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Mössbauer Effect for Fe^{57} in Ferroelectric $BaTiO_3$. II. The Vacancy-Impurity Associated State

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In the study of ferroelectric $BaTiO_3$ using the Fe^{57} Mössbauer probe, a variety of environments are encountered by the impurity probes. Velocity spectra have been analyzed to show that the Ti^{4+} substitution by the probe $(Co^{57})^{2+} \rightarrow (Fe^{57m})^{3+}$ or stable $(Fe^{57})^{3+}$ results generally in localized charge-compensating oxygen vacancies. Polarization experiments show that the impurity-vacancy complexes are rotatable. The oxygen vacancies are believed to be of the axial type (OI oxygens) in tetragonal $BaTiO_3$. Large nonstoichiometry in reduced samples has been shown to induce an Fe^{2+} state.

I. INTRODUCTION

In an earlier paper[1] (hereafter referred to as I), we have demonstrated the efficacy of the Mössbauer effect in the study of ferroelectric $BaTiO_3$. Such a study can, in principle, be made either by employing a Co^{57}:$BaTiO_3$ source or a Fe^{57}:$BaTiO_3$ absorber. In both these systems the impurity ions, Co^{2+} and Fe^{3+}, substitute for Ti^{4+} ions,[2] producing simultaneously charge-compensating, oxygen vacancies. An important aspect concerning the impurity substitution is the spatial distribution of these vacancies. Earlier investigations on the ferroelectric perovskites $BaTiO_3$,[3] $PbTiO_3$,[4] and $SrTiO_3$,[5] have not yielded any definite evidence for localized charge compensation when divalent or trivalent transition-metal ions replace the tetravalent titanium ions. Recently, however, Kirkpatrick *et al.*[6] have identified the strong axial EPR spectrum in cubic Fe^{3+}:$SrTiO_3$ as originating from the Fe^{3+}-vacancy pairs.

In I, it has been shown that if Co^{57}:$BaTiO_3$ crystals are heated in air at elevated temperatures and then suddenly quenched, a majority of the Mössbauer probes see nearly perfect-lattice local environment and reflect the true crystalline electric field gradient (EFG) normally experienced by the Ti ions. If, however, the Mössbauer probes are associated with charge-compensating oxygen vacancies, then the EFG and also the s-electron density experienced by probes would be different. Indeed, the large quadrupole splitting observed for trivalent iron in oxide systems $La_{1-x}SrFeO_y$,[7] $BaFeO_{2.5-3.0}$,[8] and $SrFeO_{2.5-3.0}$[9] have been explained in terms of vacancy association. Evidence for the defect-pair association has also come through the Mössbauer study of Co^{57}:KCl,[10] Co^{57}:NaCl,[11] and Co^{57}:NaF systems.[12] It was therefore thought that the Mössbauer study of Co^{57}:$BaTiO_3$ systems which are differently heat-treated might give some evidence for the impurity-vacancy association in these systems. The results reported here for slow-cooled, air-fired, and hydrogen-fired Co^{57}:$BaTiO_3$ sources as well as for Fe^{57}:$BaTiO_3$ absorbers suggest the formation of impurity-vacancy complexes.

II. EXPERIMENTAL AND GUIDE LINES FOR THE IDENTIFICATION OF SPECTRA

Four Co^{57}-doped $BaTiO_3$ single-crystal sources were prepared in the manner described in I. Two of these were annealed in air at 1150°C for 4 h and then slow-cooled to room temperature over a period of 12 h. The other two sources were heated at 1000°C for 30 min in hydrogen and then slow-cooled. The reducing atmosphere produced crystals with deep red coloration, $T_c \simeq 110°C$ and a peak value of the dielectric constant at T_c rising by a factor of 2 over the room-temperature value of 1800.

$BaTiO_3$ absorbers containing 1–5 mole percent of iron were prepared following the usual ceramic techniques, the starting materials being C.P. Grade $BaTiO_3$ and Fe_2O_3. For one of the samples Fe^{57}-enriched Fe_2O_3 was used. As reported by Nishioka *et al.*[13] the Curie temperature of these absorbers was found to decrease with increasing iron content, with the result that the 5% composition was cubic at room temperature.

