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Paramagnetic Fe^{3+} in $LiAl_5O_8$: Magnetic Field Effects in the Mössbauer Spectrum*

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$^{57}Fe^{3+}$ Mössbauer absorption spectra were collected for powder specimens of $LiFe_xAl_{5-x}O_8$ with $x = 0.005$. The effects on the spectra of applied magnetic fields with strength less than 1 kOe are interpreted in detail. A comparison of the calculated spectra using EPR parameters to the data is made. This comparison indicates (a) that the observed resonances which are sensitive to applied magnetic fields are associated with the ±1/2-spin Kramers's doublet of the ionic ground term; (b) that for zero applied field the field-sensitive resonances are affected drastically by dipolar fields originating from neighboring nuclei. The sign of the zero-field-splitting parameter D is found to be negative. The value of the ground-state hyperfine-coupling constant is $A_g = (-2.45 \pm 0.03)$ mm/sec, and that of the quadrupole-coupling constant is $2P = (+0.67 \pm 0.03)$ mm/sec.

I. INTRODUCTION

Paramagnetic hyperfine structure (PHS) is observed in Mössbauer spectra when the nuclear magnetic moment can follow the fluctuating hyperfine field produced by the electronic moment. Many examples illustrating this effect have appeared in the literature in recent years. The electronic relaxation is due to (i) spin-spin interactions between paramagnetic ions which can be minimized by diluting the ions in a diamagnetic host and (ii) spin-lattice interactions which are usually overcome by doing experiments at low temperatures (~4 K). One of the remarkable properties of iron-doped lithium aluminate ($LiAl_5O_8$) is the persistence of the PHS in the Mössbauer spectrum of the trivalent ^{57}Fe impurity as the temperature is increased to well above room temperatures. This was first reported by Epstein and Wachtel[1] in their Mössbauer-effect investigation of a fluorescent material[2] in which iron was believed to be the active center. As part of our work we established that iron-doped $LiAl_5O_8$ was responsible for the unusual fluorescent and Mössbauer-effect properties.

The fluorescence and excitation spectra of trivalent iron doped in lithium aluminate has been measured concomitantly with this present Mössbauer study using the same samples and the results can be found elsewhere.[3]

In this paper we are concerned with the interpretation of the Mössbauer spectra of powder specimens of paramagnetic iron-doped $LiAl_5O_8$; specifically $LiFe_xAl_{5-x}O_8$ with $\frac{1}{5}x \leq 0.01$.

Crystallographic studies have shown that $LiAl_5O_8$ forms a modified inverse-spinel-like structure whose unit cell contains four formula units. The oxygen ions are arranged in a cubic close-packed lattice with both tetrahedral (A) and octahedral (B) sites.[4] The distribution of the cations among these sites varies according to the temperature of the compound. Here we will present results related to the low-temperature phase of lithium aluminate, the ordered phase. The crystallographic description of this ordered phase is described by Datta and Roy.[4] For the ordered aluminate system, Folen made electron-paramagnetic-resonance (EPR) measurements[5] on single crystals of $LiFe_xAl_{5-x}O_8$ with $x = 0.0025$ and he proposed that a substantial number of the Fe^{3+} ions enter the lattice substitutionally for Al^{3+} on tetrahedrally coordinated A-type sites. In our optical investigation of the fluorescence of Fe^{3+} in this aluminate[3] we present further experimental evidence for the tetrahedral-site preference of this ion. In addition, based on those fluorescence studies, we propose a model which accounts for the unusual relaxation and fluorescence properties of the Fe^{3+} impurity.

The Fe^{3+} ion exists in a $^6S_{5/2}$ state which is split by axially symmetric crystal fields into three Kramers's doublets. Since the separation in energy between any two of these doublets is much greater than the hyperfine interaction, in the limit of very long electronic relaxation times the Mössbauer spectrum consists of a superposition of three spectra—one from each Kramers doublet, each contribution weighted by the appropriate Boltzmann factor determined by the temperature of the system.

In previous studies of the relaxation properties of the three Kramers doublets of Fe^{3+} it was shown that the electronic spin-lattice relaxation time is longest for the $\pm\frac{5}{2}$ doublet and shortest for the $\pm\frac{1}{2}$ one.[6–8] Furthermore, it has been indicated[8] that at low temperatures, dipolar relaxation involving the spins of neighboring nuclei is an important process which again affects the $\pm\frac{1}{2}$-doublet most severely.

In the investigation[9] of Fe-doped α-Al_2O_3 (corundum), a system which is similar to the aluminate spinel, it was pointed out that the dipolar fields associated with the neighboring ^{27}Al nuclei caused splittings in the $\pm\frac{1}{2}$ level comparable to the hyperfine interaction. Considering that these fields are random in magnitude and direction, it was assumed that the $\pm\frac{1}{2}$ hyperfine structure would be washed out and in general would be difficult to observe.

