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Mössbauer Study of Electronic Spin-Flip Processes in $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

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Relaxation-broadened Mössbauer spectra of ferric alum have been obtained in the temperature range 85–250 K, with 0–5-kG applied magnetic field. In fields above a few kG the spectra are only influenced by hyperfine fields fluctuating parallel to the applied-field direction. In low applied fields the spectra are also influenced by components of the hyperfine field fluctuating perpendicular to the applied-field direction, thereby inducing transitions between the nuclear sublevels. In the case of high applied fields, a simple model permits the determination of the spin-correlation time. In 5-kG applied fields, the spin-correlation time was found to decrease from 1.6 ± 0.15 nsec at 85 K to 0.50 ± 0.05 nsec at 245 K due to spin-lattice interactions. It is shown that these results cannot be compared with the values obtained by high-frequency susceptibility measurements.

I. INTRODUCTION

Mössbauer spectra of paramagnetic compounds are often influenced by fluctuating hyperfine fields. This has been described in a number of publications.^{1–12} In undiluted ferric compounds a broadening of the lines can often be found.^{13–15} Sufficient dilution with aluminum or other nonmagnetic ions can result in the appearance of magnetically split spectra.^{16,17}

The Mössbauer spectrum of $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (ferric alum) has been investigated by several authors.^{14–22} Highly magnetized samples exhibit magnetic splitting with anomalous line broadenings and line displacements.^{18–20} At room temperature the spectrum consists of a single broad line which in low fields becomes considerably narrower.^{14,15} In zero field the linewidth depends on the temperature in a complicated way.²²

II. EXPERIMENT

Mössbauer spectra of polycrystalline $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ were obtained in order to examine the spin-flip processes. The temperature was varied from 85 to 250 K. Magnetic fields in the range 0–5 kG were applied parallel and perpendicular to the γ -ray direction. A 10-mCi Co^{57} source in Pd was used. The absorbers were prepared with a thickness of 150 mg/cm^2 and cooled immediately in order to prevent water absorption. During each measurement the absorber temperature was controlled to within ± 1 K. The measurements were carried out with an ordinary constant-acceleration Mössbauer spectrometer with the multichannel analyzer in the PHA mode.

III. THEORY

A. Mössbauer Line Broadening

An increasing number of papers^{1–12} deal with

the influence of fluctuating hyperfine fields on the Mössbauer spectra of paramagnetic compounds. The hyperfine interaction is generally described⁴ by the Hamiltonian $\hat{H} = \hat{\mathbf{I}} \cdot \hat{\mathbf{A}} \cdot \hat{\mathbf{S}}$, where $\hat{\mathbf{S}}$ is the atomic spin, $\hat{\mathbf{I}}$ is the nuclear spin, and $\hat{\mathbf{A}}$ is a tensor, which depends on the crystal field as well as the nuclear properties. However, as demonstrated by Afanas'ev and other workers,^{23,24} a rather small magnetic field (~ 100 G in the case of Fe^{3+}) is sufficient to secure the validity of an effective-field Hamiltonian, $\hat{H} = a \hat{\mathbf{S}} \cdot \hat{\mathbf{I}} = H_{\text{eff}} \hat{\mathbf{I}}$, where a is a constant. In ferric alum this Hamiltonian must be valid as the field H_i at one ferric ion arising from the neighboring iron ions is about 450 G on the average.²⁵

In ferric alum diluted with aluminum the crystal-field splitting is small, about 0.12 K.^{26–28} It is reasonable to assume a splitting of the same order in the pure compound. Therefore, the crystal-field interaction is comparable to the magnetic dipole-dipole interaction between neighboring ferric ions. This means that the ionic spin, and hence the hyperfine field, will vary in direction according to the magnitude and direction of H_i relative to the crystal-field axis. If a magnetic field H_0 , large compared to H_i , is applied along the z direction, the ionic spins will precess around this direction and the hyperfine field will only fluctuate along the same direction.