Velocity spectra were obtained using the mechanical drive and the associated electronic described in I. The

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* Work supported by the National Bureau of Standards, Washington, D. C.

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TABLE I. Experimentally determined and computed EFG, V_{zz} (in 10^{14} esu cm^{-3}) for trivalent iron nuclei.

Heat treatment of Co^{57}:$BaTiO_3$	Probable probe environment	Computed lattice-sum for[a]		Experimental[b]
		100% ionicity	60% ionicity	
Heating in air followed by quenching	Perfect	−0.457	−0.513	−0.52
Heating in air followed by gradual cooling	OI(z or u)[c]	2.873	2.050	
	OI vacancy			1.25
	OI($-z$ or l)[c]	1.636	0.406	
Heating in hydrogen atmosphere	OI or OII or both types of vacancies. Also, possibility of electron-trapped oxygen-deficient sites.[d]	Estimates impossible since material is expected to be highly nonstoichiometric.		−0.89

[a] Computed from the lattice sums of monopoles and dipoles in a unit-cell-shaped volume measuring 10 lattice parameters along the respective cell edges.
[b] Computed from $\Delta E=\frac{1}{2}e^2(1-\gamma_\infty)qQ_{Fe^{57m}}$ with $\gamma_\infty=-9.14$ and $Q_{Fe^{57}}=0.18$b.
[c] See Fig. 4 in Ref. 1.
[d] Yu. L. Danilyuk and E. V. Kharitonov, Fiz. Tverd. Tela **6**, 322 (1964) [English transl.: Soviet Phys.—Solid State **6**, 260 (1964)].

spectra, in general, were rather complicated because of the possible existence of *Auger-electron-produced* charge states and/or the different local (vacancy-associated and perfect-lattice) environments of the probes. The procedure for curve analysis was similar to that reported in I. The resolved curves were identified with the aid of the systematics of isomer shift.[14] The computation of the crystal-field gradient at the Ti^{4+}-replaced Fe^{3+} ion was also qualitatively useful in the assignment of the spectra. Table I lists some values for $\mathbf{V}_{zz}$ at the impurity nucleus associated with different types of charge-compensating defects, it being obvious that any environment below T_c would produce a quadrupolar splitting. Such an analysis for Fe^{2+} ions is not useful because the $Fe^{2+}(3d^6)$ state is not spherically symmetric and hence carries with it its own field gradient which is difficult to compute. The temperature variation of the spectra gave a further clue as to whether the Mössbauer probe is in perfect-lattice local environment or is influenced by the charge-compensating vacancy.

A further check on the assignment of the spectra and particularly on the computed sign of $\mathbf{V}_{zz}$ was obtained through the orientation and polarization experiments. Assuming the isotropy of the Lamb-Mössbauer factor, the ratio of the intensities of the two components $I(\pi)$ and $I(\sigma)$ of the quadrupole-split spectra is given by[15,16]:

$$R=I(\pi)/I(\sigma)=(1+u^2)/(5/3-u^2)\,, \qquad (1)$$

where $u\equiv\cos\theta$, θ being the angle between the emission direction and the principal EFG axis, V_{zz}. If, however, the Lamb-Mössbauer factor is anisotropic, then the ratio R for the random orientation of the crystallites (with the assumption of a harmonic approximation) is given by

$$R=\frac{\int_0^1 (1+u^2)\exp(-\epsilon u^2)du}{\int_0^1 (5/3-u^2)\exp(-\epsilon\mu^2)du}\,, \qquad (2)$$

where $\epsilon=k^2[\langle z^2\rangle-\langle x^2\rangle]$, $\mathbf{k}$ is the gamma-ray wave vector, and $\langle z^2\rangle$ and $\langle x^2\rangle$ are the mean-square amplitudes of the nuclear displacements along the perpendicular to V_{zz}. Small but measurable difference in these two displacements have been reported for Fe^{57} in graphite and iron-organic complexes and for Sn^{119} in tin-organic complexes.[16]

In tetragonal $BaTiO_3$, the Ti^{4+} vibrations are known to be anisotropic. From neutron-diffraction studies[17] it is seen that $\langle z^2\rangle=0.54\times10^{-18}$ cm^2 and $\langle x^2\rangle=0.86\times10^{-18}$ cm^2, so that $\epsilon=-0.16$. Flinn *et al.*[15] have evaluated the integrals in Eq. (2) for various values of ϵ and have given a plot of R against ϵ. Assuming that the Fe^{3+} probe has displacements similar to those of Ti^{4+}, we have $R=1.02$ for $\epsilon=-0.16$ indicating that $I(\pi)$ is just 2% stronger than $I(\sigma)$. This difference in the intensity is not measurable in our spectra.

