

## Orbit-lattice interaction and Mössbauer quadrupole splitting of ferrous ions in ferrous diphenyl sulfoxide chlorate

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The effect of vibronic coupling between low-lying electronic states on the temperature dependence of the Mössbauer quadrupole splitting of  $\text{Fe}^{2+}$  ions in  $\text{Fe}[(\text{C}_6\text{H}_5)_2\text{SO}]_6(\text{ClO}_4)_2$  is theoretically analyzed over 4.2 to 340 K. This results in a better agreement between theoretical and experimental data. It shows that the orbit-lattice interaction is important for ferrous ions and its effect should be duly included in the interpretation of Mössbauer observables as a function of temperature.

### I. INTRODUCTION

The orbit-lattice interaction (or vibronic coupling) is an important factor in producing the temperature dependence of Mössbauer quadrupole splitting of  $^{57}\text{Fe}^{2+}$  ( $3d^6$ ,  $^5\text{D}$ ) ions in inorganic<sup>1,2</sup> and biological<sup>3,4</sup> systems. This interaction is expected to affect Mössbauer spectra as the nuclear energy levels are mainly produced by means of magnetic and electrostatic interactions with the ion's own electronic charge cloud, which by itself can be modulated by lattice vibrations. Sams and Tsin<sup>5</sup> have measured the Mössbauer quadrupole splitting ( $\Delta E_Q$ ) of  $\text{Fe}^{2+}$  ions in  $\text{Fe}[(\text{C}_6\text{H}_5)_2\text{SO}]_6(\text{ClO}_4)_2$  over 8.8 to 331 K, and to explain the results theoretically they have used the intraionic spin-spin coupling (i.e., the fine-structure term)  $\sim 23 \text{ cm}^{-1}$  along with spin-orbit coupling to modify the energy of the electronic states, which is rather unrealistic. For a free  $\text{Fe}^{2+}$  ion the strength of the spin-spin coupling is regarded to be  $< 1 \text{ cm}^{-1}$  (Refs. 6 and 7) and it should not be much different in various compounds. It is worth mentioning that while fitting  $\Delta E_Q$  vs  $T$  data, both Ingalls<sup>8</sup> and Gibb<sup>9</sup> have treated the effects of crystalline-fields and spin-orbit coupling on the quadrupole splitting in octahedral  $\text{Fe}^{2+}$  systems and omitted the intraionic spin-spin coupling because it has very little effect. Price, Johnson, and Maartense<sup>10</sup> have also ignored the intraionic spin-spin interaction because it is expected to be very small. It is therefore obvious that a reinterpretation of the observed data is needed. In the present work, an attempt has been made to explain the temperature dependence of  $\text{Fe}^{2+}$  quadrupole splitting in  $\text{Fe}[(\text{C}_6\text{H}_5)_2\text{SO}]_6(\text{ClO}_4)_2$  by taking into account the effect of orbit-lattice interaction as a perturbation over the static crystal-field potential which is expected to be important in this organometallic system with low Debye temperature. Such a study is supposed to elucidate the importance of orbit-lattice interaction in Mössbauer studies.

### II. ELECTRONIC STATES OF $\text{Fe}^{2+}$

In  $\text{Fe}[(\text{C}_6\text{H}_5)_2\text{SO}]_6(\text{ClO}_4)_2$ , the ferrous ions occupy tetragonally distorted octahedral sites<sup>5</sup> and experience a

strong crystal-field potential given by<sup>10,11</sup>

$$H_{\text{cr}} = B_4^0 [O_4^0 - 20\sqrt{2}O_4^3] + B_2^0 O_2^0 + \lambda L \cdot S, \quad (1)$$

