Iron(57) Mössbauer Effect and Spin Correlation Time in Ammonium Hexafluoroferrate(III)

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The Mössbauer effect studies of ^{57}Fe in the paramagnetic $(NH_4)_3FeF_6$ reported by Mørup and Thrane (*Phys. Rev. B* **8**, 1020, 1973) were extended to high values of applied external magnetic field up to 50 kG and low temperatures. At 4.2 K the Mössbauer spectra of partly magnetized $(NH_4)_3FeF_6$ show a broadening of the hyperfine structure lines, reflecting the paramagnetic spin fluctuations. The results are discussed in terms of the theoretical calculations given by Wegener (*Z. Phys.* **186**, 498, 1965). The data can be fitted using a maximum internal field $H_{max} = 603(5)$ kG and two atomic spin correlation times $\tau_c \simeq \tau_c' = 0.22$ nsec. It is concluded that in $(NH_4)_3FeF_6$ the electronic relaxation is independent of the temperature. © 1985 Academic Press, Inc.

Introduction

For ammonium hexafluoroferrate(III) $(NH_4)_3FeF_6$ and some other strongly related compounds, as the cubic Elpasolites $A_2^I Na$ FeF_6 (A^I = K, Rb, Cs), an ionic disorder model is discussed (*1*). The assumption that the cubic crystal symmetry might only be a result of the positional disorder of the FeF_6^{3-} ions (*2*) is supported by the Mössbauer evidence (*3*) revealing a very strong line broadening in the spectra incompatible with an octahedral ionic symmetry (*4*). This line broadening in the spectra can be explained by a statistical distribution of differently distorted FeF_6^{3-} ions causing a statistical distribution of the electric field gradients at the Fe^{3+} position (*3*). However, from a study of the lineshape of $(NH_4)_3FeF_6$ in moderate external magnetic fields, Mørup and Thrane (*5*) inferred the anomalous line broadening by electronic relaxation. In the following this study is extended to higher values of the applied external magnetic field and to lower temperatures, assuming that at 4.2 K the electronic spins of the Fe^{3+} ions are considerably polarized, inducing a resolved magnetic hyperfine splitting. These results which one might expect may be discussed in the light of the theoretical relaxation model given by Wegener (*6*).

Experimental

The sample of $(NH_4)_3FeF_6$ was prepared as described in (*4*). The Mössbauer measurements were performed by use of a 20-mCi source of ^{57}Co in rhodium. An ordinary constant-acceleration Mössbauer spectrometer was used in connection with a multichannel analyzer in the multiscaling

mode. The data were handled on a computer TR 440 (Telefunken), using a least-squares-fitting procedure for analyzing the electronic relaxation processes as stated below.

A Mössbauer absorption linewidth at half-height of 0.25 mm/sec was obtained using an iron metallic absorber. The $(NH_4)_3FeF_6$ absorber investigated was a polycrystalline sample containing 10 mg/ cm^2 of natural iron. With the aid of a superconducting magnet an external magnetic field was applied only to the absorber. The direction of the field was normal to the plane of the absorber and parallel to the γ-ray propagation direction. Field strengths from 0 to 50 kG were used. During the measurements, source and absorber were kept at 4.2 K.

Results and Discussion

X-Ray powder diffraction work by Steward and Rooksby (7) for $(NH_4)_3FeF_6$ showed a face-centered cubic lattice and a tetragonal lattice at room temperature and at 93 K, respectively. The phase transition was found at 263 K in a Mössbauer linewidth study by Mørup and Thrane (5). In the low-temperature phase, the quadrupole splitting causes an additional line broadening. However, as in the cubic phase, one supposes that the electronic relaxation affects the lineshape in a complex way (8). The mechanism of the phase transition was discussed by Massa (4), who assumed that formation of H-bonds is responsible for the crystallographic transition and proposed a mechanism of simultaneous rotation of all FeF_6^{3-} octahedra and NH_4^+ tetrahedra, which may lead to a preponderant tetrahedral coordination of the NH_4^+ ions suitable to strong hydrogen bonding. In a similar way the phase transition in $(NH_4)_2NaFeF_6$ at 159.5 K was explained by Pebler et al. (9). With the aid of temperature-dependent X-ray powder photographs, Massa (4) re-

vealed that the site symmetry of FeF_6^{3-} ion in ammonium hexafluoroferrate(III) is lower than axial in the low-temperature phase below 263 K. Obviously, the tetragonal symmetry given in the literature (7) yields only the pseudosymmetry of the lattice. This is also in agreement with the Raman data (1). However, the observed deviation from axial symmetry is very small (a = 9.009 Å; b = 9.013 Å; c = 9.268 Å; α = 90.26°; β = 90.28°; γ = 90.28° at 260 K); so we can assume in the following that the electric field gradient (efg) is axially symmetric in a good approximation.