Our $BaTiO_3$ single crystals were essentially c plates. But on diffusion of Co^{57}, it was found that the multiplicity of domains and with it the randomization of the V_{zz} axes increased. Consequently $I(\pi)$ and $I(\sigma)$ were almost equal. In ferroelectrics one can align the V_{zz} axes in the entire crystal by polarizing the crystal. On conversion of the crystal into a single-domain c plate, the ratio R is expected to change to 3:1 [Eq. (1)]. This result was helpful in identifying the quadrupole-split partners and also in determining the sign of V_{zz}.

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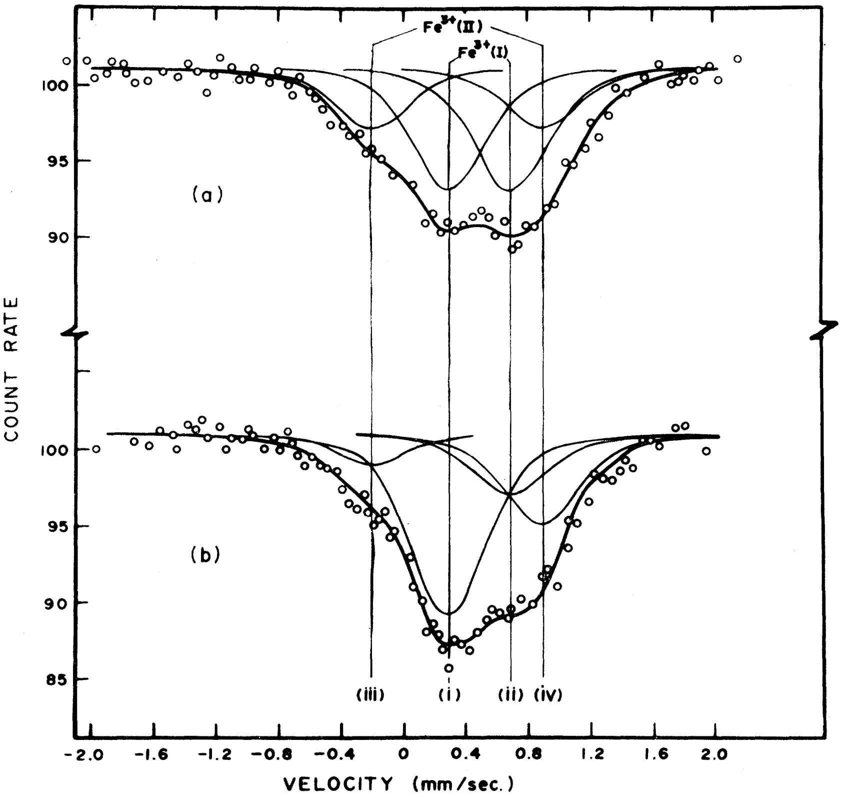

FIG. 1. Typical spectra for the air-fired, slow-cooled Co^{57}:BaTiO$_3$ source at room temperature. (a) Multi-domain single crystal (random distribution of the tetragonal *c* axes). (b) Crystal biased with a field of 5 kV/cm in the direction of detected gamma emission (crystal-face perpendicular).

The observed spectra along with the synthesized resonances are shown in Figs. 1–3. The data from these curves are summarized in Table II. It is to be noted that although the errors due to the imparted velocity and the counting statistics amounted to less than ±0.02 mm/sec, the uncertainty in the analyzed line positions was much more (generally ±0.05 mm/sec).