where  $B_n^m$  and  $O_n^m$  ( $n=2,4$  and  $m=0,3$ ) are the static crystal-field parameters and Stevens' equivalent operators compiled by Orbach.<sup>12</sup> The first term refers to the strong octahedral crystal field which splits the  $^5\text{D}$  state of a free  $\text{Fe}^{2+}$  ion into a lower orbital triplet ( $^5T_{2g}$ ) and an upper orbital doublet ( $^5E_g$ ) with energy separation  $|180B_4^0| \simeq 9600 \text{ cm}^{-1}$ .<sup>5,8</sup> At ordinary temperature the effect of the upper doublet ( $^5E_g$ ) is neglected. The tetragonal crystal-field potential  $B_2^0 O_2^0$  splits the triplet ( $^5T_{2g}$ ) into a ground singlet ( $\phi_0$ ) and an excited doublet ( $\phi_{\pm 1}$ ) with an energy difference  $|9B_2^0| = \Delta$ . These electronic orbital states are<sup>11</sup>

$$\begin{aligned} \phi_0 &= |0\rangle, \\ \phi_{-1} &= \sqrt{2/3}|2\rangle - \sqrt{1/3}|-1\rangle, \\ \phi_1 &= \sqrt{2/3}|-2\rangle + \sqrt{1/3}|1\rangle. \end{aligned} \quad (2)$$

The spin-orbit coupling  $\lambda L \cdot S$  removes the orbital degeneracy of the doublet ( $\phi_{\pm 1}$ ) and also produces a substantial mixing with the singlet ( $\phi_0$ ). The 15 basis spin-orbital states are the product functions  $|\phi, M_s\rangle$  (where  $\phi = \phi_0, \phi_{-1}, \phi_1$  and  $M_s = \pm 2, \pm 1, 0$ ) and, in general, the resulting 15 electronic eigenfunctions will be a linear combination of these basis states. To include vibronic coupling between all these electronic states is a potentially complicated problem, but as pointed out by Price<sup>13</sup> and Sinha and co-workers,<sup>2,14</sup> the essential features of the problem can be retained by assuming the spin degeneracy to be equal to two, say  $M_s = \pm 2$  only. This will eliminate the off-diagonal terms arising from  $(\lambda/2)(L_+ S_- + L_- S_+)$ , but at the same time remove the orbital degeneracy. In effect one obtains three doublets given by  $|\phi_0, \pm 2\rangle$ ,  $|\phi_{\pm 1}, \mp 2\rangle$ , and  $|\phi_{\pm 1}, \pm 2\rangle$  in order of increasing energy as shown in Fig. 1. The orbit-lattice interaction will now be considered among these states keeping in mind that this interaction does not operate on the spin functions and hence only states with

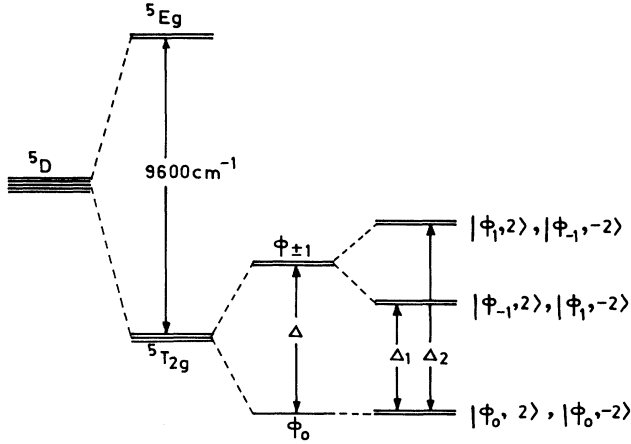


FIG. 1. Electronic energy level scheme of  $\text{Fe}^{2+}$  in  $\text{Fe}[(\text{C}_6\text{H}_5)_2\text{SO}]_6(\text{ClO}_4)_2$ .

the same spin quantum number will be vibronically mixed. The components of the electric-field gradient (EFG) obtained from these vibronically perturbed states will be used to calculate the net quadrupole splitting ( $\Delta E_Q$ ).

