTiO_4$–$NaFeTiO_4$ (*4*), and is indeed general to all of the systems so far reported in the literature: as Fe^{3+} concentration increases above 1 or 2 atom %, dipole–dipole or superexchange interactions between Fe^{3+} ions, not necessarily next neighbors, lead to a sharp decrease in the relaxation time of the electronic spin states. At concentrations where nearest neighbor interactions predominate, the electron spin resonance spectra are also affected, and an absorption at $g' = 2$ characterizing exchange coupled Fe^{3+} pairs has been found to result (*9*). This ESR behavior has been observed for a number of oxide solid solutions containing Fe^{3+} (*4*) and was not further studied in the present series.

In the $NaScTiO_4$–$NaFeTiO_4$ series, the Mössbauer spectrum of $NaFeTiO_4$ at 4 K showed this compound to be magnetically ordered, and by analogy with isostructural $CaFe_2O_4$ it is presumably antiferromagnetic (*12*, *13*). However, at 80 K $Na_{0.9}Fe_{0.9}Ti_{1.1}O_4$ did not show a Mössbauer spectrum characteristic of magnetic ordering, and in a separate study neutron diffraction powder patterns showed no evidence of magnetic ordering at 4 K (*14*).

In $Na_xFe_xTi_{2-x}O_4$ the chains of edge-shared octahedra repeat in edge-shared groups of four, rather than in pairs as in $NaFeTiO_4$, and this structural difference has presumably led to a much greater degree of spin randomization.

TiO_2 and TiO_2–$FeNbO_4$ system. In the tetragonal rutile structure, metal–oxygen octahedra repeat by edge-sharing in the 2.9 Å *c* axis direction, and the resulting octahedral strings are each joined by corner sharing to four similar strings rotated through 90° with respect to the first. The local symmetry of each metal atom site is orthorhombic, D_{2h}, with the local symmetry axes of the two equivalent sites in each unit cell being mutually perpendicular. All atoms lie in one or other of the two planes which diagonally bisect the unit cell in its *c* axis direction. The strong axial field at each site results in a large zero-order splitting of the electronic ground state of Fe^{3+} ions substituted for Ti^{4+}, as demonstrated by their ESR spectra (*15*). Mössbauer observations by Alam, Chandra and Hoy (*16*) of Fe^{3+} in the TiO_2 lattice showed a rather poorly defined hfs at 300 K. A six-line spectrum due to interaction with the ±5/2 electronic state, together with a broad central line, was observed at 78 K. In the present work, examining 0.4 atom % of $^{57}Fe^{3+}$ in TiO_2, we find a well-defined hfs at both 80 and 295 K, with however a central doublet still remaining.

The spectrum observed for 0.2 atom % of $^{57}Fe^{3+}$, Fig. 2b, more closely resembles that reported by Alam, Chandra and Hoy (*16*). Alam, Chandra and Hoy report a quadrupole splitting of +0.25 mm/sec and a magnetic field of 554 ± 20 kg for 0.22% ^{57}Fe in TiO_2. Our spectra show no evidence in the magnetic spectrum for such a quadrupole splitting and we find magnetic fields of 530 kg for both the 0.4 and 0.2% concentrations.

Ti^{4+} ions in TiO_2 occupy half of the available octahedral sites in the hexagonal close-packed oxygen lattice. Fe^{3+} could either substitute for Ti^{4+}, thereby creating nearby oxygen vacancies, or occupy otherwise empty sites. In this latter case Fe^{3+} and Ti^{4+} ions will occupy face-shared octahedral sites, with a consequent increase in overall metal:oxygen ratio. At the low concentrations employed, local oxygen vacancies rather than the long-range ordering of face-shared sites observed in the reduced rutiles Ti_nO_{2n-1}, (*17*)

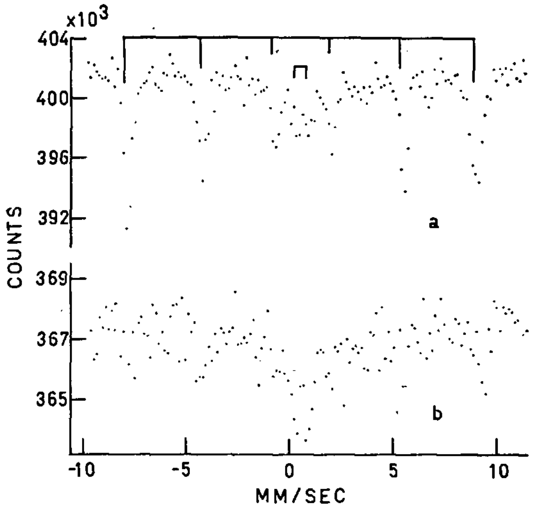

FIG. 2. Mössbauer spectrum at 80 K of (a) 0.4% ^{57}Fe in TiO_2; (b) 0.2% ^{57}Fe in TiO_2.

