

Crystal-Field Studies of Fe²⁺ in FeNb₂O₆ by the Mössbauer Effect*

M. EIBSCHÜTZ

Department of Electronics, The Weizmann Institute of Science, Rehovoth, Israel

AND

U. GANIEL†

Department of Physics, The Weizmann Institute of Science, Rehovoth, Israel

AND

S. SHTRIKMAN

Department of Electronics, The Weizmann Institute of Science, Rehovoth, Israel

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Mössbauer absorption spectra in FeNb₂O₆ were measured over a temperature range from 25 to 950°K. Assuming a certain orbital-level scheme, the effect of the spin-orbit interaction on the eigenfunctions and on the energy levels was calculated. The results obtained were used to calculate the temperature dependence of the quadrupole splitting of the Mössbauer line, with the crystal-field splitting δ as one parameter and the spin-orbit coupling λ as another. By fitting the theoretical expression to the experimental results we get: $\delta = (520 \pm 20)^\circ\text{K}$, $\lambda = (-90 \pm 10)^\circ\text{K}$.

INTRODUCTION

AS part of a series of investigations on divalent iron compounds being carried out in our laboratories, we studied FeNb₂O₆ using the Mössbauer effect. Because of a deviation from cubic symmetry at the site of the Fe²⁺ ion, the Mössbauer absorption line is split by the interaction of the quadrupole moment Q of the first excited level of the Fe nucleus, with the electric field gradient (EFG) at that site. This splitting is temperature-dependent, and from its temperature dependence one can deduce some crystal-field parameters, if some information on the point symmetry at the lattice site of the Fe²⁺ ion is available. It was found that in this specific case, the spin-orbit interaction is of major importance, so that it was essential to take it into account in the interpretation of the results.

EXPERIMENTAL

FeNb₂O₆ was prepared by mixing Fe₂O₃, Nb₂O₅, and Fe in stoichiometric proportions. The mixture was heated to the temperature of 1050°C in an evacuated silica capsule and kept there for 24 h.

X-ray powder photographs were taken using a Norelco Straumanis camera with a diameter of 114.6 mm, and cobalt radiation filtered through an iron foil. The patterns obtained contained no lines except for those consistent with the known space group of this material,¹ namely $Pcam(D_{2h}^{14})$. Lattice constants were calculated by Cohen's analytical least-squares method,² using the CDC 1604 computer. The results are given in

Table I, where Brandt's data¹ are also reproduced for comparison.

The Mössbauer spectra were obtained using a constant-velocity automatic-recording spectrometer.³ The absorber was contained in an improved version of a cryofurnace described by Sharon and Treves,⁴ and the spectra were taken over a temperature range between 25 and 950°K. The source was ⁵⁷Co in Pd.⁵ The spectra were recorded directly on an x - y recorder, and the quadrupole splitting was determined from the distance between the centers of gravity of the two peaks. The results are given in Fig. 1, where the experimental points give the quadrupole splitting in mm/sec versus temperature. At 80°K we found $|\frac{1}{2}e^2qQ| = (2.35 \pm 0.03)$ mm/sec, while at 1000°K we get (0.64 ± 0.03) mm/sec. This rather strong temperature dependence can be explained easily by a relatively small crystal-field splitting of the electronic levels.

THEORETICAL INTERPRETATION

FeNb₂O₆ has an orthorhombic structure with four molecules per unit cell.⁶ All four Fe²⁺ ions are in equivalent positions. Each ferrous ion is surrounded by a nearly regular octahedron of oxygen atoms. The point

TABLE I. Lattice constants of FeNb₂O₆ (in Å).

	Brandt (Ref. 1)	Present work
a	5.616	5.616 ± 0.003
b	13.96	14.07 ± 0.02
c	4.992	4.978 ± 0.003

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¹ K. Brandt, Arkiv. Kemi, Mineral. Geol. A17, No. 15 (1943).

² M. V. Cohen, Rev. Sci. Instr. 6, 68 (1935).

³ Mössbauer Effect Spectrometer, produced by "Elron" Electronics Industries, Haifa, Israel.

⁴ B. Sharon and D. Treves, Rev. Sci. Instr. 37, 1252 (1966).