III. RESULTS

A. Slow-Cooled Air-Fired Samples

Two of the typical spectra obtained with slow-cooled air-fired Co^{57}:BaTiO$_3$ sources matched against 310 stainless steel are shown in Fig. 1. These spectra are quite complex and were analyzed following the guide lines indicated above. The composite spectra at room temperature in Fig. 1(a) are seen to be made up of four resonances, (i)–(iv), with resonances (i) and (ii) forming one quadrupole-split pair and (iii) and (iv) forming the other. Resonances (i) and (ii) are identified from the quadrupole splitting and center shift as due to Fe^{3+} experiencing perfect-lattice local environment as in I. An increase in temperature of the source results in the merging of these two resonances at and above T_c, thus confirming the assignment. The other pair, if regarded as a quadrupole-split spectrum, has the isomer shift $\delta = 0.34 \pm 0.05$ mm/sec, characteristic of Fe^{3+} state and an unusually large splitting $\Delta E = 1.12 \pm 0.05$ mm/sec, which persists even beyond T_c. On the application of an electric field 5 kV/cm along the crystal-face perpendicular, resonances (iii) and (iv) adjust to the intensity ratio of approximately 3:1, confirming the inference that they are the partners of the quadrupole-split spectrum. Further, it is seen that the component with higher energy corresponds to the transition $\pm(\frac{3}{2})_{ex} \rightarrow (\frac{1}{2})_{gd}$, indicating that ΔE is positive. The negative sign for the other pair checks with the earlier observations in I. The polarization experiments also enable us to infer that the principal EFG axis, V_{zz}, for both sites Fe^{3+}(I) [resonances (i) and (ii)] and Fe^{3+}(II) [resonances (iii) and (iv)] are directed along the tegragonal *c* axis and rotate with domain alignment. In view of the fact that the $(Co^{57})^{2+} \rightarrow (Fe^{57})^{3+}$ probes can occupy only the Ti^{4+} sites, the large ΔE at Fe^{3+}(II) site can be tentatively assigned to impurity-vacancy association. If the simple electrostatic computation of the EFG based on the lattice-sum method gives any indication—at least for the sign of V_{zz}—then the ΔE at Fe^{3+}(II) site can be ascribed to the axial or OI-type associated oxygen vacancy.

The low isomer shift for Fe^{3+}(II), $\delta = 0.34 \pm 0.05$ mm/sec, is understandable since a localized oxygen vacancy implies a reduction in the number of near-neighbor oxygens from 6 to 5. Consequently, there is a reduction in the electronic contribution to the 3*d* orbital of Fe^{3+}. Such a decrease in δ can also be inferred from