### III. ORBIT-LATTICE INTERACTION

In the long-phonon-wavelength approximation the orbit-lattice interaction is given by

$$H_{\text{ol}} = \sum_k \sum_{n,m} \left[ \frac{\hbar}{2M\omega_k} \right]^{1/2} k V_n^m(L)(a_k + a_k^*), \quad (3)$$

where the terms have their usual meaning.<sup>2</sup> Assuming that the orbit-lattice interaction acts as a small perturbation, the vibronically perturbed ground state may be written as

$$\psi_0 = A_0 [ |\phi_0, 2, n_k\rangle + \alpha_1 |\phi_{-1}, 2, n_k + 1\rangle + \beta_1 |\phi_{-1}, 2, n_k - 1\rangle + \alpha_2 |\phi_1, 2, n_k + 1\rangle + \beta_2 |\phi_1, 2, n_k - 1\rangle ], \quad (4)$$

where

$$\begin{aligned} \alpha_1 &= \frac{\langle \phi_0, 2, n_k | H_{\text{ol}} | \phi_{-1}, 2, n_k + 1 \rangle}{\Delta_1 + \hbar\omega_k}, \\ \beta_1 &= \frac{\langle \phi_0, 2, n_k | H_{\text{ol}} | \phi_{-1}, 2, n_k - 1 \rangle}{\Delta_1 - \hbar\omega_k}, \\ \alpha_2 &= \frac{\langle \phi_0, 2, n_k | H_{\text{ol}} | \phi_1, 2, n_k + 1 \rangle}{\Delta_2 + \hbar\omega_k}, \\ \beta_2 &= \frac{\langle \phi_0, 2, n_k | H_{\text{ol}} | \phi_1, 2, n_k - 1 \rangle}{\Delta_2 - \hbar\omega_k}. \end{aligned} \quad (5)$$

Here  $|n_k\rangle$  represents the phonon-occupation number (or phonon state) of the system.

The normalization constant  $A_0$  satisfies the relation

$$A_0^2 = [1 + (\alpha_1^2 + \beta_1^2) + (\alpha_2^2 + \beta_2^2)]^{-1}. \quad (6)$$

Similarly, the vibronic perturbed excited states may be

expressed as

$$\begin{aligned} \psi_{-1} &= A_{-1} [ |\phi_{-1}, 2, n_k\rangle + \alpha_3 |\phi_0, 2, n_k + 1\rangle \\ &\quad + \beta_3 |\phi_0, 2, n_k - 1\rangle \\ &\quad + \alpha_4 |\phi_1, 2, n_k + 1\rangle + \beta_4 |\phi_1, 2, n_k - 1\rangle ] \end{aligned}$$

and

$$\psi_1 = A_1 [ |\phi_1, 2, n_k\rangle + \alpha_5 |\phi_0, 2, n_k + 1\rangle + \beta_5 |\phi_0, 2, n_k - 1\rangle + \alpha_6 |\phi_{-1}, 2, n_k + 1\rangle + \beta_6 |\phi_{-1}, 2, n_k - 1\rangle ], \quad (7)$$

where

$$A_{-1}^2 = [1 + (\alpha_3^2 + \beta_3^2) + (\alpha_4^2 + \beta_4^2)]^{-1}$$

and

$$A_1^2 = [1 + (\alpha_5^2 + \beta_5^2) + (\alpha_6^2 + \beta_6^2)]^{-1}. \quad (8)$$

It can be seen that

$$\begin{aligned} \alpha_1^2 + \beta_1^2 &= \alpha_3^2 + \beta_3^2, \\ \alpha_2^2 + \beta_2^2 &= \alpha_5^2 + \beta_5^2, \end{aligned} \quad (9)$$

and

$$\alpha_4^2 + \beta_4^2 = \alpha_6^2 + \beta_6^2,$$

where

$$\begin{aligned} \alpha_4 &= \frac{\langle \phi_{-1}, 2, n_k | H_{\text{ol}} | \phi_1, 2, n_k + 1 \rangle}{(\Delta_2 - \Delta_1) + \hbar\omega_k}, \\ \beta_4 &= \frac{\langle \phi_{-1}, 2, n_k | H_{\text{ol}} | \phi_1, 2, n_k - 1 \rangle}{(\Delta_2 - \Delta_1) - \hbar\omega_k}. \end{aligned} \quad (10)$$