The ideal case where the hyperfine field fluctuates only parallel to the z axis has been investigated theoretically by several authors. Wegener⁵ considers only short relaxation times (10^{-9} – 10^{-12} sec) whereas other authors^{1–4,7–12} also consider longer relaxation times. In the limit of fast relaxation all these theories give essentially the same result, namely, a broadening of the absorption lines proportional to $\tau \langle h^2 \rangle_{\text{av}} \nu^2(m_e, m_g)$. Here, τ is the spin-flip time or the spin-correla-

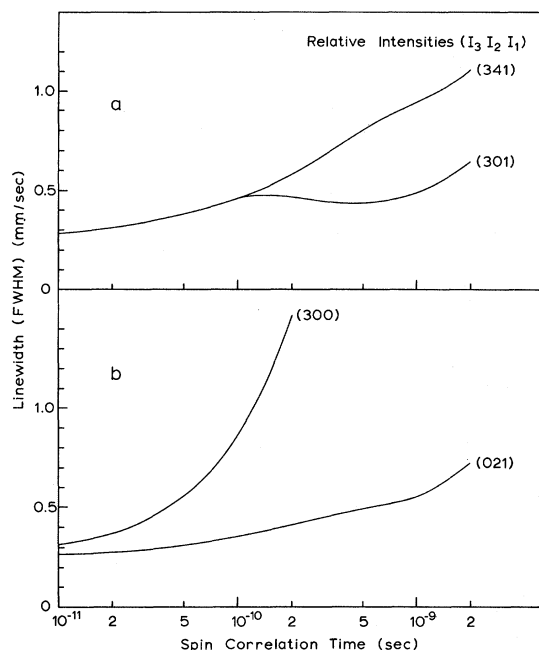


FIG. 1. Computed linewidth (FWHM) as a function of the spin-correlation time for $\langle h^2 \rangle_{av} = 162400 \text{ kG}^2$ and $\Gamma_0 = 0.25 \text{ mm/sec}$. Relative intensities of the three components are given in parentheses. (341) and (301) correspond to external magnetic field perpendicular and parallel to the γ -ray direction, respectively. (300) and (021) correspond to the two lines in the case of quadrupole splitting.

tion time, h is related to the magnitude of the fluctuating hyperfine field, and $\nu(m_e, m_g)$ is the difference between the z components of the nuclear magnetic moments of the initial state and the final state of the individual γ transitions. The various theories differ at most in the definitions of $\langle h^2 \rangle_{av}$ and τ .

In the present work we have applied the short-correlation-time approximation of van der Woude's theory⁸ as derived by van Zorge *et al.*⁹

Neglecting the average magnetic field $\langle \vec{H}_0 + \vec{H}_{hf} \rangle_{av}$ and the electric field gradient at the nucleus, the absorption spectrum will consist of three equally positioned Lorentzian lines corresponding to the different nuclear transitions. The linewidths are

$$\Gamma = \Gamma_0 + \langle h^2 \rangle_{av} \nu^2(m_e, m_g) \tau, \quad (1)$$

where $\langle h^2 \rangle_{av}$ is the average value of the squared hyperfine field. As $H_{hf} = aS_z$ and $S = \frac{5}{2}$, we get

$$\langle h^2 \rangle_{av} = a^2 \langle S_x^2 \rangle = a^2 \frac{35}{12}. \quad (2)$$

τ is the spin-correlation time and Γ_0 is the experimental linewidth in the limit of very fast fluctuating fields. The relative integral inten-

sities of the three Lorentzians are 3:4:1 and 3:0:1 for the applied magnetic field perpendicular and parallel to the γ -ray direction, respectively.

The total linewidth, full width at half-maximum (FWHM), of an absorption line has often been connected to the correlation time τ . In Fig. 1(a) is shown the calculated total linewidth (FWHM) for parallel and perpendicular field as a function of τ for $\Gamma_0 = 0.25 \text{ mm/sec}$ and $\langle h^2 \rangle_{av} = 162400 \text{ kG}^2$ ($H_{hf} = 590 \text{ kG}$ for $S_x = \frac{5}{2}$). In parallel field the linewidth is a decreasing function of τ for $0.15 \leq \tau \leq 0.45 \text{ nsec}$. In the perpendicular case the linewidth is an increasing function of τ as expected, but the slope is not pronounced. Hence a fitting procedure is necessary when one wants to derive the spin-correlation time from a Mössbauer spectrum.