More recently, Afanas'ev and Kagan[10] have shown that the Mössbauer spectra associated with the $\pm\frac{3}{2}$ and $\pm\frac{5}{2}$ doublets are insensitive to local dipolar fields when axial symmetry is present.

These observations suggest that the Mössbauer spectrum could be stabilized by the application of external fields of magnitude large enough to decouple the nuclear and electronic spin.

In comparison to similar compounds, iron-doped LiAl$_5$O$_8$ in its ordered phase presents a unique opportunity to study the effects of small external fields on the PHS because of the unusual quality and sharpness of the zero-field spectrum.

The purpose of this investigation is first to interpret the spectra obtained with the application of external magnetic fields of strengths less than 1000 Oe and then to extrapolate these results to the zero-field case.

II. EXPERIMENTAL

The powder specimens were prepared according to the LiFe$_x$Al$_{5-x}$O$_8$ formula unit; details of its preparation can be found elsewhere.[11]

External magnetic fields up to 1 kOe in magnitude and homogeneous to 0.6% over the target volume were produced by two parallel air-core water-cooled solenoids. The solenoids were arranged so that the field could be applied either parallel or perpendicular to the γ-ray beam. Absorber temperatures below 300 K were achieved with a cryostat in which the specimen was clamped to a copper extension of the coolant reservoir.

Figure 1(a) shows the ^{57}Fe Mössbauer-effect absorption spectra of a powder specimen of LiFe$_x$Al$_{5-x}$O$_8$ with $x = 0.005$ (0.1 at.%) in the temperature range 295–4.2 K. These data illustrate the weak relaxation of the electronic spins even at room temperature. In Fig. 1(b) a comparison of the spectra obtained for specimens with $x = 0.005$ and $x = 0.25$ at 295 K is shown. As can be seen, the complex PHS of the more diluted system collapses into a doublet when enough iron is introduced into the aluminate system to allow spin-spin relaxation to become important. Our investigation of specimens with higher concentrations of iron[12] indicates that the doublet can be associated with a single quadrupole interaction.

Presented in Fig. 2 are the data collected at 4.2 K as a function of H, the external magnetic field strength for the situation where the external-field direction is parallel to the Mössbauer γ-ray beam.

Comparing the 0- and 80-Oe data one notes that there is a definite sharpening of the absorption spectra as well as an enhancement of certain resonances. This enhancement continues as the external field increases to 280 Oe and in addition there is an indication of new resonances in the negative-velocity region marked by the arrow. From an examination of the 565- and 905-Oe data, it is evident that the position of this resonance, as well as the one in the positive-velocity region

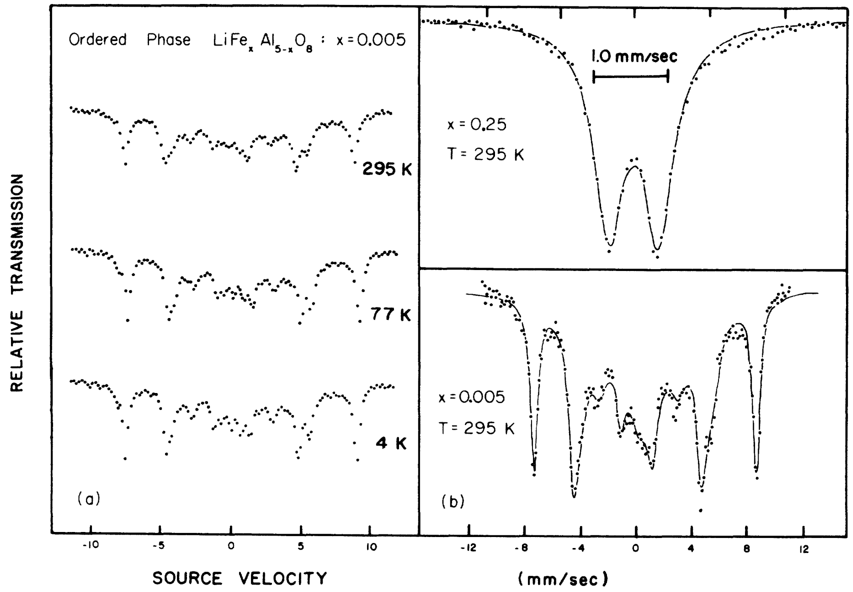

FIG. 1. Mössbauer spectra of powdered LiFe$_x$Al$_{5-x}$O$_8$, $x = 0.005$, in zero applied field showing the paramagnetic hyperfine structure (PHS) at various temperatures. The existence of PHS at 295 K and above is a remarkable property of this material. (b) Comparison of the Mössbauer spectra showing effects of iron concentration due to spin-spin relaxation. The solid lines are Lorentzian curves consistent with the least-squares fit to the main features of the data.