I. Mössbauer Spectrum of $(NH_4)_3FeF_6$ at 4.2 K and $H_{ext} = 0$

The Mössbauer spectrum obtained at 4.2 K is an asymmetric quadrupole pattern consisting of two unresolved lines of different shapes (Fig. 1). The spectrum was computer-fitted with two Lorentzian lines of different widths Γ_i and amplitudes A_i. The values of the linewidths and ratio of the amplitudes are given in Table I. The area under both absorption lines are nearly the
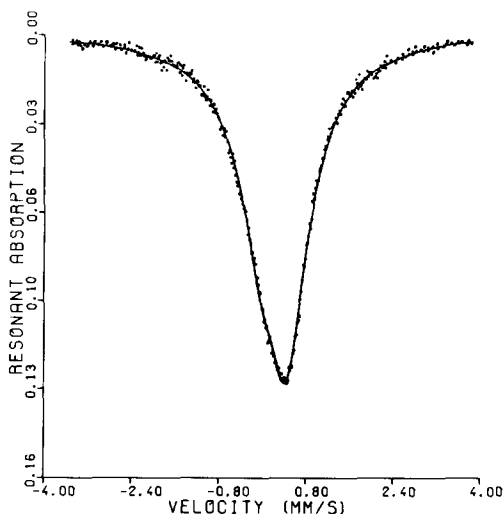

FIG. 1. Mössbauer spectrum of $(NH_4)_3FeF_6$ obtained at 4.2 K. The solid curve was also fitted to the relaxation model given in (18) with $\tau_c \simeq 0.1$ nsec.

TABLE I

RESULTS OF THE QUADRUPOLE SPLITTING ΔE^Q, ISOMER SHIFT δ, LINEWIDTHS Γ_1 AND Γ_2, AND THE CORRESPONDING AMPLITUDE RATIO A_1/A_2 OF A COMPUTER FIT AT DIFFERENT TEMPERATURES T

T (K)	ΔE^Q (mm/sec)	δ (mm/sec)	Γ_1 (mm/sec)	Γ_2 (mm/sec)	A_1/A_2
300.0	0.37(1)	0.45(1)	0.92(2)	0.92(2)	1.01
80.0	0.45(3)	0.27(1)	1.29(5)	0.98(5)	0.75
4.2	0.44(4)	0.27(2)	1.24(5)	0.89(5)	0.72

same. The quadrupole splitting is $\Delta E^Q = 0.44(4)$ mm/sec, and the center of the lines indicates an isomer shift δ = 0.27(3) mm/sec relative to Fe in Rh at 4.2 K. The δ-value is characteristic for Fe^{3+}-ferric compounds. Measurements of the magnetic susceptibility revealed the existence of the Curie–Weiss law between 4.2 K and room temperature and from this an averaged magnetic moment of 5.90(5) μ_B was calculated which is in agreement with the spin-only value expected for a paramagnetic compound with Fe^{3+} in the $^6S_{5/2}$ state (10).

A quadrupole-split Mössbauer spectrum of polycrystalline isotropic absorbers can become asymmetric for two reasons: first, the Karagin–Goldanskii effect, which is based on the anisotropy of the Debye–Waller factor in connection with the angular distribution of the γ-radiation, and second, the relaxation of paramagnetic ions causing fluctuating magnetic fields. The former effect will give lines with different areas and equal shapes, while relaxation will result in lines with different shapes and equal areas. From the data in Table I, it is obvious that the second effect influences the shape of the spectrum at 4.2 K in agreement with the results of Mørup and Thrane (8) at 78 K.