When a quadrupole splitting is present and the magnetic field is fluctuating along the axis of an axially symmetric electric field gradient, the broader line depends in a more simple way on the relaxation time [Fig. 1(b)].

In a previous paper²⁹ we have discussed the shape of the Mössbauer spectrum as a function of the applied field H_0 . For $H_0 \gtrsim 1 \text{ kG}$, the absorption line consists of broad and narrow components in agreement with the theories mentioned above. The narrowest component, arising from the $\pm \frac{1}{2} \rightarrow \mp \frac{1}{2}$ nuclear transitions is responsible for the relatively small linewidth. When the applied field is decreased, the narrow component gradually disappears. It was proposed that magnetic fields fluctuating perpendicularly to the direction of the external field induce transitions between the nuclear sublevels. If the lifetime of a nuclear sublevel is not considerably longer than the nuclear Larmor period, the components of the Mössbauer spectrum will mix.⁷ Hence, the narrow component disappears resulting in an increased linewidth. Here we shall discuss this phenomenon a little further.

In a magnetic field H_1 fluctuating perpendicularly to the direction of a large constant field, the transition rate P for transitions between nuclear sublevels is proportional to H_1^2 . Neglecting the crystal-field splitting, H_1 is, as a good approximation, equal to the component of the hyperfine field H_{hf} perpendicular to the direction of the applied field H_0 . The ionic dipole-dipole field H_i is responsible for the time dependence of the orientation of H_{hf} . For $H_1^2 \ll H_0^2$, we find

$$P \propto H_{hf}^2 \langle H_i^2 \rangle_{av} / H_0^2. \quad (3)$$

P also depends on the detailed time variation of H_1 . However, when only the amplitude of H_1 is changed, we see that if P is comparable to the nuclear Larmor frequency at moderate applied fields H_0 , an increase of H_0 by a factor of 3 will

increase the lifetime of the nuclear sublevels so much that the transitions can hardly be observed. We believe that this is the explanation of the observed line narrowing.

The above explanation is supported by the fact that the line narrowing is obtained with smaller applied field in compounds diluted with aluminum, where H_i is smaller.³⁰ This suggests that the Mössbauer effect can give information about phenomena related to transverse relaxation. The detailed calculations still remain to be carried out.

B. Spin-Flip Processes

Transitions between the eigenstates of the atomic spin \hat{S}_z are induced by spin-spin interactions and by spin-lattice interactions. Generally, the spin-correlation time measured by Mössbauer spectroscopy cannot be compared with the relaxation time measured in high-frequency susceptibility experiments, as the latter does not take into account spin-flip processes which leave the total magnetization of the sample unchanged. An example is the simultaneous transitions of two spins S_1 and S_2 induced by the operator $\hat{S}_1^+ \hat{S}_2^- + \hat{S}_1^- \hat{S}_2^+$. These processes are energy conserving, contrary to other spin-flip processes caused by spin-spin interaction. Hence these processes are most important when the separation between the ionic

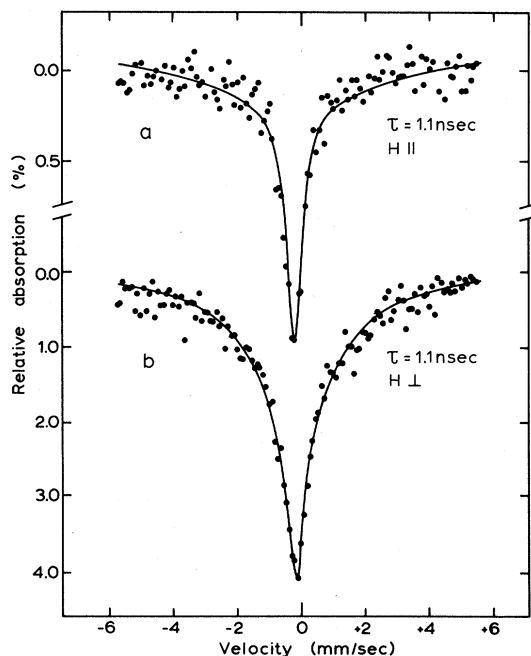


FIG. 2. Mössbauer absorption spectra of ferric alum at 120 K in a 5-kG external field. (a) and (b) correspond to the external field parallel and perpendicular to the γ -ray direction, respectively. The solid lines represent computed spectra for $\tau = 1.1$ nsec.