⁵ Purchased from New England Nuclear Corporation, U.S.A.

⁶ R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1951), Vol. II.

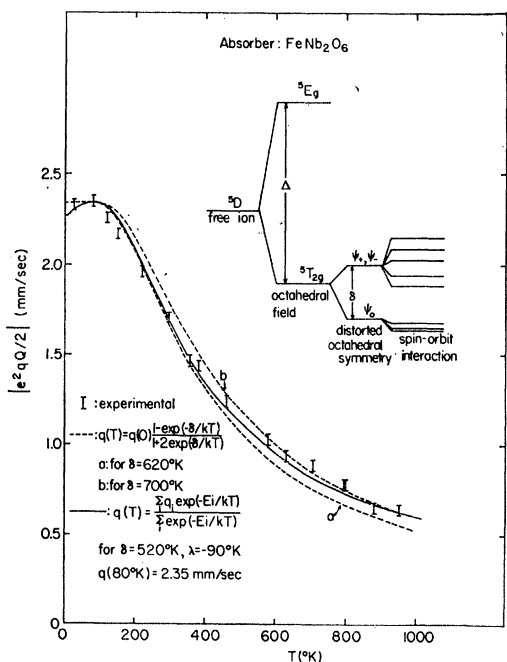


FIG. 1. Quadrupole splitting as a function of temperature. In the insert we show the assumed orbital-level scheme of Fe^{2+} in FeNb_2O_6 as well as the splitting due to the spin-orbit interaction (not to scale).

symmetry at the site of the Fe^{2+} ion gives only one twofold axis.⁷

In an octahedral field, the orbital ground state of the free Fe^{2+} ion 5D splits into two levels, the lower being the orbital triplet T_{2g} , and the upper is the orbital doublet E_g . These two are separated by an amount Δ , which is typically of the order of 10 000 cm^{-1} in ferrous compounds.⁸ The lower triplet wave functions can be written in cubic axes as (normalization factors omitted) xy , yz , and xz .⁹

We first chose the z axis perpendicular to the twofold axis, which then bisects the angle between the x and y axes. If we form the combinations

$$\begin{aligned}\phi_1 &\propto xz + yz, \\ \phi_2 &\propto -xz + yz, \\ \phi_3 &\propto xy,\end{aligned}\quad (1)$$

we find that ϕ_1 , ϕ_2 , and ϕ_3 are eigenfunctions of the operator R_2 , which represents a rotation by π around the twofold axis, since

$$\begin{aligned}R_2\phi_1 &= -\phi_1, \\ R_2\phi_2 &= \phi_2, \\ R_2\phi_3 &= \phi_3.\end{aligned}\quad (2)$$

⁷ *International Tables for X-ray Crystallography* (Kynoch Press, Birmingham, England, 1952), Vol. I.

⁸ D. Palumbo, *Nuovo Cimento* **8**, 271 (1958).

⁹ C. J. Ballhausen, *Ligand Field Theory* (McGraw-Hill Book Company, Inc., New York, 1962).

A rotation of the axes by $\frac{1}{4}\pi$ around the z axis will give us the functions in the form

$$\begin{aligned}\phi_1 &\propto xz, \\ \phi_2 &\propto yz, \\ \phi_3 &\propto \frac{1}{2}(x^2 - y^2).\end{aligned}\quad (3)$$

For convenience in the calculation of the spin-orbit interaction, we rotate the axes by $\frac{1}{2}\pi$ around the new y axis, so that the twofold axis now becomes the z axis. Written in this coordinate system, our functions become

$$\begin{aligned}\phi_1 &\propto xz, \\ \phi_2 &\propto xy, \\ \phi_3 &\propto \frac{1}{2}(z^2 - y^2).\end{aligned}\quad (4)$$

Our calculations are all done in the subspace of the orbital triplet T_{2g} , since the splittings inside T_{2g} are much smaller¹⁰ than Δ and hence mixing from the states of E_g is entirely negligible.