The asymmetric Mössbauer spectrum reflects the fact that the $|\pm\frac{3}{2}\rangle \to |\pm\frac{1}{2}\rangle$ transitions, which give rise to the low-velocity component of the quadrupole doublet, relax at higher frequencies than do the $|\pm\frac{1}{2}\rangle \to$ $|\pm\frac{1}{2}\rangle$ and $|\pm\frac{1}{2}\rangle \to |\pm\frac{1}{2}\rangle$ transitions, which cause the high-velocity component because of their differing Zeeman precession frequencies. From this we conclude that the electric field gradient is negative, meaning that the FeF_6^{3-} octahedron is compressed along the nearly symmetry axis. This is in agreement with the idea of formation of strong N–H · · · F bonding bridges perpendicular to the symmetry axis (within the (a,b) plane) as explained above.

This spectrum of $(NH_4)_3FeF_6$ at 4.2 K can also be fitted on the basis of the well-known electronic relaxation model given by Blume (11). However, in the case of fast relaxation we can reveal more precisely the relaxation time with the appearance of an external magnetic field and in the light of the Wegener model (6).

II. Mössbauer Spectra at 4.2 K in an External Magnetic Field up to 50 kG

Figure 2 shows the measured hfs spectra of $(NH_4)_3FeF_6$ in a external magnetic fields H_{ext} up to 50 kG. The direction of the magnetic field was parallel to the propagation direction; therefore, the spectra consist of two outer and two inner pairs of absorption lines. The observed separations and the linewidths of the inner and outer absorption lines ΔV_i, ΔV_0 and Γ_i, Γ_0, respectively, are given for all our measurements in Table II. Reducing the external magnetic field H_{ext}, the separations decrease and the outer pair of lines appear progressively much broader in respect to their linewidths Γ_0 and smaller in amplitude. In sharp contrast, the widths Γ_i and amplitudes of the inner pair of lines nearly appear to be independent of H_{ext} within statistical error. A similar behavior was observed in the case of ferric alum for the first time (12).

The broadening of the outer lines as a function of an external magnetic field may be an indication of time-dependent magnetic hyperfine field fluctuations, which will be treated in the following. However, in
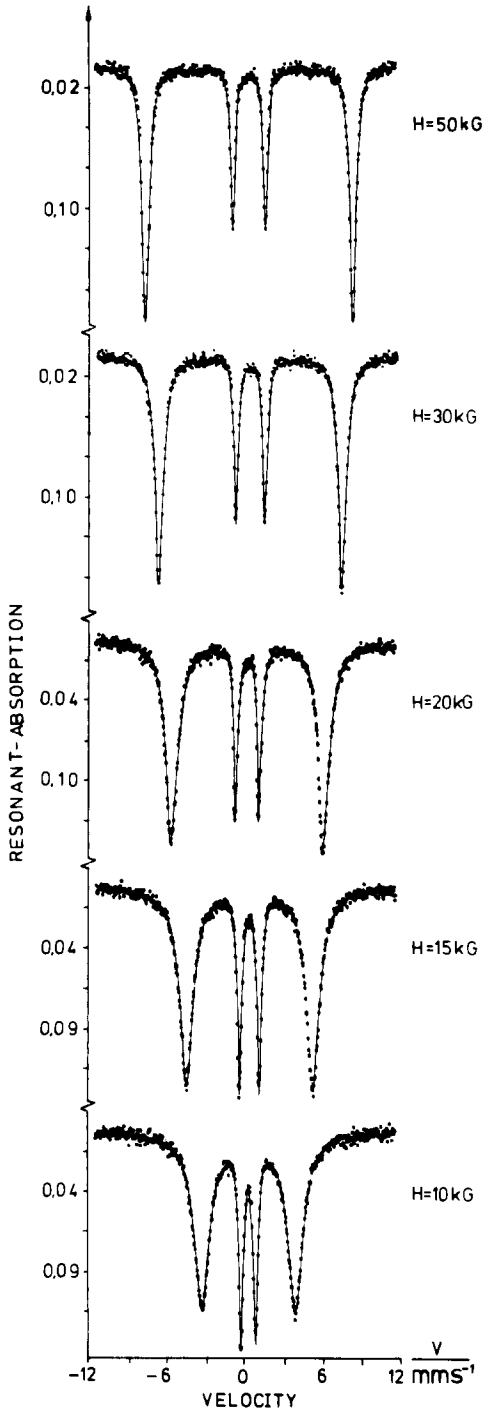
FIG. 2. The hfs spectra for $(NH_4)_3FeF_6$ are shown for the external magnetic fields H_{ext} between 10 and 50 kG at 4.2 K.

this procedure we have to realize that in our polycrystalline sample the efg principal axis is randomly distributed in respect to the magnetic field direction causing a definite and constant contribution $\Delta\Gamma_Q$ to the linewidths Γ_0 of the outer line pair. Considering the observed quadrupole splitting (Table I) and integrating $\overline{q(\theta)}$ over all angles θ to the quantization axis (13), we can estimate $\Delta\Gamma_Q$ = 0.17(3) mm/sec.