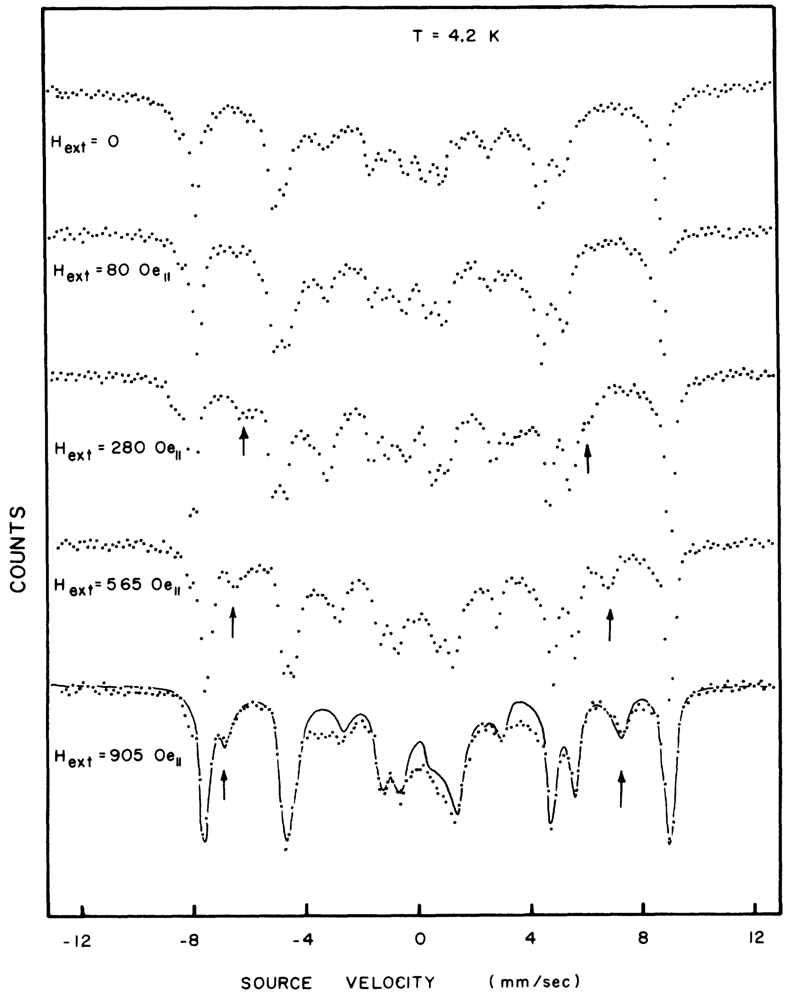

FIG. 2. Spectra of powder samples of $LiFe_xAl_{5-x}O_8$, $x = 0.005$, taken at 4.2 K in magnetic fields parallel to the γ beam. The arrows indicate the field-sensitive resonances, and the solid curve is a spectrum calculated with the spin-Hamiltonian parameters given in the text.

indicated by an arrow, is sensitive to the magnitude of the external field.

In Fig. 3 the results where the external field is perpendicular to the γ-ray beam are shown. In comparison with Fig. 2, we note that the spectra depend upon magnetic field orientation indicating that we have decoupled the electronic and nuclear spins and in some sense polarized the former.

Figure 4 shows data taken in 900 Oe and at 2.1 K. Comparing this spectrum with that obtained at 4.2 K (see Fig. 3), one sees that the line intensities vary with temperature. The 2.1-K spectrum led to our assignment of the $\pm\frac{5}{2}$ Kramers's doublet as lowest in energy.

III. INTERPRETATION

A. Spin Hamiltonian

The data are compared to spectra generated by a computer program for a spin Hamiltonian with adjustable parameters. Combining all of the interactions, the appropriate spin Hamiltonian for the present analysis can be written

$$\mathcal{H} = \mathcal{H}_{CF} + g\mu_B \vec{H}\cdot\vec{S} + A\vec{I}\cdot\vec{S} + \mathcal{H}_Q - g_n\mu_N \vec{H}\cdot\vec{I}\,.$$

$\mathcal{H}_{CF}$ describes the interaction of the electronic spin with crystal fields of cubic and axial symmetry. In each unit cell the Fe^{3+} ion can occupy one of four possible tetrahedral sites, each having a different orientation of the symmetry axes. However, it is not necessary to consider more than one of them, since we average over all the possible orientations of the crystals for comparison to the powder samples used in our experiments.

Combining the cubic and axial terms, $\mathcal{H}_{CF}$ becomes

$$\mathcal{H}_{CF} = \left(D + \frac{95}{72}(a-F)\right)S_z^2 - \frac{7}{36}(a-F)S_z^4 + \frac{a\sqrt{2}}{36}\left[S_z(S_+^3 + S_-^3) + (S_+^3 + S_-^3)S_z\right],$$

where z is the trigonal symmetry axis along the [111] direction relative to the local cubic axes.