or their chromia substituted analogues $Cr_2Ti_{n-2}O_{2n-1}$ (*18–20*), appears more likely. Detailed examination of the ESR spectra of low concentrations of Cr^{3+} in rutile has shown (*21*) that the CrO_6 octahedra are complete, and that there appear to be oxygen vacancies at the second and third neighbor sites. Thus there is a strong ESR spectrum arising from CrO_6 octahedra with the site symmetry expected for the host lattice, together with weaker spectra having the symmetry expected from coupling to second and third neighbor vacancies. Uncompensated Fe^{3+} ions can be expected to reproduce a similar arrangement of vacancies, and the strong primary ESR spectrum of Fe^{3+} in rutile is certainly characteristic of intact FeO_6 octahedra with host lattice symmetry (*15*).

We have recently found (*22*) that TiO_2 forms continuous rutile-type solid solutions with $FeNbO_4$, even though $FeNbO_4$ has the rutile structure only above 1380°C (*23*). The Mössbauer effect is particularly sensitive to small interactions between the nucleus and the orbital electrons, and the spectrum of $^{57}Fe^{3+}$ compensated with Nb^{5+} in TiO_2, at composition $Ti_{0.992}Fe_{0.004}Nb_{0.004}O_2$, showed significant differences from that for uncompensated Fe^{3+}.

The relaxation time for compensated Fe^{3+} was also noticeably decreased, indicative of a higher local symmetry than in the uncompensated case. Wickman and Wertheim have calculated the shape of the hfs spectra for Fe^{3+} in polycrystalline absorbers [Ref. (*2*), p. 582, Fig. 11.10], and judging from the collapse of the hfs spectrum of the charge compensated Fe^{3+} to give a central peak with weaker outer lines, Fig. 3, the relaxation time is less than 2.5×10^{-9} sec at 295 K, compared with approximately 7.5×10^{-9} sec for uncompensated Fe^{3+}. The relaxation time is evidently sensitive to the presence of vacancies, and presumably also to their concentration and disposition. The variations in Fe^{3+} electron spin relaxation times reported for different samples of rutile (*24*) may well be due to differences in both the concentration and disposition of vacancies associated with Fe^{3+} in samples prepared under varying conditions.

SnO_2 also has the rutile structure, and the Mössbauer (*5*, *25*, *26*) spectra of uncompensated

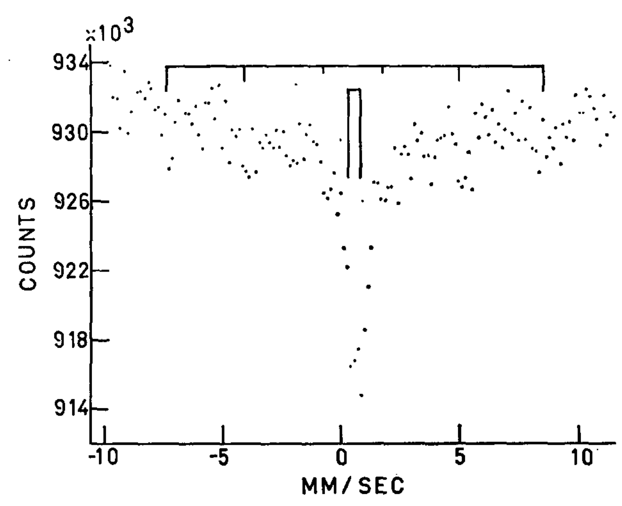

FIG. 3. Mössbauer spectrum at 80 K of 0.4% ^{57}Fe NbO_4 in TiO_2.

Fe^{3+} in this host recently have been reported. As expected for this structure, Mössbauer hyperfine structure was observed at low Fe^{3+} concentrations, with resolution of the spectra arising from the ±3/2 and ±5/2 spin states. The ESR spectra were similar to those observed for Fe^{3+} in TiO_2.