III. Magnetic Hyperfine Structure in the Presence of Rapid Fluctuating Longitudinal Relaxation and Spin Correlation Time

A common spin Hamiltonian of a high-spin Fe^{3+} ion in a low (axial, orthorhombic) symmetry can be written as a sum of the electronic Zeeman interaction $\hat{H}_z$, the crystal field interaction $\hat{H}_{cf}$, the magnetic dipole–dipole interaction $\hat{H}_{dd}$, the exchange interaction $\hat{H}_{ex}$, and the hyperfine interaction $\hat{H}_{hf}$. $\hat{H}_{ex}$ may be neglected because the distance between the magnetic ions exceeds about 6.44 Å in $(NH_4)_3FeF_6$ (4). Because of the spherically symmetric distribution of the electronic charge, the crystal field interaction $\hat{H}_{cf}$ can be expressed as a sum of an axial term $\hat{H}_{ax}$, a rhombohedral term $\hat{H}_{rh}$, and a cubic term $\hat{H}_{cub}$. Considering our approximation of any nearly axially symmetric efg, the dominating term in $\hat{H}_{cf}$ may be $\hat{H}_{ax}$ which may give rise to a splitting of the ionic states of several cm^{-1}, whereas $\hat{H}_{cub}$ normally contributes with less than 0.1 cm^{-1} (14).

The electronic Zeeman interaction has the form

$$\hat{H}_z = g\mu_B\mathbf{H}_{ext} \cdot \mathbf{S} \qquad (1)$$

where μ_B is the Bohr magneton and g is close to the free electron value in ferric compounds.

The dipole–dipole interaction $\hat{H}_{dd}$

$$\hat{H}_{dd} = g\mu_B\mathbf{H}_d \cdot \mathbf{S} \qquad (2)$$

can be described in terms of an internal

TABLE II

The Observed Separations of the Absorption Minima ΔV_0 and ΔV_i, the Linewidths Γ_0 and Γ_i for the Outer and Inner Line Pairs, Respectively, the Averaged Total Magnetic Hyperfine Field H_{Tot} (See Text) and the Calculated Values of $\overline{h^2}/\overline{H^2_{max}}$ and $\overline{h^3}/\overline{H^3_{max}}$ (6) are Given to the Corresponding External Magnetic Field H_{ext} and the Reduced Magnetization M/M_{max}

H_{ext} (kG)	$\dfrac{M}{M_{max}}$	ΔV_0 (mm/sec)	ΔV_i (mm/sec)	Γ_0 (mm/sec)	Γ_i (mm/sec)	ΔV_0^* (mm/sec)	ΔV_i^* (mm/sec)	$\dfrac{\Delta V_0^*}{\Delta V_i^*}$	H_{Tot} (kOe)	$\dfrac{\overline{h^2}}{\overline{H^2_{max}}}$	$\dfrac{\overline{h^3}}{\overline{H^3_{max}}}$
3.0	0.11	2.50(5)	0.38(2)	1.50(5)	0.42(3)	2.60	0.40	6.50	80(6)	0.329	0.033
5.0	0.18	3.90(5)	0.63(2)	1.53(5)	0.40(3)	4.06	0.65	6.25	127(6)	0.323	0.051
7.5	0.27	5.84(5)	0.92(2)	1.53(5)	0.38(3)	6.08	0.96	6.33	188(6)	0.311	0.0712
10.0	0.35	7.23(5)	1.15(2)	1.44(5)	0.38(3)	7.55	1.20	6.29	235(5)	0.294	0.0876
15.0	0.49	9.81(5)	1.53(2)	1.24(5)	0.35(3)	10.29	1.61	6.39	317(5)	0.256	0.1045
17.5	0.55	11.14(4)	1.74(2)	1.16(5)	0.39(3)	11.70	1.83	6.39	360(4)	0.235	0.1059
20.0	0.61	11.80(3)	1.84(1)	1.14(5)	0.34(3)	12.44	1.94	6.41	384(4)	0.213	0.1038
25.0	0.69	13.26(3)	2.09(1)	1.03(5)	0.38(3)	14.16	2.21	6.41	437(3)	0.174	0.0923
30.0	0.76	14.17(2)	2.24(1)	0.88(3)	0.35(3)	15.13	2.39	6.33	470(3)	0.140	0.0766
35.0	0.81	14.93(2)	2.36(1)	0.86(3)	0.35(3)	16.04	2.53	6.34	498(3)	0.113	0.0611
40.0	0.85	15.50(2)	2.44(1)	0.73(3)	0.34(3)	16.79	2.64	6.36	520(3)	0.091	0.0477
50.0	0.90	16.05(2)	2.52(1)	0.68(3)	0.32(3)	17.66	2.77	6.37	550(2)	0.061	0.0285
	1.00[a]					19.43[a]	3.07[a]		603(10)[a]		