The second term of $\mathcal{H}$ is the interaction between

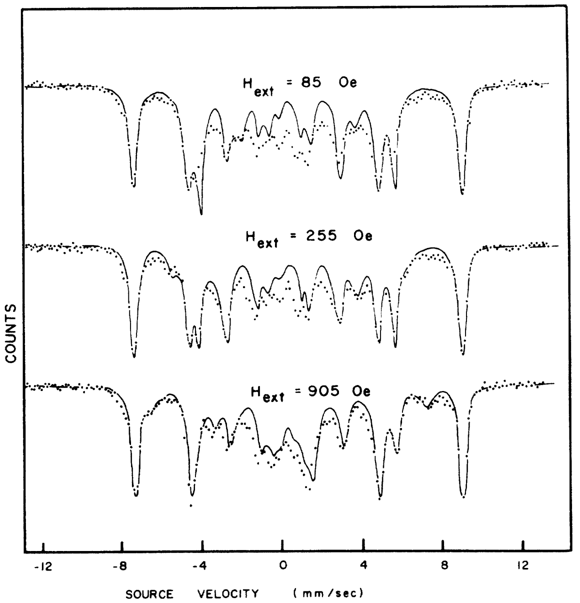

FIG. 3. Spectra of powder samples of $LiFe_xAl_{5-x}O_8$, $x=0.005$, taken at 4.2 K in magnetic fields transverse to the γ beam. Comparison with Fig. 2 shows the polarization effects of the applied magnetic field. The solid curves are calculations using the spin-Hamiltonian parameters $D=-0.104$ cm^{-1}, $|a|=0.01$ cm^{-1}, $a-F=-0.0166$ cm^{-1}, $A=-2.45$ mm/sec, and $\Delta E_Q=0.67$ mm/sec.

the electronic spin and the applied magnetic field H; the third term describes the hyperfine interaction between the electronic and nuclear spins, while the last term represents the direct effect of the applied field on the nuclear magnetic moment. This last term is quite negligible for the field strengths ($\leq$ 900 Oe) discussed in this paper. Finally, with the axial symmetry present at these tetrahedral sites, the quadrupole interaction $\mathcal{H}_Q$ in the $I=\frac{3}{2}$ nuclear state of ^{57}Fe is given by

$$\mathcal{H}_Q=\tfrac{1}{4}e^2Qq(I_z^2-\tfrac{5}{4})\equiv P(I_z^2-\tfrac{5}{4}) .$$

The magnitudes of D and $a-F$ and the spectroscopic-splitting factor g are known from EPR studies[5] of $LiFe_xAl_{5-x}O_8$ with $x=0.0025$. The values are $|D|=0.104$ cm^{-1}, $|a-F|=0.0166$ cm^{-1}, $|a|\simeq 0.01$ cm^{-1} with $g=2.006\pm 0.006$ and $D/(a-F)>0$. The magnitude of the quadrupole-interaction energy was initially assumed to have the same value [$|P|=(0.335\pm 0.009)$ mm/sec] determined experimentally for the aluminate system with higher concentrations of iron.[12] The value of A is determined from this work to be -2.45 mm/sec for the nuclear ground state.

The Hamiltonian matrices operating on the electronic nuclear-product states $|SM_S\rangle\,|IM_I\rangle$ were diagonalized in order to obtain the transition energies and probabilities.