Sc_2O_3. Sc_2O_3 has the C-rare earth oxide structure (*27*) and thus contains Sc atoms in two different crystallographic sites. These comprise distorted octahedra derived from the eightfold cubic coordination of fluorite-type structure by omission of two oxygen atoms from cube corners—in one case from opposite ends of a body diagonal leading to 3-fold axial symmetry, and in the other from opposite ends of a face diagonal, leading to rhombic local symmetry.

Although the ESR spectrum of 1% of Fe^{3+} substituted for Sc^{3+} in Sc_2O_3 lattice showed a number of strong absorptions extending over a wide range of apparent *g* values, and attributable to splitting of the Fe^{3+} ground state levels by strong axial and rhombic fields, the Mössbauer spectrum did not show hyperfine structure (Table II) presumably because of very short relaxation times.

$LiScO_2$. $LiScO_2$ is tetragonal, with $a = 4.183$, $c = 9.318$ Å (*28*) and an arrangement of metal and oxygen atoms which is based on that in the rocksalt structure. However Li and Sc atoms are ordered into parallel double rows which extend through the structure in one of the *a* axis directions. Three nonequivalent twofold axes intersect at each metal atom site, and a rhombic crystal field should thus be evident at these sites. The ESR spectrum of 1% of Fe^{3+} substituted for Sc^{3+} in $LiScO_2$ showed a very strong signal at $g' = 4.3$, indicating that in fact the rhombic spin Hamiltonian parameters D and E were close to the limiting ratio (*10*, *11*, *27*) of $E/D = 1/3$. Similar ESR spectra have been reported for Fe^{3+} in a number of host lattices (*4*, *9*). As expected from this result, the Mössbauer spectra showed a well-resolved contribution from the ±5/2 state and partial resolution of the ±3/2 state. At 295 K a much poorer spectrum was obtained (Fig. 4b) with the ±5/2 spectrum barely discernible. The Mössbauer spectrum of the $LiFeO_2$ polymorph which is isostructural with $LiScO_2$ has been found to show a magnetic hyperfine splitting arising from antiferromagnetic spin-ordering (*29*). Intermediate concentrations, e.g., $LiSc_{0.9}Fe_{0.1}O_2$, gave only a simple quadrupole-split absorption, as was similarly the case for a number of other Fe^{3+} containing solid solutions which exhibited hfs at very low and very high Fe^{3+} concentrations (*4*). A small quadrupole splitting was noted in the hyperfine spectrum.

$MgAl_2O_4$. In the spinels $MgAl_2O_4$ and $MgFe_2O_4$, Mg^{2+} occupies tetrahedral sites and Al^{3+} or Fe^{3+} occupy octahedral sites. It can be expected that Fe^{3+} substituted at low concentrations for Al^{3+} in $MgAl_2O_4$ will also occupy octahedral sites exclusively. The strong axially directed crystal fields which the Al^{3+} atoms, or Fe^{3+} substituted for them, experience in the octahedral sites of the spinel structure lead to pronounced splitting of Fe^{3+} ground state levels,

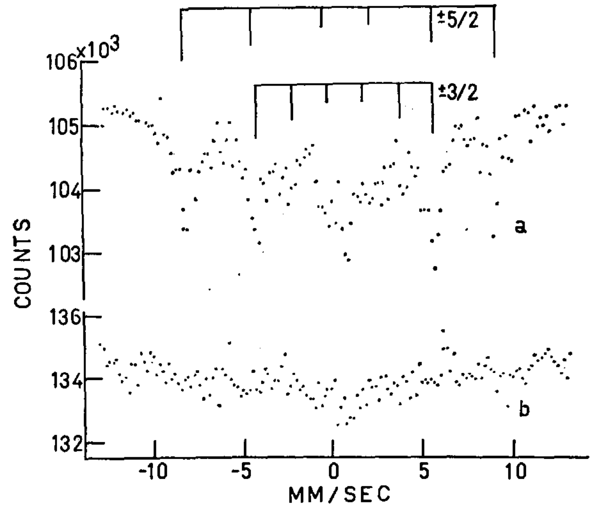

FIG. 4. Mössbauer spectrum of Li $^{57}FeO_2$ in $LiScO_2$ at (a) 80 K; (b) 295 K.