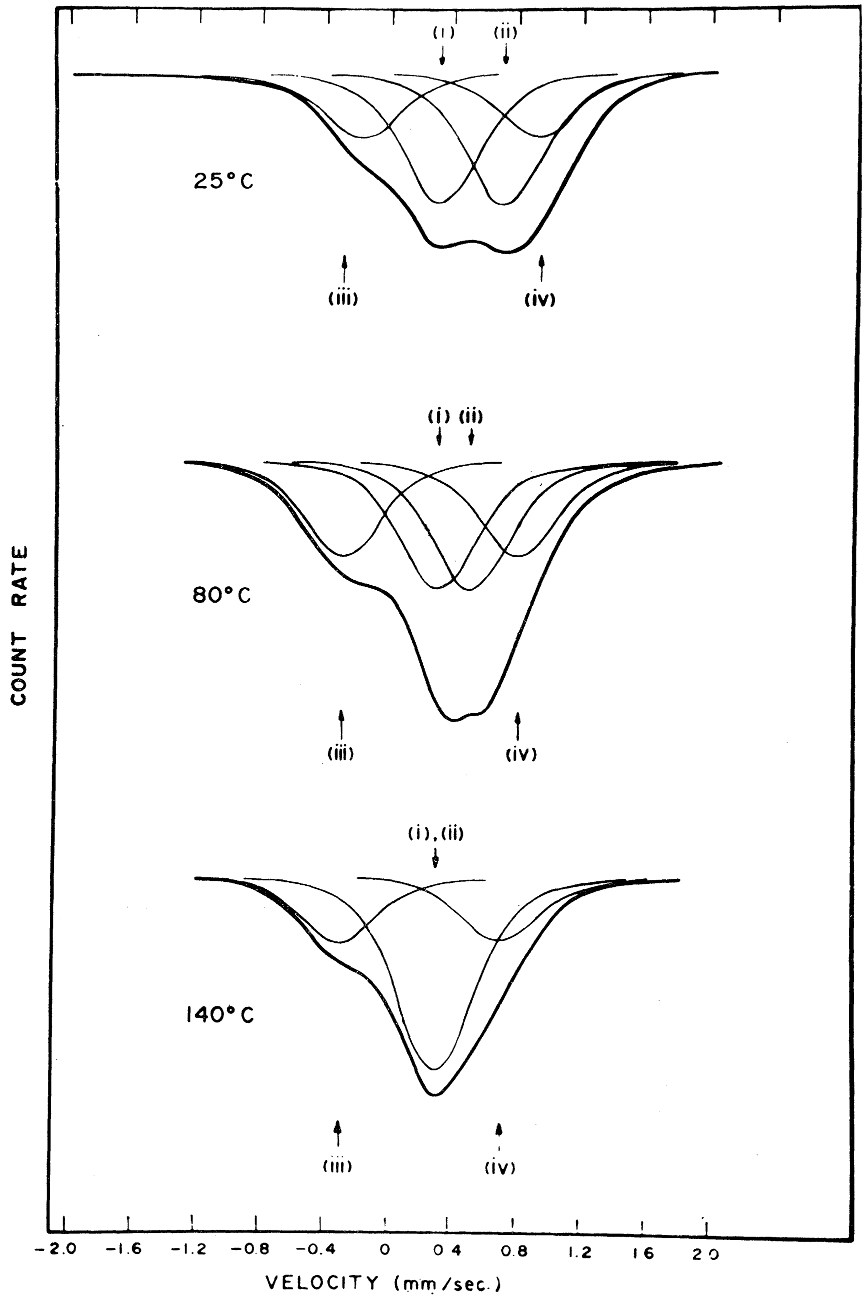

FIG. 2. Three Mössbauer resonances for the air-fired Co^{57}:$BaTiO_3$ source. The spectra indicate the merging of the inner two resolved components when the temperature is raised beyond the Curie point.

the observations of Shimony and Knudsen[7] and Gallagher *et al.*[8,9] for Fe^{3+} ion in the oxygen deficient perovskites, $SrFeO_{3-x}$ and $BaFeO_{3-x}$.

B. Slow-Cooled Hydrogen-Fired Sources

For these sources it was found that the spectrum shape depended sensitively upon the extent of the heat treatment. Figure 3(a) shows the composite spectrum and the synthesized resonances for a source which was biased with an electric field 5 kV/cm along the crystal-face perpendicular (which was also the direction of gamma detection). There are four resonances made up of two pairs with the intensity ratio of approximately 3:1, indicating that they are the two sets of quadrupole-split spectra. Figure 3(b) represents the spectra obtained with the same source but inclined so that the observed emission lies between 55° and 90° with respect to the crystal-face perpendicular. The intensities of the resonances adjust themselves because of the angular dependence of $I(\pi)$ and $I(\sigma)$ and aid in the identification of the spectra. On the basis of isomer shift they appear to be due to Fe^{3+} [resonances (i) and (ii)] and Fe^{2+}