The deviation from octahedral symmetry can, in principle, split T_{2g} into three levels. We see, however, from Eq. (2), that ϕ_2 and ϕ_3 can mix (belonging to the same irreducible representation of the subgroup C_2), but ϕ_1 cannot mix with any of them. We perform our calculations assuming ϕ_1 to be the (orbital) ground-state function, while ϕ_2 and ϕ_3 are assumed to represent energetically equal states (accidentally degenerate). The latter assumption simply leaves us with one crystal-field parameter to be determined, namely, the energy difference δ between the two orbital levels. The actual situation may be more complicated, since if we do not make this assumption, we have to add two more parameters, namely, the energy difference between the states ϕ_2 and ϕ_3 , and the amount of mixture between them.

It should be noted, however, that the crystal-field splittings within T_{2g} are rather small. Hence we have a case where the spin-orbit interaction cannot be neglected, its magnitude not being negligible compared to the crystal-field splitting.¹¹ It is this feature which we intend to stress in the present analysis, and hence we stick to the simplifying assumption mentioned above. It should be noted, however, that the theoretical curve thus derived is in very good agreement with the experimental points, so that the calculations made seem to give a rather good picture of the physical situation.

Writing the spin-orbit interaction matrix $\mathbf{L} \cdot \mathbf{S}$ in the manifold of the function ϕ_1 , ϕ_2 , and ϕ_3 gives us

$$\mathbf{L} \cdot \mathbf{S} = \begin{vmatrix} \phi_1 & \phi_2 & \phi_3 \\ 0 & \frac{1}{2}i(S^+ + S^-) & \frac{1}{2}(S^+ - S^-) \\ -\frac{1}{2}i(S^+ + S^-) & 0 & iS_z \\ -\frac{1}{2}(S^+ - S^-) & -iS_z & 0 \end{vmatrix}$$

¹⁰ This is easily seen from the fact that the quadrupole splitting at 950°K is about a quarter of its value at 80°K (see Fig. 1).

¹¹ See, e.g., the analysis for GeFe_2O_4 by Eibschütz *et al.*, *Phys. Rev.* **151**, 245 (1966).

where $S^\pm = S_x \pm iS_y$ and S_x, S_y, S_z are the usual spin-operator 5×5 matrices for $S=2$.

Transforming to a new set of functions:

$$\begin{aligned}\psi_0 &= \phi_1 = -(d_1 - d_{-1})/\sqrt{2}, \\ \psi_+ &= (i\phi_2 + \phi_3)/\sqrt{2} = \frac{3}{4}d_2 - \frac{1}{4}d_{-2} + \frac{1}{2}(\sqrt{\frac{3}{2}})d_0, \\ \psi_- &= (\phi_2 + i\phi_3)/\sqrt{2} = i(-\frac{1}{4}d_2 + \frac{3}{4}d_{-2} + \frac{1}{2}(\sqrt{\frac{3}{2}})d_0),\end{aligned}\quad (5)$$

where d_m are the eigenfunctions of L^2, L_z for $L=2, L_z=m$, respectively, we get

$$\mathbf{L} \cdot \mathbf{S} = \begin{vmatrix} \psi_0 & \psi_+ & \psi_- \\ 0 & -S^-/\sqrt{2} & iS^+/\sqrt{2} \\ -S^+/\sqrt{2} & S_z & 0 \\ -iS^-/\sqrt{2} & 0 & -S_z \end{vmatrix}. \quad (6)$$

Since the spin-orbit interaction $\lambda(\mathbf{L} \cdot \mathbf{S})$ leaves the ground-level orbital ψ_0 degenerate to first order, we used second-order degenerate perturbation calculation in order to get the energy levels. We calculated the perturbed eigenfunctions by the usual perturbation procedure, and using these functions we calculated the components of the EFG tensor in each of the 15 states of our subspace. This is done easily, using the immediate results