[a] Extrapolated to $M/M_{max} \rightarrow 1$.

magnetic field $\mathbf{H_d}$, fluctuating randomly. The value of $\mathbf{H_d}$ at the Fe^{3+} position is a function of the arrangement of the neighboring ions and the direction of their magnetic dipole moments (15). Qualitatively, the term $\hat{H}_{dd}$ induces a fluctuation of the atomic spins described by a relaxation time between transitions among the eigenstates of the Fe^{3+} ions. $\mathbf{H_d}$ is of the order of 0.1–10 kG, depending on the separation of the magnetic ions.

The hyperfine interaction between the iron nucleus and its surroundings may be expressed by the Hamiltonian

$$\hat{H}_{hf} = \hat{H}_Q + \hat{H}_M(t) \qquad (3)$$

where $\hat{H}_Q$ represents the quadrupole interaction assuming it is time independent. $\hat{H}_M(t)$ describes the magnetic interactions

$$\hat{H}_M(t) = -g_N \cdot \mu_N \mathbf{I}(\mathbf{H_e}(t) + \mathbf{H_{ext}})$$
$$= g_N \cdot \mu_N \mathbf{I}(\mathbf{H_k}(t)$$
$$+ \mathbf{H_d}(t) + \mathbf{H_{ext}}) \qquad (4)$$

where g_N is the gyromagnetic factor of the nuclear state and $\mu_N = 3.15$ eV/G is the nuclear magneton. The electron–nucleus magnetic interaction is assumed to be iso-tropic and is described by an effective hyperfine field $\mathbf{H_k}(t) = A \cdot \mathbf{S}(t)$. $\mathbf{H_{ext}}$ is the applied magnetic field which defines the z axis.

Now we can predict the direction of the fluctuation of the magnetic hyperfine field $\mathbf{H_e}$. In the light of our previous discussion of the essential interaction terms, it is valid for $(NH_4)_3FeF_6$: $\hat{H}_Q \neq 0$ and $\hat{H}_{ax} \gg \hat{H}_{dd} + \hat{H}_{ex} + \hat{H}_{cub} + \hat{H}_{rh}$ (see (8)). In the absence of an applied magnetic field $\mathbf{H_{ext}}$, $\mathbf{H_e}$ fluctuates along the z direction defined by the efg principal axis. For large applied fields, one obtains $\hat{H}_z \gg H_{ax}$; and the hyperfine field now fluctuates along the direction of $\mathbf{H_{ext}}$. Now $H_e(t)$ can be divided up into two parts

$$H_e(t) = \overline{H} + h(t). \qquad (5)$$

$\overline{H}$ is the average of $H_e(t)$ during a time interval which is long, compared with the spin correlation time. The $h(t)$ is the remaining part of fluctuations and the instantaneous magnetic field deviation from $\overline{H}$. Because of the results that the magnetization of $(NH_4)_3FeF_6$ is a function of H_{ext} at 4.2 K, which is described by a Brillouin function of $S = \frac{5}{2}$ and $g = -2$, the electronic spins of the Fe^{3+} ions in $(NH_4)_3FeF_6$ are considera-