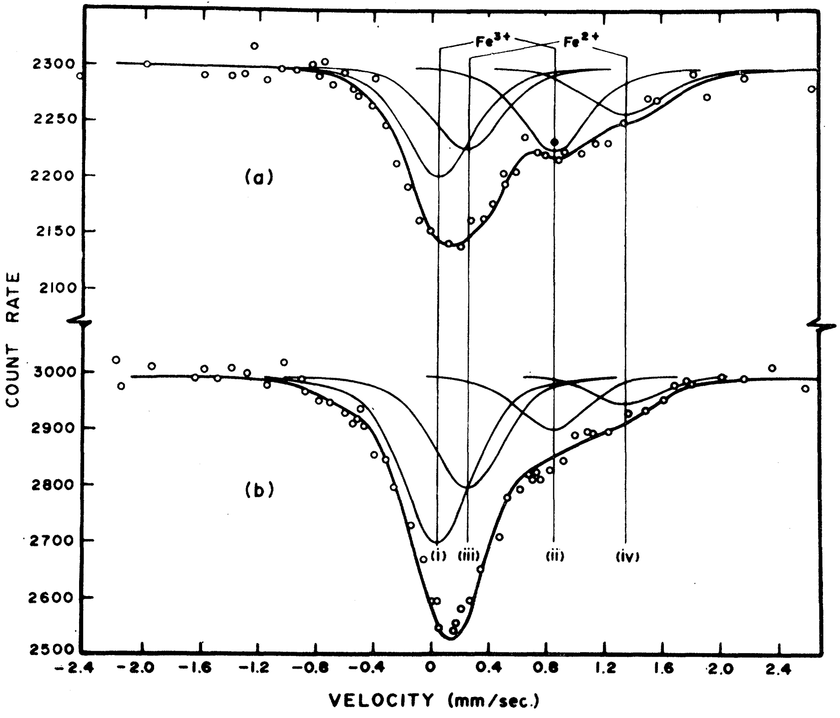

FIG. 3. Typical spectra for the hydrogen-fired Co^{57}:$BaTiO_3$ source. For these spectra the source was electrically biased with a field of 5 kV/cm along the crystal-face perpendicular. (a) Detected gamma emission 55° and 90° with respect to the face perpendicular. (b) Detected gamma emission along the face perpendicular.

[resonances (iii) and (iv)] states. Further, since the quadrupole splitting is found to persist beyond T_c, it seems that the Mössbauer probes are associated with neighboring vacancies. It is necessary to point out that since the intensities of the partners can be modified by the application of an electric field, V_{zz} axes seem to be along the crystal c axis and can be oriented together with the domains. It is perhaps of interest to note that the effect of the application of the electric field is maintained for quite some time after the field is removed.

It is of interest to examine whether the simultaneous observation of Fe^{2+} and Fe^{3+} spectra is due to the aftereffects of Co^{57} decay or to the possibility of Fe^{2+} and Fe^{3+} being the stable states in the highly reduced $BaTiO_3$ lattice. Although the intensities of Fe^{2+} and Fe^{3+} resonances are almost equal in the present case, they were found to be very sensitive to the duration of heating of samples in hydrogen. Indeed, for the untreated samples only the Fe^{3+} lines were observed whereas prolonged heating in hydrogen progressively reduced the Fe^{3+} intensity. This result compares well with EPR experiments for Fe^{3+} in $BaTiO_3$ wherein it is observed that continuous firing in hydrogen atmosphere causes a progressive disappearance of the Fe^{3+} spectrum.[3] For samples heated in hydrogen for different durations, the linewidths of Fe^{2+} and Fe^{3+} spectra were nearly equal. Wertheim and Guggenheim[12] have analyzed the limit of detectibility of nonequilibrium charge states and the corresponding linewidths. They have shown that the linewidth of the nonequilibrium charge state should be a function of the intensity since both the parameters are determined by the lifetime of the nonequilibrium state. It appears from these observations that Fe^{2+} and Fe^{3+} are the equilibrium charge states in the reduced $BaTiO_3$ samples. Evidence indicating that the impurity charge state depends upon the

TABLE II. Data from the velocity spectra of air-fired Co^{57}:$BaTiO_3$ and hydrogen-fired Co^{57}:$BaTiO_3$ sources matched against 310 stainless steel (in mm/sec).[a]

	Air-fired source (Fig. 1)				Hydrogen-fired source (Fig. 3)			
	Fe^{3+}(I)		Fe^{3+}(II)		Fe^{3+}		Fe^{2+}	
Resonance	(i)	(ii)	(iii)	(iv)	(i)	(ii)	(iii)	(iv)
Analyzed line positions	+0.28	+0.70	−0.22	+0.90	+0.04	+0.86	+0.26	+1.35
Isomer shift, δ	+0.49		+0.34		+0.45		+0.81	
Quadrupole splitting, ΔE[b]	−0.42		+1.12		−0.82		−1.09	

[a] The errors in δ and ΔE are ±0.05 mm/sec.

[b] The sign has been obtained from polarization experiments.