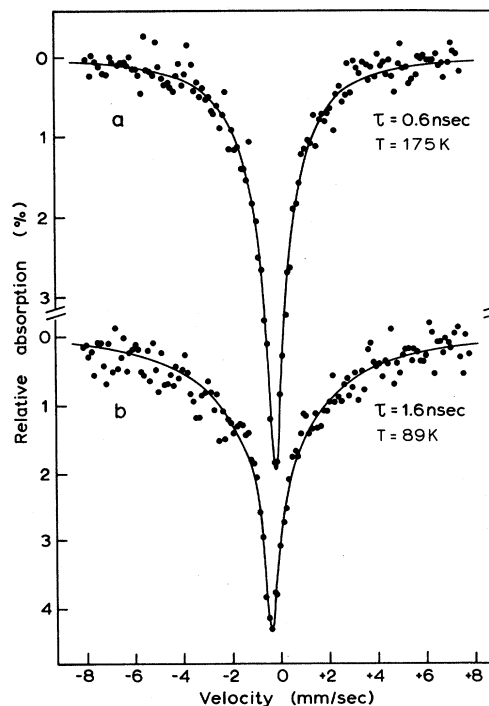


FIG. 3. Mössbauer absorption spectra of ferric alum in an external magnetic field of 5 kG perpendicular to the γ -ray direction. (a) $T = 175$ K; (b) $T = 89$ K. The solid lines represent computed spectra for the indicated spin-correlation times.

levels is large relative to the dipole-dipole interaction energy. Having this in mind, one should describe the time-constant characteristic for the fluctuating hyperfine field not as a relaxation time but rather as a spin-correlation time or a spin-flip time.

The spin-spin interaction is essentially temperature independent unless the separation between the ionic levels is comparable to the thermal energy giving rise to an unequal population of the levels, as in the case of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ³¹ and ferric hemin.³² In contrast, spin-lattice interaction is normally strongly temperature dependent.

In ferric compounds the spin-lattice interaction is usually considered to be negligible compared to spin-spin interaction. However, in diluted compounds spin-spin processes are slowed down, and spin-lattice processes have been observed in a few cases.^{16,21,33} In a recent work by Svetozarov³⁴ it was shown that the spin-flip rate due to interaction with the lattice vibrations is proportional to T^5 for temperatures well below the Debye temperature. In the high-temperature limit a proportionality to T^2 was found. Suzdalev *et al.*³³ have calculated the detailed temperature dependence on basis of the Einstein model and the Debye model for the phonon spectrum.

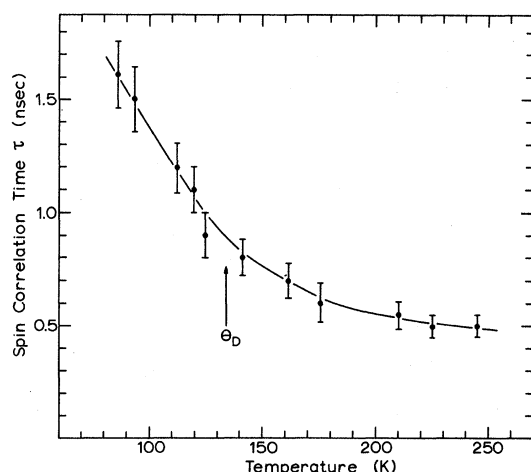


FIG. 4. Estimated values of the spin-correlation time τ of ferric alum as a function of temperature in a 5-kG external field applied perpendicular to the γ -ray direction.

In the following we shall denote the time constants for spin-spin and spin-lattice interactions by τ_{ss} and τ_{sl} , respectively. The resulting spin-correlation time is denoted τ .

