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Vibronic effects on the Mössbauer quadrupole splitting of Fe(II) in ferrous fluo-silicate ($\text{FeSiF}_6 \cdot 6 \text{H}_2\text{O}$)

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Résumé. — La résolution quadrupolaire Mössbauer du $^{57}\text{Fe}(\text{II})$ dans $\text{FeSiF}_6 \cdot 6 \text{H}_2\text{O}$ décroît quand la température croît de 77 à 300 K et ceci ne peut être complètement expliqué sur la seule base de l'interaction de champ cristallin statique qui est habituellement utilisée pour obtenir les états orbitaux électroniques et l'interaction quadrupolaire résultante. Dans le présent article, nous avons considéré le mélange entre les états orbitaux dû à l'interaction orbite-réseau, nous avons obtenu les états perturbés électrons-phonons et avons ensuite calculé la résolution quadrupolaire à partir de ces états en fonction de la température. Les résultats théoriques ainsi obtenus sont en accord raisonnable avec les données expérimentales.

Abstract. — The Mössbauer quadrupole splitting of $^{57}\text{Fe}(\text{II})$ in $\text{FeSiF}_6 \cdot 6 \text{H}_2\text{O}$ decreases with increasing temperature from 77 to 300 K and this cannot be fully explained on the basis of the static crystal field interaction only which is usually used to obtain the electronic orbital states and the resulting quadrupole interaction. In the present work we have considered the mixing between orbital states due to orbit-lattice interaction, obtained the perturbed electron-phonon states and then calculated the quadrupole splitting from these states as a function of temperature. The theoretical results thus obtained agree reasonably well with the experimental data.

1. Introduction.

Mössbauer technique has been widely used to study the crystal field and lattice dynamical interactions involving $^{57}\text{Fe}(\text{II})$ ions in various compounds. The temperature dependence of the quadrupole splitting of Fe(II) in various fluo-silicates over 4.2 to 300 K has been reported by Varret and Jehanno [1], but the same cannot be fully explained by a theoretical model which includes the static crystal field interaction and spin-orbit coupling to obtain the electronic states of the ferrous ion [1]. The inadequacy of the static crystal approach is quite pronounced in the case of $\text{FeSiF}_6 \cdot 6 \text{H}_2\text{O}$ where the observation shows a substantial decrease of quadrupole splitting between 77 to 300 K but the theory predicts a much smaller decrease [1]. During the last few years the orbit-lattice interaction has been used to explain the temperature dependence of the quadrupole splitting of ferrous ions in some compounds and the theoretical works of Bacci [2], Price [3], Srivastava [4] and Srivastava and Choudhary [5] are important in this context. The present work is a step in the same

direction where orbit-lattice interaction is regarded as a perturbation [3, 4] over the static crystal field in order to analyse the temperature variation of the quadrupole splitting in $\text{FeSiF}_6 \cdot 6 \text{H}_2\text{O}$. It is understood that in the case of ferrous ions the quadrupole interaction arises mainly from the valence electrons and any lattice contribution remains small and unchanged over the temperature range.

2. Electronic states of Fe(II).

In $\text{FeSiF}_6 \cdot 6 \text{H}_2\text{O}$ the ferrous ions occupy trigonally distorted octahedral sites [1] and experience a strong crystal field potential given by

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

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 [6]. Here the parameter B_4^0 refers to the [111] direction of the cube as the axis of symmetry and its magnitude is only 2/3 of the value when the [001] direction is taken as the

symmetry axis. The strong octahedral field splits the 5D state of a free Fe(II) ion into a lower triplet ($^5T_{2g}$) and an upper doublet (5E_g) with energy separation $|180 B_4^0| \simeq 10^4 \text{ cm}^{-1}$ [7, 8]. At ordinary temperatures the effect of the upper doublet is neglected. The trigonal field potential $B_2^0 O_2^0$ splits the triplet into a ground singlet (ϕ_0) and an excited doublet ($\phi_{\pm 1}$) with energy difference $\Delta = |9 B_2^0|$. The sign of the quadrupole interaction confirms that the singlet is the ground state [1]. These electronic orbital states are [3, 7]:

$$\begin{aligned} \phi_1 &= -\sqrt{2/3} Y_2^{-2} - \sqrt{1/3} Y_2^1 \\ \phi_{-1} &= \sqrt{2/3} Y_2^2 - \sqrt{1/3} Y_2^{-1} \\ \phi_0 &= Y_2^0. \end{aligned} \quad (2)$$

The spin-orbit coupling $\lambda L \cdot S$ removes the orbital degeneracy of the doublet and also produces a substantial mixing with the singlet. The 15 basis spin-orbital states are the product functions $|\phi, M_s\rangle$ (where $\phi = \phi_1, \phi_{-1}, \phi_0$ and $M_s = \pm 2, \pm 1, 0$) and in general the electronic eigenfunctions will be linear combinations of these basis states. To include vibronic coupling between all these electronic states is a potentially complicated problem, but as pointed out by Price [3] the essential features of the problem can