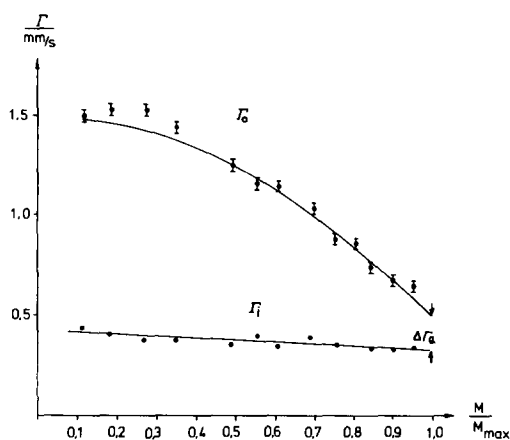FIG. 3. The total linewidths at half height of the outer and inner lines in the Mössbauer spectra of $(NH_4)_3FeF_6$, respectively, as a function of the reduced magnetization M/M_{max}. The drawn curve of the upper data is calculated from (6).

bly polarized by an external magnetic field; and the reduced magnetization M/M_{max} is proportional to the time averaged value $\overline{H}/H_{max}$. At a given instant of time, the magnetic field at the Fe^{3+} nucleus is then essentially given by the sum of the external magnetic field H_{ext} and the field calculated from the magnetic hyperfine splittings in the Mössbauer spectra.

In Fig. 3 the experimentally measured linewidths of the inner and outer line pairs Γ_i and Γ_0, and in Fig. 4 the reduced splittings $\Delta V_i^*/\Delta V_{im}^*$ and $\Delta V_0^*/\Delta V_{0m}^*$ are plotted versus M/M_{max}, respectively (see Table II). The experimentally measured splittings ΔV_0 and ΔV_i contain a certain contribution from the interaction of the externally applied magnetic field with the nucleus which is in an antiparallel direction to the hyperfine field H_e. Therefore, in order to get the total magnetic hyperfine field H_{Tot} we have added to ΔV the corresponding velocity $\Delta V(H_{ext})$ yielding ΔV^*. It may be seen from Fig. 4 that in contrast to our investigations of $(NH_4)_2NaFeF_6$ (9) one notices for $(NH_4)_3FeF_6$ some deviations from the linearity of ΔV_i^* and ΔV_0^* as a function of M/M_{max}. However, the ratio of $\Delta V_0^*/\Delta V_i^*$ is

within statistical error nearly constant (Table II). The extrapolation of ΔV_i^* to magnetic saturation $M/M_{max} \rightarrow 1$ yields $\Delta V_{im}^* = 3.07$ mm/sec, which corresponds to an internal magnetic hyperfine field of 603(10) kOe. The observed nonlinearity of $\Delta V(M/M_{max})$ may be caused by the small deviation from the axial symmetry.

Wegener has developed a theory for Mössbauer spectra in the presence of rapid longitudinal relaxation (6). In this theory it is assumed that the quadrupole splitting is zero. This model is easily extended to the case where an axially symmetric quadrupole interaction is present. Wegener (6) found that for fast fluctuations induced by the magnetic dipole–dipole interaction among the paramagnetic ions, the lines have Lorentzian shape but are broadened by

$$\Delta\Gamma = 2\nu^2(m_e, m_g)h^{-1}\overline{h^2}(t) \cdot \tau_c \qquad (6)$$

and shifted from the normal positions ΔV (defined by $H_e + H_{ext}$) by

$$\Delta = \tfrac{2}{3}\nu^3(m_e, m_g)h^{-2}\overline{h^3}(t)\tau_c'^2 \qquad (7)$$
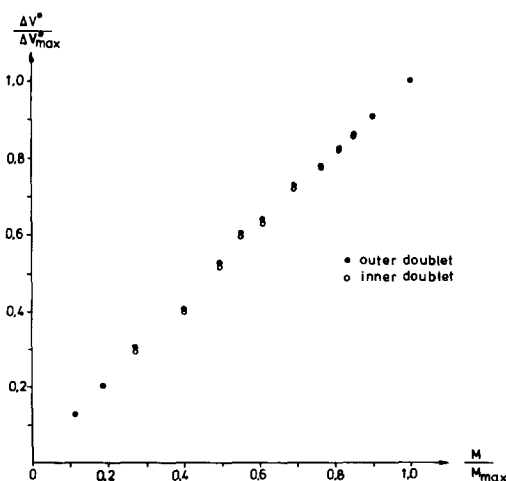