IV. RESULTS

A number of spectra have been obtained with the absorber in a magnetic field of 5 kG and at temperatures in the range 85–250 K. The spectra were computer fitted with the simple model described in Sec. III. In all fittings Γ_0 was 0.35 mm/sec and $\langle h^2 \rangle_{av} = 162400 \text{ kG}^2$. The value of $\langle h^2 \rangle_{av}$ has been estimated from the measurements of Campbell and DeBenedetti on $\text{NH}_4(\text{AlFe})(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$,^{17,21} which showed a magnetic field of $H_{\text{max}} = 590 \text{ kG}$ for the $\frac{5}{2}$ state, in good agreement with the results of Bruckner *et al.*^{19,20} on highly magnetized diluted and undiluted ferric alum, which indicated $H_{\text{max}} = 595 \pm 10 \text{ kG}$. In the actual temperature range the average magnetic field at the place of the iron nuclei can be neglected since the external field is partly compensated by the induced average hyperfine field. The quadrupole splitting was assumed to be zero. Examples of the fitting are shown in Figs. 2 and 3.

Figure 2 shows spectra obtained at 120 K in a 5-kG external field parallel and perpendicular to the γ -ray direction. The successful fitting with intensity ratios 3:0:1 and 3:4:1, and a common spin-correlation time $\tau = 1.1 \text{ nsec}$ seems to justify the application of the simple model.

In Fig. 3 are shown two typical spectra obtained in a 5-kG perpendicular field at 175 and 89 K. The full lines indicate the theoretical spectra.

In Fig. 4 the estimated values of τ are shown

as a function of the temperature. The temperature dependence of the correlation time is evident. In the actual temperature range and with a field of 5 kG the populations of the ionic states are almost constant. Hence τ_{ss} should be almost constant. Therefore, the temperature dependence must be due to spin-lattice interactions. Even if τ_{sl} is assumed to be long for S-state ions like Fe^{+3} , this result is not surprising in the light of measurements on $\text{NH}_4(\text{Fe, Al})(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$,^{16,17,21} indicating a temperature-dependent spin-correlation time.

V. DISCUSSION

It is interesting to compare our results with the existing theories for spin-lattice processes in S-state compounds. We find that the slope of τ versus temperature is more pronounced below the Debye temperature Θ_D than above. $\Theta_D = 134 \text{ K}$ was derived from the temperature dependence of the integral intensity of the Mössbauer absorption line. These observations agree well with the theories.^{33,34} A separation of τ_{ss} and τ_{sl} could in principle have been made on the basis of one of the models by Suzdalev *et al.*³³ This has been tried but the results were considered doubtful as none of the models agreed in detail with our measurements. The deviation can be due to the simplicity of the models. The theories only deal with transitions induced by modulation of a temperature-independent crystal field in the absence of external fields. However, the crystal-field parameters vary as a function of temperature^{27,28} and furthermore our results are obtained in a 5-kG field.

Gleason and Walker²² have measured the linewidth and line area of Mössbauer spectra of ferric alum in zero applied field. The linewidth was found to depend in a complicated way on the temperature. Above 140 K the linewidth was found to increase with temperature. This was considered to be due to an increasing spin-correlation time contrary to our results in the same temperature range. A more pronounced increase of the linewidth as function of the temperature in a 700-G external field has later been found.³⁵ However, these results cannot directly be compared with ours as we have applied a 5-kG external field. It is uncertain whether the linewidth in zero and low fields can be related to the spin-correlation time since transverse relaxation may complicate the situation considerably. The crystal field, as well as an external magnetic field, gives rise to a more or less strong polarization of the ferric ions. Therefore, a change in the crystal-field parameters may influence the Mössbauer spectra in a way similar to a change in the magnitude of the external field. ESR measurements^{27,28} have

shown a strong temperature dependence of the crystal-field parameters although the total splitting is limited to about 0.1–0.2 K. This could be the explanation of the above-mentioned data obtained in 0 and 700 G.

VI. CONCLUSION

We have found that Mössbauer spectroscopy is a useful tool for measurements of spin-correlation times in undiluted ferric compounds when computer fitting is used. The simple model used gives results in good agreement with experiments.

The measured spin-correlation times give information about the spin fluctuations which cannot

be found from bulk measurements. The low-field spectra are affected by fluctuations both parallel and perpendicular to the z direction. The detailed line shape has not yet been calculated for this case.

It has been shown clearly that spin-lattice interactions play an important role in ferric alum and the temperature dependence of the spin-lattice interaction is in qualitative agreement with theory.

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