In an earlier paper<sup>15</sup> the matrix elements over orbit-lattice interaction have been obtained by using the properties of phonon annihilation and creation operators and following the same procedure one obtains that

$$\begin{aligned} \alpha_1^2 + \beta_1^2 &= aI(T)T^4, \\ \alpha_2^2 + \beta_2^2 &= bI(T)T^4, \end{aligned} \quad (11)$$

and

$$\alpha_4^2 + \beta_4^2 = cI(T)T^4,$$

where

$$\begin{aligned} a &= \left[ \frac{\hbar}{4\pi^2\rho v^5} \right] \frac{\left| \langle \phi_0 | \sum_{n,m} V_n^m | \phi_{-1} \rangle \right|^2}{\Delta_1^2} \left[ \frac{k_B}{\hbar} \right]^4, \\ b &= \left[ \frac{\hbar}{4\pi^2\rho v^5} \right] \frac{\left| \langle \phi_0 | \sum_{n,m} V_n^m | \phi_1 \rangle \right|^2}{\Delta_2^2} \left[ \frac{k_B}{\hbar} \right]^4, \\ c &= \left[ \frac{\hbar}{4\pi^2\rho v^5} \right] \frac{\left| \langle \phi_{-1} | \sum_{n,m} V_n^m | \phi_1 \rangle \right|^2}{(\Delta_2 - \Delta_1)^2} \left[ \frac{k_B}{\hbar} \right]^4, \end{aligned} \quad (12)$$

$$I(T) = \int_0^{\Theta_D/T} \frac{x^3(e^x + 1)}{e^x - 1} dx,$$

$\rho$  is the density,  $v$  the velocity of sound, and  $\Theta_D$  the Debye temperature of the crystal. It has been assumed that  $\Delta_1$  and  $\Delta_2 \gg \hbar\omega_D$ , where  $\hbar\omega_D$  is the Debye energy.

Now the expectation values of the EFG operators are

$$\begin{aligned} \langle V_{zz} \rangle_{\psi_0} &= \langle \psi_0 | V_{zz} | \psi_0 \rangle \\ &= A_0^2 [ \langle \phi_0 | V_{zz} | \phi_0 \rangle + (\alpha_1^2 + \beta_1^2) \langle \phi_{-1} | V_{zz} | \phi_{-1} \rangle + (\alpha_2^2 + \beta_2^2) \langle \phi_1 | V_{zz} | \phi_1 \rangle ] \\ &= A_0^2 |e| \langle r^{-3} \rangle [ 1 - \frac{1}{2}(\alpha_1^2 + \beta_1^2) - \frac{1}{2}(\alpha_2^2 + \beta_2^2) ] \\ &= \frac{4}{7} |e| \langle r^{-3} \rangle \frac{1 - 0.5aI(T)T^4 - 0.5bI(T)T^4}{1 + aI(T)T^4 + bI(T)T^4}. \end{aligned} \quad (13)$$

Similarly,

$$\langle V_{zz} \rangle_{\psi_{-1}} = \frac{4}{7} |e| \langle r^{-3} \rangle \frac{-0.5 + aI(T)T^4 - 0.5cI(T)T^4}{1 + aI(T)T^4 + cI(T)T^4} \quad (14)$$

and

$$\langle V_{zz} \rangle_{\psi_1} = \frac{4}{7} |e| \langle r^{-3} \rangle \frac{-0.5 + bI(T)T^4 - 0.5cI(T)T^4}{1 + bI(T)T^4 + cI(T)T^4},$$

where we have used the standard values of the EFG (Ref. 8) produced by the pure orbitals given by

$$\langle \phi_0 | V_{zz} | \phi_0 \rangle = \frac{4}{7} |e| \langle r^{-3} \rangle, \quad (15)$$

and

$$\langle \phi_{\pm 1} | V_{zz} | \phi_{\pm 1} \rangle = -\frac{2}{7} |e| \langle r^{-3} \rangle.$$

The EFG remains axially symmetric even after vibronic coupling. Similarly, the calculations can be done by considering the states with  $M_s = -2$  and the results will remain the same. Because both the components of a given doublet produce identical EFG the thermal average of the EFG will remain the same as can be obtained by considering only three states with  $M_s = 2$  or  $-2$ . The thermal average of the EFG is finally obtained as

$$\langle V_{zz} \rangle_T = \frac{\langle V_{zz} \rangle_{\psi_0} + \langle V_{zz} \rangle_{\psi_{-1}} \exp(-\Delta_1/k_B T) + \langle V_{zz} \rangle_{\psi_1} \exp(-\Delta_2/k_B T)}{1 + \exp(-\Delta_1/k_B T) + \exp(-\Delta_2/k_B T)}. \quad (16)$$