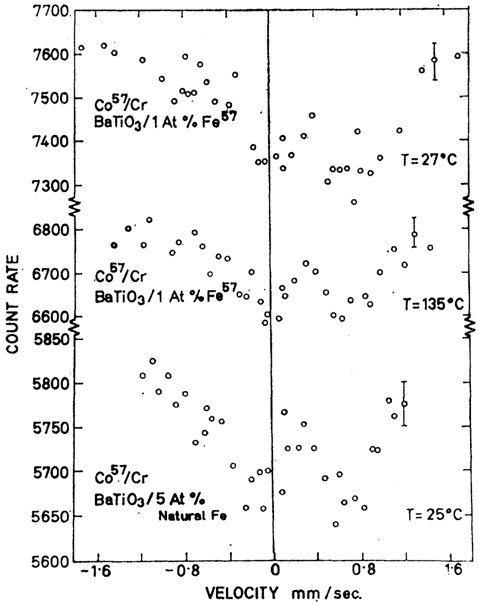

FIG. 4. Mössbauer spectra for iron-doped $BaTiO_3$ absorbers. The quadrupole splitting persists beyond the Curie temperature and also for the cubic 5-mole-percent composition.

local environment has been reported by Wertheim and Guggenheim[12] for Co^{57}:NaF and by Mullen[11] for Co^{57}:NaCl.

C. Fe^{57}:$BaTiO_3$ Absorbers

Three typical spectra obtained with iron-doped absorbers are shown in Fig. 4. All these correspond to Fe^{3+} quadrupole doublets. The quadrupole splitting persists even beyond T_c and is exhibited also by the 5% mole-percent composition which is cubic at room temperature. For 1 mole-percent composition the Mössbauer data, δ and ΔE, are closely similar to the Fe^{3+} data for hydrogen-fired Co^{57}:$BaTiO_3$ sources. It also agrees within experimental errors with that of Nicholson and Burns,[18] (who also resport the insensitivity of ΔE to impurity concentration). These results show that the ΔE values revealed by these sources are not due to the perfect lattice and are dominated by some sort of defect association. It is also of interest to point out that impurity-vacancy association seems to be more probable in the iron-doped absorbers as compared to the air-fired Co^{57}:$BaTiO_3$ sources.

IV. DISCUSSION

The present work on Co^{57}:$BaTiO_3$ sources and Fe^{57}:$BaTiO_3$ absorbers clearly indicates that the transition-metal ions generally remain associated with their charge-compensating oxygen vacancies. Although the structure of the associated vacancies in reduced Co^{57}:$BaTiO_3$ source and Fe^{57}:$BaTiO_3$ absorber is similar (probably because the starting material for absorber may be oxygen-deficient) it cannot be elucidated from our experiments. The associated vacancies in the air-fired Co^{57}:$BaTiO_3$ source, however, are of the axial type. This is understandable because it is known that among the six Ti-O bonds in a unit cell of $BaTiO_3$, the axial Ti-OI(l) (see Fig. 4 in I) is believed to be weakest of all.[19] Indeed, conjecture about axially associated vacancies has been made earlier by Gainon[4] to explain the strong axial EPR spectrum of Fe^{3+} in the structurally similar ferroelectric, $PbTiO_3$.

It is interesting to note that Hornig *et al.*[3] had observed considerable broadening of certain EPR resonances of Fe^{3+}:$BaTiO_3$ which were attributed to spreaded values of the crystalline fields stemming essentially from the presence of defects. Indeed, Gainon[20] has identified EPR resonances from $Fe^{3+}-V_0$ pairs in $BaTiO_3$. The reasons for the ease of obtaining impurity-vacancy pairs in the Mössbauer absorber rather than in the EPR samples may be the following:

(1) The amounts used for the two types of measurement differ considerably. In the EPR work the paramagnetic impurity content is usually in the range 0.01–0.05 mole percent, whereas the present Mössbauer measurements could be successfully made with a doping concentration of at least one mole percent. Higher concentration of impurity ions is known to increase the probability of impurity-associated charge-compensation effects. Indeed, Low and Shaltiel[21] have observed that the intensity of the normal EPR spectrum of Fe^{3+}:$BaTiO_3$ did not increase proportionally with impurity content varying from 0.1 to 0.5 mole percent.

(2) The fraction of recoil-free gammas,

$$f=\exp[-k^2\langle x^2\rangle],$$

from the vacancy-associated probes may be significantly larger than that from probes with normal perfect-lattice environment. With the reduction in the nearest-neighbor oxygens from 6 to 5, better packing may be achieved, resulting in a decreased value of f.