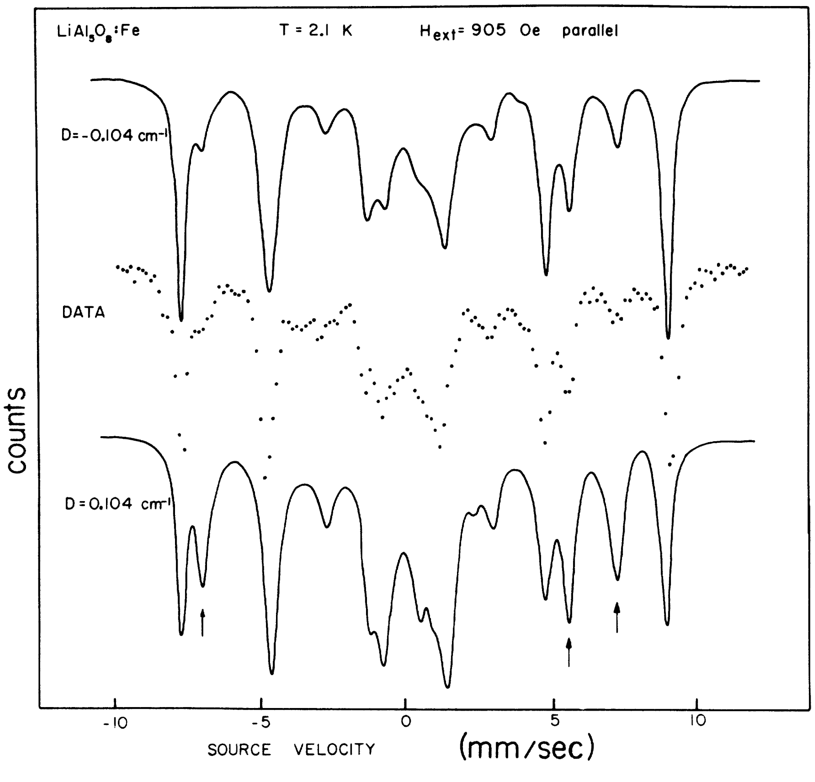

FIG. 4. Mössbauer data taken at 2.1 K where significant variation in the populations of the electronic states can occur. By comparison of the data with the calculated spectra the sign of D was found to be clearly negative. The arrows indicate the greatest discrepancies between calculation assuming $D>O$ and data. The applied field is parallel to the γ beam.

Theoretical spectra were computed for each of many orientations of the magnetic field relative to the axes of the crystal equally spaced over the unit sphere, and added together with equal weight to simulate the random orientations of the absorber.

The line shape was taken into account by folding a Lorentzian of full width at half-maximum (FWHM) equal to 0.4 mm/sec into the theoretical spectra. Since in this study the Zeeman splittings of the Kramers doublets are always smaller than the initial crystal field splittings, it is possible to divide the complete set of hyperfine transitions into three groups. Each group is associated with one of the three Kramers doublets. For convenience these three groups are *labeled* by $M_S = \pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2}$. It should be realized that this labeling does not refer to the actual electronic spin state due to the fact that $a \neq 0$ and $H \neq 0$. A typical result is given in Fig. 5 where the separate contributions of each Kramers doublet to this total spectrum are shown.

B. Comparison of Calculated and Experimental Spectra in Moderate Fields

The theoretical spectra for magnetic fields in the range $100 \leq H \leq 900$ Oe, and calculated as described in Sec. III A, are plotted as solid lines in Fig. 3. We discuss our $H < 100$ Oe data in Sec. III C.

From these spectra a value of $A_g = (-2.45 \pm 0.03)$ mm/sec was obtained for the ground-state hyperfine-coupling constant by matching the theoretical splitting between the two extreme energy peaks to the experimental data. P was found to be $(+0.335 \pm 0.03)$ mm/sec; its sign was determined as positive from the asymmetry observed in the experimental data. Within our experimental error the magnitude of P is the same as that reported for the aluminate system with higher concentrations of iron.[12]

As seen in Fig. 5(b) the set of resonances labeled $S = \frac{1}{2}$ is greatly influenced by the strength of the applied field. Our calculations indicate that the positions of these resonances are sensitive to the external magnetic field H and the initial zero-field splittings of the electronic states which in turn are a function of D and $a - F$. Our measurements are in agreement with the EPR values for $|D|$ and $|a - F|$.

On the other hand the amplitude of the resonances depends on the relative Boltzmann population of the ionic states, and these are controlled by the sign of D and $a - F$ separately. At 2.1 K and 900 Oe the populations of these levels vary significantly with the sign of D (see Fig. 4) and by comparison with the theory we were able to determine that both D and $a - F$ are negative.

C. Comparison of Calculated and Experimental Data in Small Applied Fields

For zero applied field we were unable to observe any resonance associated with the $\pm\frac{1}{2}$ electronic doublet [Fig. 6(a)]. The arrows in this figure mark the predicted resonances of the $\pm\frac{1}{2}$ spectrum. It would be tempting to assign the shoulder on the lowest-energy resonance of the $\pm\frac{5}{2}$ spectrum as a $\pm\frac{1}{2}$ resonance. This shoulder, as is shown in Sec. III D, is not part of the main spectrum. From this