FIG. 4. The quantities $\Delta V_0^*/\Delta V_{0max}^*$ and $\Delta V_i^*/\Delta V_{imax}^*$ are plotted versus M/M_{max} (see text and Table II). The extrapolation to magnetic saturation yields $\Delta V_{0max}^* = 19.43$ mm/sec and $\Delta V_{imax}^* = 3.07$ mm/sec. The internal magnetic hyperfine field estimated from these saturation values of ΔV_{0max}^* and ΔV_{imax}^* is $H = 603(10)$ kOe.

with $\nu(m_e,m_g) = g_e\mu_N m_e - g_g\mu_N m_g$. The $\tau_c \simeq \tau'_c$ is the longitudinal correlation time of the magnetic field fluctuations. Note that ν enters the equation for $\Delta\Gamma$ and Δ with the second and third power, respectively, so that the outer lines have a ν^2 value 38 times larger and a ν^3 value 242 times larger than the inner absorption lines. Therefore, the influence of ν upon the lineshape and position of the inner absorption lines is negligibly small. The formulae for $\Delta\Gamma(m_e,m_g)$ and $\Delta(m_e,m_g)$ are approximations obtained under the assumptions that the atomic spin Lamor precession is much faster than the Lamor precession of the nucleus and that the correlation time τ_c is not larger than the precession time of the nucleus. As an example the sample of $(NH_4)_3FeF_6$ may be described on the basis of these assumptions.

From Eq. (6) the line broadening of the outer lines caused by the time-dependent fluctuations of the magnetic hyperfine field may be written as

$$\Delta\Gamma_0 = \Gamma_0 - \Gamma_i - \Delta\Gamma_Q$$
$$= 0.037\overline{h^2} \cdot \tau_c \frac{\text{mm/sec}}{(G)^2 \text{sec}^2} \quad (8)$$

where $\Delta\Gamma_Q$ is the difference between $\Gamma_0 - \Gamma_i$ in the limit of magnetic saturation $M/M_{max} \to 1$ and where $\overline{h^2}(t)$ and $\overline{h^3}(t)$ approach zero. From Fig. 3 one can see that the value of $\Delta\Gamma_Q(M/M_{max} \to 1) = 0.18$ mm/s is in a fair agreement with our previous estimation at page 6. The fluctuating part of the field ($\overline{h^2} = \overline{f \cdot H^2_{max}}$) in Eq. (8) is given in $(\text{Gauss})^2$ and τ_c in seconds. H_{max} has the meaning $H_e(M/M_{max} \to 1) + H_{ext} = 603$ kOe. Calculating $\overline{h^2}$ and $\overline{h^3}$ from Eq. (32) in (6), we get from the least-squares-fitting procedure of Eq. (6) (with the border conditions mentioned above) to our experimental data of $\Gamma_0(M/M_{max})$, the upper curve shown in Fig. 3. This fit which seems to be quite a good approximation to the data gives a correlation time of $\tau_c = 0.22$ nsec.

From Eq. (7) the shift Δ of the outer absorption lines from their normal positions can be formulated as

$$\Delta = 14.6 \cdot \overline{h^3} \cdot \tau^2_c \frac{\text{mm/sec}}{(G)^3 \text{sec}^2}. \quad (9)$$

With $\overline{h^3}$ in Table II and assuming the spin correlation time about $\tau'_c = 0.22$ nsec we estimate a shift $\Delta = 0.016$ mm/sec at $M/M_{max} = 0.61$, which is nearly outside of the accuracy of our measurements. The correlation time of 0.22×10^{-9} sec does not affect the Δ-shift defined in Eq. (7).

We emphasize that although the principal axis of the efg is randomly distributed in respect to the magnetic field direction H_{ext}, there should be, besides the observed line broadening $\Delta\Gamma_Q$, a rest of quadrupole splitting, which is not noticeable in our spectra. Within statistical error, the splittings ΔV_0 are nearly equidistant. In polycrystalline samples as in the low-temperature phase of $(NH_4)_3FeF_6$, there may be a smaller probability for the applied field to be nearly parallel to the symmetry direction than to be nearly perpendicular to this direction. Therefore, for $\hat{H}_z \gg H_{cf}$ the spectra may resemble those expected where the angle between the hyperfine field direction and the efg principal axis is between 0 and 90°, averaging the rest of quadrupole splitting.