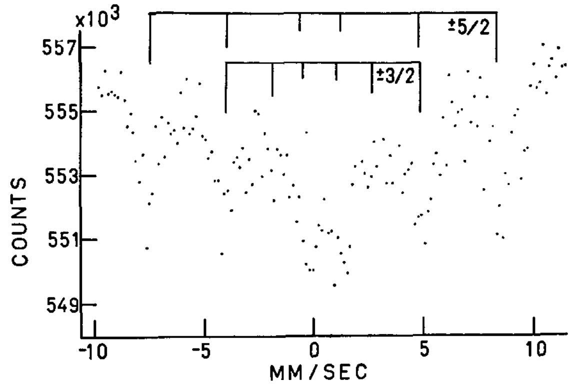

FIG. 5. Mössbauer spectrum of ^{57}Fe in $MgAl_2O_4$ at 80 K.

as the ESR spectra show (*30*). This strong field leads to partially resolved hyperfine structure in the Mössbauer spectrum of Fe^{3+} in spinel, Fig. 5 and Table II. Despite the low counting statistics due to the low concentrations of Fe^{3+} employed, partial resolution of superimposed hfs due to both ±3/2 and ±5/2 electronic states is evident. One also notes (Fig. 5) that there is little build up in the central region of the spectrum suggesting that even the ±1/2 state may have been partially resolved. In $MgFe_2O_4$, an incompletely inverted spinel, both tetrahedral and octahedral sites contain Fe^{3+}, and the associated antiferromagnetism causes hyperfine splitting for both sites (*31*).

Discussion

The present examples, Table II, and a number previously discussed [Refs. (*1–5*, *32–37*)] show that nuclear hyperfine structure (hfs) can be obtained for paramagnetic $^{57}Fe^{3+}$ in a variety of host lattices. The requirements for the observation of this phenomena are that the spherical symmetry of the $3d^5$ electron spin system is reduced by crystalline fields sufficiently strong to split the ground state levels into discrete Kramer's doublets, and that the relaxation time of the individual spin states ±5/2, ±3/2 and ±1/2 are sufficiently long, specifically, greater than $\sim 10^{-8}$, the nuclear precession time. The ±5/2 state often has a sufficient lifetime, but the ±3/2 and particularly the ±1/2 states have such short relaxation times that hyperfine spectra due to them are seldom observed.

Splitting of the $3d^5$ ground state into Kramer's doublets necessarily results in electron spin resonance spectra containing transitions among these doublets, and anisotropic ESR spectra will always be observable in situations where nuclear hyperfine structure can be observed in the Mössbauer spectra. However, as the magnetic field at the nucleus arises mainly from the polarization of the *s*-electrons by unpaired $3d^5$ electrons, an effect which depends on the spatial configuration of the $3d$ system and the net spin alignment with respect to the crystal field, the actual value of the Kramer's doublet separations has little direct effect on the internal magnetic field. For the ±5/2 state, where all five spins are parallel, in all of the examples so far observed, the internal field is ~500 kG, even though the Kramer's doublet separations vary widely in the range 0.08 to 1 cm^{-1} (*3*, *9–11*, *15*, *25*, *26*). Much the same internal field value is also observed for the single six-line hfs spectrum occurring in typical antiferromagnet Fe^{3+} oxides, e.g., $LiFeO_2$ (*29*), Fe_2O_3 (*6*), $LiFeTiO_4$ (*4*) and $MgFe_2O_4$ (*31*).

It is evident that the primary effect of the crystal field in producing observable nuclear hfs is to align the $3d^5$ spin system in one configuration or another for a sufficiently long period. Qualitatively, the stronger the crystal field the more firmly the $3d^5$ system is "locked" in a particular configuration, and the more the relaxation time is increased. This concept appears to be borne out in the present studies, but a detailed investigation of calculated crystal field, observed Kramer's doublet separations and associated spin-relaxation times would be necessary to establish whether a real functional dependence exists among these parameters.

The necessity for an anisotropic local crystal field for production of nuclear hfs Mössbauer spectra implies that in general an electric field gradient should also occur at the nucleus and quadrupole coupling should therefore also result. Such an effect was noticeable for $^{57}Fe^{3+}$ in $LiScO_2$ (Table II), but may of course often be obscured by the lack of resolution of the spectra and the relatively small size of the effect.

Acknowledgments

The authors are indebted to Mrs. C. Li for skilled experimental assistance, and to Mr. F. Looney, Division of Applied Chemistry, CSIRO for assistance in obtaining the ESR spectra. The N.R.C. of Canada is thanked for financial support.