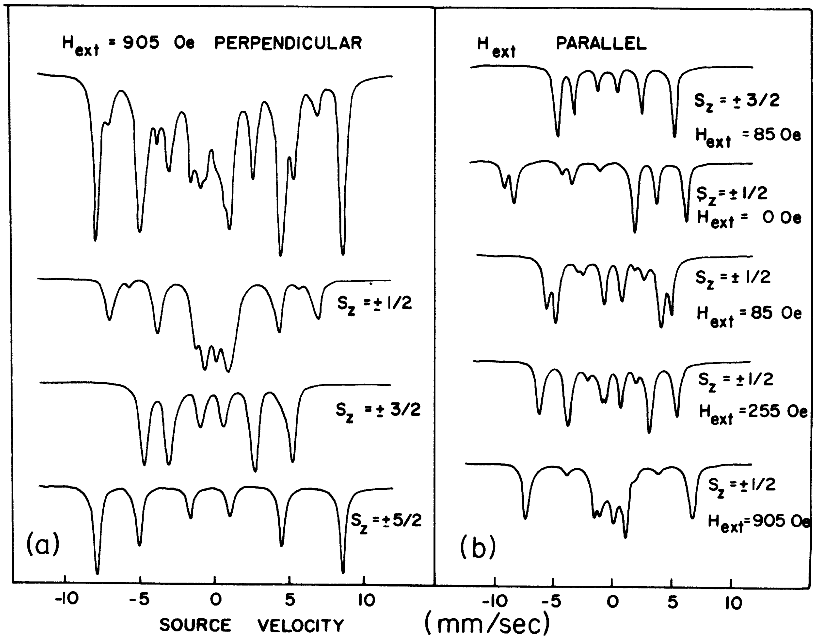

FIG. 5. (a) Calculated spectra using the spin-Hamiltonian parameters appropriate for $LiFe_xAl_{5-x}O_8$ in the long-relaxation-time limit. The total spectrum (upper left) is the superposition of contributions from each of the three Kramers doublets labeled $\pm\frac{1}{2}$, $\pm\frac{3}{2}$, $\pm\frac{5}{2}$. The applied magnetic field is perpendicular to the γ beam. (b) Predicted effect of a magnetic field on the $\pm\frac{1}{2}$ spectrum. These results show that the field-sensitive resonances (Fig. 2) are associated with the $\pm\frac{1}{2}$ states. The $\pm\frac{3}{2}$ spectrum (upper right) overlaps the main features of the $\pm\frac{1}{2}$ spectrum at low fields. The applied field here is parallel to the γ beam.

figure it can be seen that the major deviations from the static-model predictions in zero field are associated with the $\pm\frac{1}{2}$ electronic doublet.

The failure to experimentally resolve the zero-field contribution of the $S_z = \pm\frac{1}{2}$ doublet to the spectrum in systems similar to Fe-doped $LiAl_5O_8$ has been mentioned in Sec. I of this paper. Of all the factors which perturb this doublet, the static and dynamic effects of dipolar fields originating from the neighboring ^7Li and ^{27}Al nuclei should be the two most important ones.

There is clear evidence that all Kramers doublets are relaxing very slowly compared to the nuclear precession time. This is certainly the case at 4.2 K as indicated by the extremely sharp resonances in the spectra and the good fits obtained using a static model for the data taken in applied fields of moderate strength. This evidence and the well-known sensitivity to very small magnetic fields of the resonance lines associated with the $S_z = \pm\frac{1}{2}$ doublet [Fig. 5(b)] led us to examine the static effects of dipolar fields originating from neighboring nuclear moments.

The correct approach to the zero-field data involves a modification of the Hamiltonian of Sec. III by adding to $\mathcal{H}$ the terms

$$\sum_{i=1}^{n} \vec{I}_i \cdot \overleftrightarrow{B}_i \cdot \vec{S} ,$$

where $\vec{I}_i$ is the nuclear spin of the ith neighbor. The solution involves the diagonalization of a $(2I_{\mathrm{Fe}}+1)(2S+1)\prod_{i=1}^{n}(2I_i+1)$-dimensional matrix and $8[(2S+1)\prod_{i=1}^{n}(2I_i+1)]^2$ Mössbauer transitions which is a formidable computational problem even if we know how many neighbors (n) to consider and the strength of the interaction tensor ($\overleftrightarrow{B}_i$) for each neighbor. To make an approximation which is solvable, we assume that all the neighboring nuclear moments together produce an effective magnetic field at the site of the Mössbauer ion which is randomly oriented and whose strength is to be determined. Thus we have set

$$\sum_{i=1}^{n} \vec{I}_i \cdot \overleftrightarrow{B}_i \cdot \vec{S} = \langle \mu_B \vec{H} \cdot \overleftrightarrow{g} \cdot \vec{S} \rangle ,$$

where the average is taken over the orientations of $\vec{H}$ with respect to $\vec{S}$. This keeps the dimensionality of the matrix and the number of Mössbauer transitions the same.

In order to examine the effects of static fields, a calculation was made with $|H|$ fixed at values of 5 and 10 Oe and directed to all possible angles with the z axis. The theoretical spectra obtained in this manner for 10 Oe "random" field is shown in Fig. 6(a). As is indicated some of the prominent resonances associated with the zero-field $\pm\frac{1}{2}$ doublet have disappeared with the inclusion of