For the cubic phase, Mørup and Thrane (8) found a spin correlation time of $\tau_c = 1.19 \times 10^{-10}$ sec, which is in fairly good agreement with our relaxation time of 2.2×10^{-10} sec for the low-temperature phase, revealed from the line broadening of $\Delta\Gamma_0$ as a function of H_{ext}. This conformity may be an indication that the electronic relaxation effect of the atomic spins in $(NH_4)_3FeF_6$ is temperature independent and that the spins of the Fe^{3+} ions fluctuate along the principal axis of the efg in zero external magnetic field. Otherwise, if the hyperfine field would fluctuate perpendicular to this direction, we would expect a temperature dependence of the correlation time τ_c (16).

Finally, we remark that in comparison

with the results discussed above, the smaller spin correlation time $\tau_c = 0.04$ nsec previously observed in $(NH_4)_2NaFeF_6$ (9), can be explained by the shortening of the Fe–Fe separation from 6.44 Å in $(NH_4)_3FeF_6$ to 5.99 Å in $(NH_4)_2NaFeF_6$, causing a stronger dipole–dipole interaction and therefore a faster spin relaxation. This is in agreement with most recent measurements of the ^{57}Fe Mössbauer effect in $(NH_4)_3Fe_xAl_{1-x}F_6$ showing an increase of the spin correlation time by reducing the dipole–dipole interaction with increased Al^{3+} concentration. For $x = 0.5$ and $M/M_{max} = 0.61$ we estimate from the spectra $\tau_c = 0.5(1)$ nsec and a Δ shift of $\Delta = 0.12(2)$ mm/sec. Detailed investigations of this behavior of the spin correlation time and its influence on the linebroadening observed in the Elpasolites (3), formally mentioned, are in progress (17).

Acknowledgment

References

1. K. MORIYA, T. MATSUO, H. SUGO, AND S. SEKI, *Bull. Chem. Soc. Jpn.* **50**, 1920 (1977).
2. D. BABEL, *Struct. Bonding* **3**, 23 (1967).
3. J. PEBLER, K. SCHMIDT, R. HAEGELE, AND D. BABEL, *Z. Naturforsch. B* **31**, 1039 (1976).
4. W. MASSA, Habilitationsschrift: "Strukturchemische Anomalien bei Fluorometallaten," Marburg 1982.
5. S. MØRUP AND N. THRANE, *Phys. Rev. B* **8**, 1020 (1973).
6. H. WEGENER, *Z. Phys.* **186**, 498 (1965).
7. E. G. STEWARD AND H. P. ROOKSBY, *Acta Crystallogr.* **6**, 49 (1953).
8. S. MØRUP AND N. THRANE, *Phys. Rev. B* **8**, 1020 (1973).
9. J. PEBLER, E. HERDTWECK, W. MASSA, AND R. SCHMIDT, "Solid State Chemistry 1982, Proceedings of the Second European Conference, Veldhoven, The Netherlands" (1982).
10. J. PEBLER, unpublished magnetic susceptibility measurements.
11. M. BLUME, *Phys. Rev. Lett.* **14**, 96 (1965).
12. F. E. OBENSHAIN, L. D. ROBERTS, C. F. COLEMAN, D. W. FORSTER, AND J. V. THOMSON, *Phys. Rev. Lett.* **14**, 365 (1965).
13. P. GÜTLICH, H. RUMMEL, AND H. SPIERING, *J. Phys. Colloq.* (Ornay, *Fr.*) **41**, Cl-185 (1980).
14. S. MØRUP, thesis: "Paramagnetic and Superparamagnetic Relaxation Phenomena Studied by Mössbauer Spectroscopy," Lyngby, Denmark (1981).
15. A. ABRAGAM AND B. BLEANEY, "Electron Paramagnetic Resonance of Transition Ions," Oxford Univ. Press (Clarendon), London/New York (1970).
16. M. BLUME AND J. A. TJON, *Phys. Rev.* **165**, 446 (1968).
17. J. PEBLER, unpublished measurements, 1983.
18. J. PEBLER, *Phys. Status Solidi A* **78**, 589 (1983).