The quadrupole splitting is proportional to  $\langle V_{zz} \rangle_T$ . At  $T=0$  K there will be no vibronic effects and the quadrupole splitting is produced exclusively by the ground state. Therefore, one finds that

$$\begin{aligned} (\Delta E_Q)_T &= (\Delta E_Q)_0 \frac{1}{1 + \exp(-\Delta_1/k_B T) + \exp(-\Delta_2/k_B T)} \\ &\times \left[ \frac{1 - 0.5aI(T)T^4 - 0.5bI(T)T^4}{1 + aI(T)T^4 + bI(T)T^4} + \frac{-0.5 + aI(T)T^4 - 0.5cI(T)T^4}{1 + aI(T)T^4 + cI(T)T^4} \exp(-\Delta_1/k_B T) \right. \\ &\quad \left. + \frac{-0.5 + bI(T)T^4 - 0.5cI(T)T^4}{1 + bI(T)T^4 + cI(T)T^4} \exp(-\Delta_2/k_B T) \right], \end{aligned} \quad (17)$$

where  $(\Delta E_Q)_0$  is the quadrupole splitting at 0 K. This is the final expression for the variation of quadrupole splitting with temperature.

#### IV. CALCULATION OF $(\Delta E_Q)_T$

Any explicit calculation of  $(\Delta E_Q)_T$  needs a reasonably good estimate of various parameters. We have taken  $(\Delta E_Q)_0 = 3.37$  mm/sec, which is the measured value at 8.8 K assuming that the vibrational effect will be negligible at this temperature. The static parameter  $B_4^0$

obtained for these wave functions keeping in mind that these operators connect only those electronic states for which the phonon occupation numbers are the same. Then one obtains that

is obtained from the octahedral field splitting  $180B_4^0 = 9600$  cm<sup>-1</sup>. The spin-orbit coupling parameter  $\lambda = 103$  cm<sup>-1</sup> for a free Fe<sup>2+</sup> ion, but its magnitude decreases significantly due to covalency in various compounds. We have done the calculation for  $\lambda = 80$  cm<sup>-1</sup>. In order to match the theoretical and experimental values of the quadrupole splitting, an approximate value of  $\Delta \sim 500$  cm<sup>-1</sup> has already been estimated from the static crystal-field scheme.<sup>5</sup> We have generated several sets of theoretical values of  $\Delta E_Q$  as a function of temperature by taking different values of  $\Delta$  between 400 and 600 cm<sup>-1</sup>.

The static parameter  $B_2^0$  ( $9B_2^0 = \Delta$ ) and  $\Delta_1$  ( $=\Delta - 2\lambda$ ) and  $\Delta_2$  ( $=\Delta + 2\lambda$ ) are each time derived for a given value of  $\Delta$ . The agreement appears fairly good for  $\Delta = 590 \text{ cm}^{-1}$  ( $\Delta_1 = 430 \text{ cm}^{-1}$  and  $\Delta_2 = 750 \text{ cm}^{-1}$ ). These values of  $\Delta_1$  and  $\Delta_2$  are quite reasonable and well within the expected range.

The matrix elements over the dynamic crystal-field potential are obtained as

$$\begin{aligned} \langle \phi_0 | \sum_{n,m} V_n^m | \phi_{\pm 1} \rangle &= \langle \phi_0 | C_2^2 O_2^{\pm 2} + C_4^2 O_4^{\pm 2} | \phi_{\pm 1} \rangle \\ &= 2C_2^2 + 6C_4^2 \end{aligned}$$

and

$$\begin{aligned} \langle \phi_{-1} | \sum_{n,m} V_n^m | \phi_1 \rangle &= \langle \phi_{-1} | C_2^1 O_2^{\pm 1} + C_2^2 O_2^{\pm 2} + C_4^1 O_4^{\pm 1} + C_4^2 O_4^{\pm 2} | \phi_1 \rangle \\ &= -\sqrt{2}C_2^1 + C_2^2 - 2\sqrt{2}C_4^1 - 4C_4^2, \end{aligned}$$