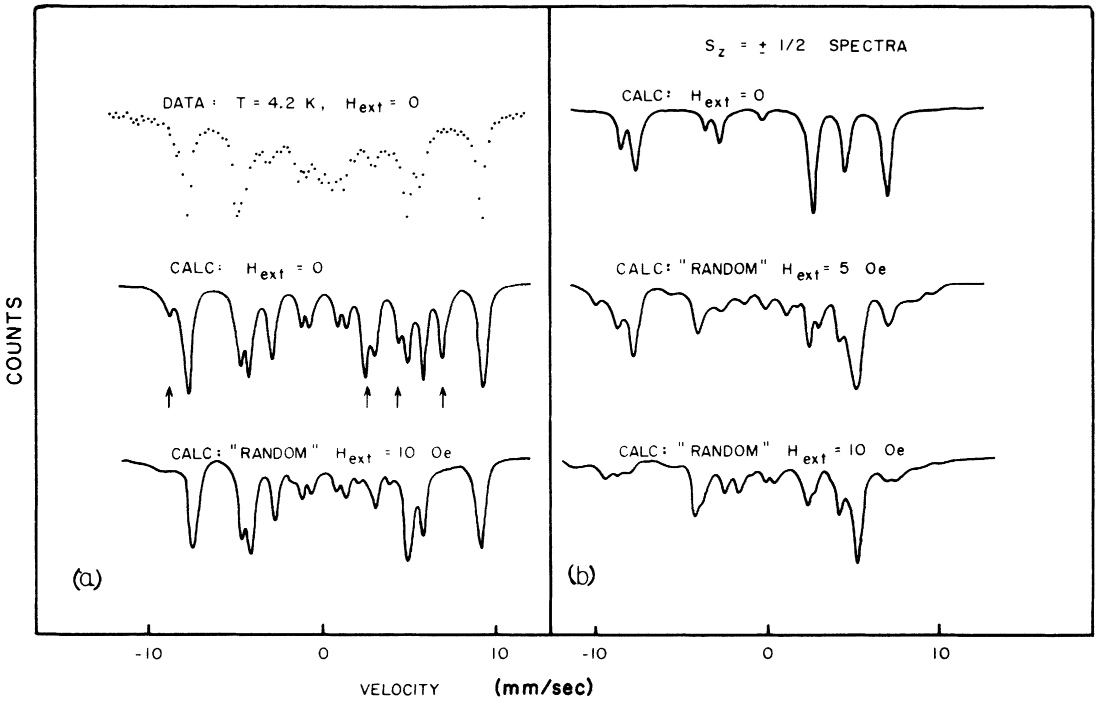

FIG. 6. (a) Experimental data taken in zero applied field—the arrows indicate missing resonances. The addition in the calculation of small random fields of about 10 Oe makes the agreement with the experimental data better. (b) Calculated effects of the small random fields in the $S_z = \pm\frac{1}{2}$ Kramers doublet.

this approximation in the calculation. Furthermore, the over-all agreement between the spectrum calculated with small "random" fields and the data is improved.

It is important to note that we have made a static average of the fields due to neighboring nuclei and not a temporal average in order to understand the behavior of the Mössbauer spectrum due to the $S_z = \pm\frac{1}{2}$ doublet. In Fig. 6(b) the comparison of the calculated $\pm\frac{1}{2}$ spectrum as a function of "random" field is shown. It is difficult, however, to determine from the aluminate data to what extent this approach characterizes the perturbed $\pm\frac{1}{2}$ spectrum, or whether these are spin-relaxation effects which modify this spectrum. Clauser and Blume[13] have worked out a method which includes the effects of spin relaxation in the $S_z = \pm\frac{1}{2}$ Kramers doublet and specific examples are forthcoming.

That the "static" dipolar-field model does have some validity, however, is indicated by some recent Mössbauer results from a study of 10^{-3} *M* acid met myoglobin *p*H 6 by Lang *et al.*[14] The spectrum observed at 4.2 K in zero applied field which is reproduced in Fig. 7 contains only resonances associated with the $\pm\frac{1}{2}$ electronic doublet because of a large positive D of approximately 10 cm^{-1}.

It is evident from Fig. 7 that the experimental data is very similar to our theoretical spectra calculated with the small random field.

The interpretation offered for the zero-field data can be extended to the low-field case in which the external magnetic field competes with the dipolar interaction in determining the electronic state. An external field of 85 Oe dominates all other interactions (except the crystal field term) and to a great degree determines the hyperfine-level scheme for the $\pm\frac{1}{2}$ doublet. This is indicated by the fact that the discrepancies between the data and the calculated spectra for this field value are minor when compared to the zero-field case.

D. Minor Discrepancies

Although the over-all agreement between the calculated and observed spectra is very good considering the complexity of the data and the assumptions of the model, there are slight obvious discrepancies. Perhaps the most significant one of these is that the calculations do not predict the shoulder present on the lowest-energy resonance of the experimental spectrum. Since the calculations are successful in reconstructing the other important aspects of the data, one is forced to draw the conclusion that this shoulder is not part of the main resonance spectrum supposedly associated with iron in tetrahedral sites. As a plausible explanation, this resonance may be due to Fe^{3+} on an octahedral site since the specimen from x-ray analysis is definitely single phase with no iron or aluminum oxide impurities.