$$\begin{aligned}\langle \psi_0 | V_{xx} | \psi_0 \rangle &= \langle \psi_0 | V_{zz} | \psi_0 \rangle = -\frac{1}{2} \langle \psi_0 | V_{yy} | \psi_0 \rangle \\ &= (2/7)e\langle 1/r^3 \rangle, \\ \langle \psi_+ | V_{xx} | \psi_+ \rangle &= \langle \psi_+ | V_{zz} | \psi_+ \rangle = -\frac{1}{2} \langle \psi_+ | V_{yy} | \psi_+ \rangle \\ &= -(1/7)e\langle 1/r^3 \rangle, \\ \langle \psi_- | V_{xx} | \psi_- \rangle &= \langle \psi_- | V_{zz} | \psi_- \rangle = -\frac{1}{2} \langle \psi_- | V_{yy} | \psi_- \rangle \\ &= -(1/7)e\langle 1/r^3 \rangle\end{aligned}\quad (7)$$

for the nonvanishing components of the EFG tensor at the nucleus, where $\langle 1/r^3 \rangle$ is the average of the inverse cubic distance between the d electron and the nucleus.¹²

Because of the axial symmetry of the EFG tensor, the quadrupole splitting of the Mössbauer line is $|\frac{1}{2}e^2qQ|$, where $eq = V_{yy}$. Since the electronic relaxation times are expected to be much smaller than $|2h/e^2qQ|$ (which is of the order of 3.10^{-8} sec at room temperature), the EFG which the nucleus "feels" becomes a thermal average of the values of eq in the different states. Hence the EFG at temperature T can be written as

$$eq(T) = e \frac{\sum_i q_i \exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)}, \quad (8)$$

where

$$eq_i = \langle i | V_{yy} | i \rangle,$$

and E_i is the energy of the state $|i\rangle$.

¹² The direct contribution of neighboring ions (including the antishielding of the electronic core) to the EFG have been neglected in this discussion.

The sum (8) contains two parameters: the spin-orbit coupling λ and the energy difference δ between the (orbital) states ψ_\pm and ψ_0 . From computer calculations we found

$$\begin{aligned}\delta &= (520 \pm 20)^\circ\text{K}, \\ \lambda &= (-90 \pm 10)^\circ\text{K}\end{aligned}\quad (9)$$

to give the best fit to the experimental data. The sum (8) as a function of temperature is plotted in Fig. 1 (solid curve) for the above values of δ and λ , taking $eq(80^\circ\text{K}) = 2.35$ mm/sec.

In the insert in Fig. 1 we show the energy-level scheme which we get from these calculations. The ground level is nondegenerate, whereas all other levels are doubly degenerate. With the values (9) for δ and λ , the energies of the eight levels turn out to be (in $^\circ\text{K}$) 0, 19, 86, 501, 600, 680, 750, 813. It could thus be of interest to perform a specific-heat measurement on this compound.

The importance of the spin-orbit interaction is clearly manifested by the broken curves in Fig. 1, which show the results of the sum (8) when the spin-orbit interaction is neglected ($\lambda=0$), for $\delta=620^\circ\text{K}$ and $\delta=700^\circ\text{K}$. The first of those curves (for $\delta=620^\circ\text{K}$) fits the experimental results at low temperatures, but deviates from them considerably at high temperatures, while the opposite is true for the second ($\delta=700^\circ\text{K}$).

One interesting consequence of our calculations is the fact (already noted by Ingalls¹³), that for suitable values of the parameters the quadrupole splitting should have its maximum at a temperature different from 0°K , since for the ground state we get from first-order perturbation calculation

$$\begin{aligned}|\text{ground state}\rangle &= |\psi_0, S_z=0\rangle + \lambda \frac{\sqrt{3}}{\delta + \lambda} |\psi_+, S_z=1\rangle \\ &\quad + \lambda \frac{i\sqrt{3}}{\delta + \lambda} |\psi_-, S_z=-1\rangle,\end{aligned}$$

and hence

$$\langle V_{yy} \rangle = -\frac{4}{7}e\left\langle \frac{1}{r^3} \right\rangle \left[1 - 3\left(\frac{\lambda}{\delta + \lambda} \right)^2 \right]$$

at 0°K , whereas neglecting the spin-orbit interaction would naturally lead to $\langle V_{yy} \rangle = -(4/7)e\langle 1/r^3 \rangle$ at 0°K . It can be seen that our result at 25°K shows a slight decrease, but we were not able to check this point further at lower temperatures.

ACKNOWLEDGMENT

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¹³ P. Ingalls, Phys. Rev. **133**, A787 (1964).