where  $C_n^m$  are the dynamic crystal-field parameters. The dynamic and static crystal-field parameters, according to Huang's approximation,<sup>16</sup> are related as

$$C_n^m \simeq (n+1)B_n^m,$$

giving

$$C_2^1 \simeq C_2^2 = 3B_2^0 = 196.5 \text{ cm}^{-1},$$

and

$$C_4^1 \simeq C_4^2 = 5B_4^0 = 266.5 \text{ cm}^{-1}.$$

An experimental value of the Debye temperature in this compound is not available, however, it is expected to be  $\sim 100 \text{ cm}^{-1}$ . In the present calculations, the Debye temperature ( $\Theta_D$ ) has been kept variable within this range and each time the velocity of sound  $v$  has been estimated from the standard phonon density-of-states relation

$$v^3 = \frac{VE_D^3}{6\pi^2 \hbar^3 N},$$

where  $N$  is the number of molecules in volume  $V$  and  $E_D$  the Debye energy. The molecular weight of this compound is  $1467 \text{ g/mol}$ , and the density  $\rho \simeq 1.75 \text{ g/cm}^3$ , which corresponds to the molar volume  $V = 838.3 \text{ cm}^3$ . The integral  $I(T)$  was performed numerically for different values of Debye temperature between 175 and 100 K. It was found that for  $\Theta_D = 125 \text{ K}$  and correspondingly  $v = 4.7 \times 10^5 \text{ cm/sec}$ , the agreement between

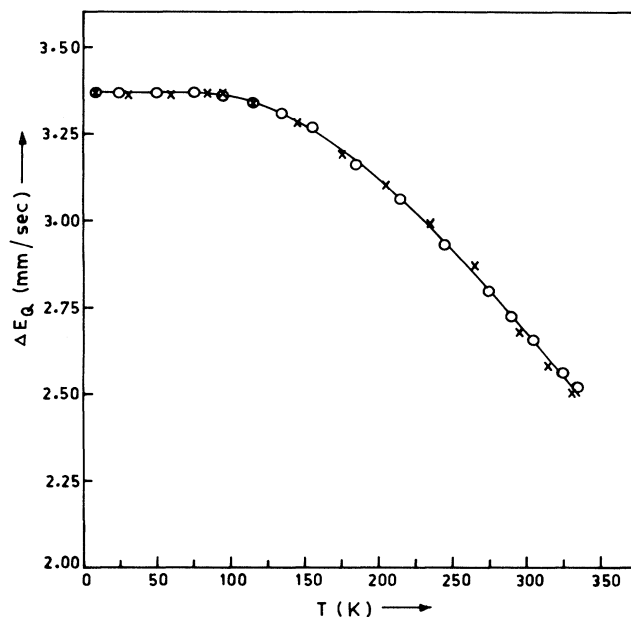


FIG. 2. Comparison of observed (×) and calculated (○) quadrupole splittings of  $\text{Fe}^{2+}$  in  $\text{Fe}[(\text{C}_6\text{H}_5)_2\text{SO}]_6(\text{ClO}_4)_2$  as a function of temperature.

calculated and observed values of  $\Delta E_Q$  was quite fair. This value of the Debye temperature is also well within the expected range. It was seen that a small change, of the order of  $\pm 25 \text{ K}$ , in the value of  $\Theta_D$  does not affect the results significantly but a larger change does. Using all these parameters,  $(\Delta E_Q)_T$  has been calculated as a function of temperature and compared with the observed data as shown in Fig. 2.

## V. CONCLUSIONS

In retrospect it appears that the orbit-lattice interaction can reasonably explain the observed temperature dependence of  $\text{Fe}^{2+}$  quadrupole splitting in  $\text{Fe}[(\text{C}_6\text{H}_5)_2\text{SO}]_6(\text{ClO}_4)_2$  over 4.2–335 K, though the model used is very simple. This interaction, though weak in general, may be quite important in the case of  $\text{Fe}^{2+}$  ( $L=2$ ) which is strongly coupled to lattice vibrations and its effect can be manifested in Mössbauer studies which can measure extremely small energy changes.

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