The second reason is probably more likely to account for the spectrum of dilutely doped air-fired Co^{57}:$BaTiO_3$. This is because the isomer shift for Fe^{3+} in this sample $\delta=0.34\pm0.05$ mm/sec, closely corresponds with that for Fe^{3+} in the tetrahedral sites of yttrium iron garnet.[22]

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Similarly low values of δ and large values of f are obtainable from the data on trivalent iron in oxygen-deficient perovskites, $BaFeO_{3-x}$ and $SrFeO_{3-x}$.[23]

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[23] From the spectra of Refs. 7–9, it must be inferred that there are quadrupole-split lines for the trivalent Fe ions. This is necessary so as to obtain a proper isomer shift and also to account for the proximity of oxygen-deficient sites. From the relative areas of the absorption dips for the unsplit Fe^{4+} line and the split Fe^{3+} lines, it becomes evident that the recoilless fraction from the vacancy-associated Fe^{3+} ions is larger than expected from its chemical proportion.

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Nuclear-Resonance Spin-Echo Study of ^{61}Ni Hyperfine Fields in Ferromagnetic Ni-Al, Ni-V, and Ni-Cr Systems

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The nuclear-magnetic-resonance line shapes of ^{61}Ni have been studied in ferromagnetic Ni-rich Ni-Al, Ni-V, and Ni-Cr powders by plotting the spin-echo amplitude as a function of frequency across the inhomogeneously broadened resonance lines. The measurements were made at 4.2°K in alloys containing concentrations of up to 12.3 at.% Al, 5.5% V, and 5.3% Cr. In all three systems, the average hyperfine fields decreased approximately linearly with increasing solute concentration. A general discussion of the relationship between the average hyperfine field and the atomic moments is presented. The major contribution to the hyperfine field is believed due to the moment on the parent atom, with a smaller contribution from moments on neighboring atoms via conduction-electron polarization. The detailed structure of the resonance spectra is analyzed. It is found that the magnetic disturbances are spatially more widespread in the Ni-Al and,Ni-V systems than in the Ni-Cr system. The Ni-Cr system in turn has a more delocalized behavior than the Ni-Co system previously studied. The results in the Ni-V and Ni-Cr systems are consistent with results obtained by Collins and Low using neutron scattering techniques.

I. INTRODUCTION

THE magnetic properties of the 3*d*-transition metals and alloys have been subjects of interest for many years. Many experimental techniques have been employed in studying the magnetic properties of these materials. Saturation magnetization measurements have been used in order to better characterize the electronic structure of these materials. In recent years neutron-scattering, Mössbauer-effect and nuclear-magnetic-resonance techniques have been used extensively in studying the microscopic magnetic properties of the transition-metal alloys.

Saturation-magnetization measurements only provide information about the average magnetic moments of the alloys. The average-magnetic-moment measurements are summarized by the well-known Slater-Pauling curve. Neutron-scattering techniques have been used to determine the magnetic moment distributions about the solute atom in several binary ferromagnetic systems. In some systems it has also been possible to estimate the magnetic moments on the host atoms which are near neighbors to a solute atom, using these techniques. Nuclear-magnetic-resonance techniques and the Mössbauer effect have also been successfully used to measure the nuclear-magnetic-hyperfine fields in many binary systems. A detailed study of the hyperfine fields in these alloys gives information about both the 3*d* atomic moments and the conduction-electron polarization. Thus, the information derived from these different experimental techniques taken together provide a more complete picture of the magnetic properties of these materials.

In a previous paper,[1] the authors have reported the results of a nuclear-resonance spin-echo study of the hyperfine fields at both the Ni and Co sites in Ni-rich Ni-Co alloys, a system which falls on the right branch of the Slater-Pauling curve. In this paper we present results of a similar study of the Ni hyperfine fields in Ni-rich Ni-V, Ni-Cr and Ni-Al alloys. These systems deviate from the right branch of the Slater-Pauling curve. The Ni-Al system has been studied for concentrations containing up to 12.3% Al (all percentages are atomic), the Ni-V system for concentrations up to 5.5%

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