References

1. G. W. Wertheim and J. P. Remeika, *Phys. Lett.* **10**, 14 (1964).
2. "Chemical Application of Mössbauer Spectroscopy," Eds. R. H. Herber and V. I. Goldanskii, Academic Press, New York, 1968: (a) J. Danon, Chap. 3; (b) V. I. Goldanskii and E. F. Makarov, Chap. 1; (c) H. H. Wickman and G. K. Wertheim, Chap. 11.
3. I. Campbell and S. Debenedetti, *Phys. Lett.* **20**, 102 (1966); *Phys. Rev.* **167**, 556 (1968).
4. T. Birchall, N. N. Greenwood, and A. F. Reid, *J. Chem. Soc. A* 2382 (1969).
5. V. G. Bhide and S. K. Date, *Inorg. J. Nucl. Chem.* **31**, 2397 (1969).
6. O. C. Kistner and A. W. Sunyar, *Phys. Lett.* **4**, 412 (1960).
7. T. Birchall, *Can. J. Chem.* **47**, 1351 (1969).
8. W. G. Mumme and A. F. Reid, *Acta Crystallogr. B* **24**, 625 (1968).
9. A. F. Reid, H. K. Perkins, and M. J. Sienko, *Inorg. Chem.* **7**, 119 (1968).
10. H. H. Wickman, M. P. Klein, and D. A. Shirley, *J. Chem. Phys.* **42**, 2113 (1965).
11. R. D. Dowsing and J. F. Gibson, *J. Chem. Phys.* **50**, 294 (1969).
12. Y. Allain, B. Boucher, P. Imbert, and M. Perrin, *C. R. Acad. Sci. Ser. B* **263**, 9 (1966).
13. E. F. Bertaut, J. Chappert, A. Apostolov, and V. Semenov, *Bull. Soc. Fr. Mineral. Cristallogr.* **89**, 206 (1966).
14. T. M. Sabine, private communication.
15. D. L. Carter and A. Okaya, *Phys. Rev.* **118**, 1485 (1960).
16. M. Alam, S. Chandra, and G. R. Hoy, *Phys. Lett.* **22**, 26 (1966).
17. S. Anderson, B. Collen, U. Kuylenstierna, and A. Magnéli, *Acta Chem. Scand.* **11**, 1641 (1957).
18. S. Anderson, A. Sundholm, and A. Magnéli, *Acta Chem. Scand.* **13**, 989 (1959).
19. L. A. Bursill, B. G. Hyde, and D. K. Philp, *Phil. Mag.* **23**, 1501 (1971).
20. O. W. Flörke and C. W. Lee, *J. Solid State Chem.* **1**, 445 (1970).
21. M. Ikebe, Y. Miyako, and M. Date, *J. Phys. Soc. Jap.* **26**, 43 (1969).
22. C. Li and A. F. Reid, unpublished data.
23. R. S. Roth and J. L. Waring, *Amer. Mineral.* **49**, 242 (1964).
24. G. J. Lichtenberger, *Can. J. Phys.* **47**, 1573 (1969).
25. W. J. Nicholson and G. Burns, *Phys. Rev.* **129**, 2490 (1963).
26. G. Sperlich, *Z. Naturforsch. A* **23**, 1967 (1968).
27. T. Castner, G. S. Newell, W. C. Holton, and C. P. Slichter, *J. Chem. Phys.* **32**, 688 (1960).
28. C. J. M. Rooymans, *Z. Anorg. Allg. Chem.* **313**, 234 (1961).
29. D. F. Cox, G. Shirane, P. A. Flinn, S. R. Ruby, and W. J. Takei, *Phys. Rev.* **132**, 1567 (1963).
30. E. Brun, H. Loeliger, and F. Waldner, *Arch. Sci.* **14**, 167 (1961).
31. V. Gonser, H. Wiedersich, and R. W. Grant, *J. Appl. Phys.* **39**, 1004 (1968).
32. L. M. Epstein and A. Wachtel, *Appl. Phys. Lett.* **10**, 246 (1970).
33. H. H. Wickman and G. K. Wertheim, *Phys. Rev.* **148**, 211 (1966).
34. A. J. Nozik and M. Kaplan, *J. Chem. Phys.* **49**, 4141 (1968).
35. G. Lang and W. T. Oosterhuis, *J. Chem. Phys.* **51**, 3608 (1969).
36. A. M. Afanas'ev and Y. M. Kagan, *JETP Lett.* **8**, 382 (1968).
37. H. Schwegler, *Phys. Status Solidi* **41**, 353 (1970).