IV. CONCLUSIONS

The PHS of powder absorbers of Fe-doped $LiAl_5O_8$ in the ordered phase was interpreted as a function of an applied magnetic field. The field-sensitive resonances were identified as transitions between hyperfine levels associated with the Zeeman electronic levels derived from the zero field $S_z = \pm\frac{1}{2}$ Kramers doublet. The field dependence of these resonances was attributed to the mixing of crystal field states (specifically the $\pm\frac{1}{2}$ states) by the component of the external field perpendicular to the crystal field axis. As a result of this interpretation it was possible, independent of EPR, to predict the magnitude and relative sign of the electronic spin-Hamiltonian parameters D and $a - F$.

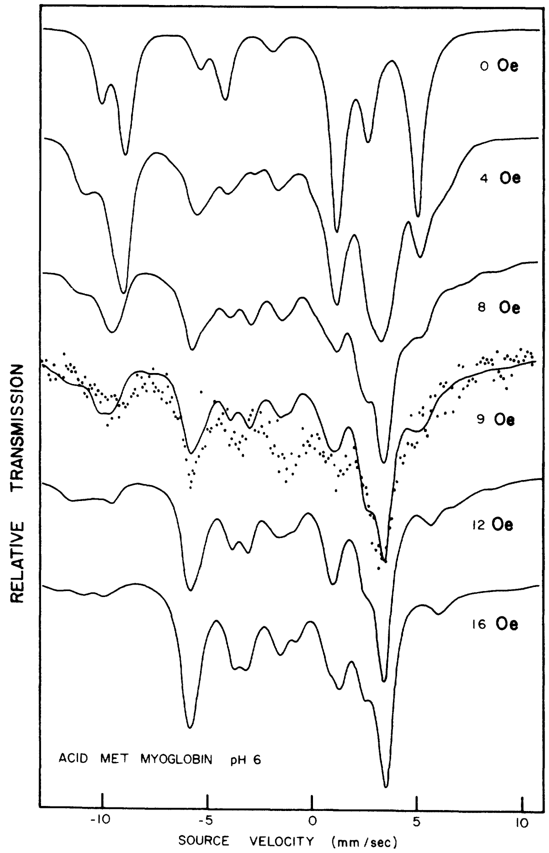

FIG. 7. Experimental data of acid met myogloblin taken by Lang *et al.* (Ref. 14) in zero magnetic field at $T = 4.2$ K. The solid curves are calculated with the spin-Hamiltonian parameters $D = 10\ cm^{-1}$, $A = -2.36$ mm/sec (nuclear ground state), $g = 2.0$, and $P = 0.65$ mm/sec and with the random-field model where the field strengths are indicated.

Consistent with the EPR results,[5] the ratio of $D/(a-F)$ was found to be positive.

The absolute sign of D is assigned to be negative. The data did not facilitate a determination of the signs of a and F. For the parameter a, such a determination may be possible through the interpretation of data collected with external fields high enough to cause the $\pm\frac{1}{2}$ and $\pm\frac{5}{2}$ electronic crystal field state to cross.[6,9]

The value of the ground-state hyperfine-coupling constant was found to be $A_g = (-2.45 \pm 0.03)$ mm/sec. The hyperfine field associated with this value is $|H| = (206 \pm 7)$ kOe per unit electronic spin. This value is compared to $|H| = 220$ kOe/spin for $^{57}\mathrm{Fe}^{3+}$ in[8] α-$\mathrm{Al_2O_3}$ and $|H| = 229$ kOe/spin for $^{57}\mathrm{Fe}^{3+}$ in $\mathrm{NH_4AlSO_4 \cdot 12H_2O}$.[6] The decrease in H for the spinel is expected in view of the covalency present at the site.[15] This value of H for the spinel is not the smallest value reported. Several of the biological molecules containing high-spin trivalent iron have H values of less than 200 kOe/spin.[14]

The sign of V_{zz}, the crystalline electric field gradient as determined by Mössbauer measurements, is found to be positive consistent with the prediction by Stauss[16] for the tetrahedral sites of ordered $\mathrm{LiAl_5O_8}$. The magnitude of the quadrupole-coupling constant $P = \frac{1}{4}e^2Qq$ for the iron-doped aluminate has the same value as that measured for the higher-concentration specimen $\mathrm{LiFe}_x\mathrm{Al_5O_8}$ with $x = 0.25$ (5 at.% Fe), i.e., for the $x = 0.005$ specimen $\Delta E_Q = 2P = (0.67 \pm 0.03)$ mm/sec, while for $x = 0.25$, $\Delta E_Q = (0.675 \pm 0.01)$ mm/sec.

A model is proposed to show how the effects of neighboring nuclear moments can appear in the zero-field Mössbauer spectrum and experimental evidence of this interaction is presented.

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