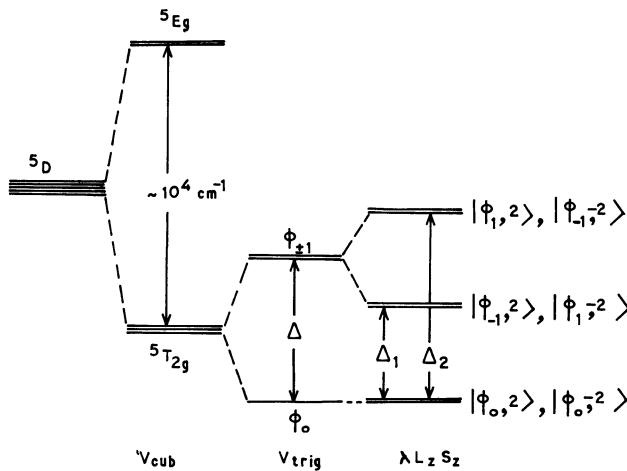


Fig. 1. — Electronic energy level scheme of Fe(II) in $\text{FeSiF}_6 \cdot 6 \text{H}_2\text{O}$.

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 3 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 figure 1. The orbit-lattice interaction will now be considered between these states keeping in mind that this interaction does not operate on the spin functions and hence only states with the same spin quantum number will be vibronically mixed. The components of the electric field gradient (e.f.g.) obtained from these vibronically perturbed states will be used to calculate the net quadrupole splitting (ΔE_Q).

3. Effect of orbit-lattice interaction.

The orbit-lattice interaction accounts for the thermal modulation of the electronic charge distribution of Fe(II) due to vibrations of the surrounding ligands. In the long phonon wavelength approximation this interaction is represented as [6, 9]:

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

where a_k and a_k^* are the phonon annihilation and creation operators, ω_k is the frequency of phonons with wavevector k , $V_n^m(L)$ is the crystal field potential with dynamic parameters and M is the mass of the crystal. Now the new basis states become the product of electron and phonon states like $|\phi, M_s, n_k\rangle$, where n_k is the phonon occupation number given by the Bose-Einstein distribution function. The energy of an electron-phonon system is given by

$$E = E_c + \sum_k \hbar\omega_k \left(n_k + \frac{1}{2} \right) \quad (4)$$

which is equal to the sum of the electronic and vibrational energies. The vibronically perturbed electronic states can be obtained by the first order perturbation method. Thus the new ground state eigenfunction is given as:

$$\begin{aligned} \psi_0 &= A_0 [|\phi_0, 2, n_k\rangle + \frac{\langle \phi_0, 2, n_k | H_{ol} | \phi_{-1}, 2, n_k + 1 \rangle}{\Delta_1 + \hbar\omega_k} |\phi_{-1}, 2, n_k + 1\rangle \\ &+ \frac{\langle \phi_0, 2, n_k | H_{ol} | \phi_{-1}, 2, n_k - 1 \rangle}{\Delta_1 - \hbar\omega_k} |\phi_{-1}, 2, n_k - 1\rangle \\ &+ \frac{\langle \phi_0, 2, n_k | H_{ol} | \phi_1, 2, n_k + 1 \rangle}{\Delta_2 + \hbar\omega_k} |\phi_1, 2, n_k + 1\rangle \\ &+ \frac{\langle \phi_0, 2, n_k | H_{ol} | \phi_1, 2, n_k - 1 \rangle}{\Delta_2 - \hbar\omega_k} |\phi_1, 2, n_k - 1\rangle] \\ &= A_0 [|\phi_0, 2, n_k\rangle + \alpha_1 |\phi_{-1}, 2, n_k + 1\rangle + \beta_1 |\phi_{-1}, 2, n_k - 1\rangle \\ &+ \alpha_2 |\phi_1, 2, n_k + 1\rangle + \beta_2 |\phi_1, 2, n_k - 1\rangle] \end{aligned} \quad (5a)$$

where α_1, β_1 , and α_2, β_2 , are the various coefficients of expression (5) and A_0 is the normalization constant given by

$$A_0^2 = [1 + (\alpha_1^2 + \beta_1^2) + (\alpha_2^2 + \beta_2^2)]^{-1}. \quad (5b)$$

The expectation values of the e.f.g. operators are now obtained for ψ_0 keeping in mind that these operators [3, 4] connect only electronic states for which the phonon occupation numbers are the same. Then one obtains that

$$\begin{aligned} \langle V_{zz} \rangle_{\psi_0} &= \langle \psi_0 | V_{zz} | \psi_0 \rangle \\ &= A_0^2 [\langle \phi_0 | V_{zz} | \phi_0 \rangle] + (\alpha_1^2 + \beta_1^2) \langle \phi_{-1} | V_{zz} | \phi_{-1} \rangle + (\alpha_2^2 + \beta_2^2) \langle \phi_1 | V_{zz} | \phi_1 \rangle \\ &= A_0^2 (-4/7) |e| \langle r^{-3} \rangle \left[1 - \frac{1}{2} (\alpha_1^2 + \beta_1^2) - \frac{1}{2} (\alpha_2^2 + \beta_2^2) \right] \end{aligned} \quad (6)$$

$$= (-4/7) |e| \langle r^{-3} \rangle X_0 \quad (6a)$$

where we have used the standard values [3, 4] of the e.f.g. produced by the pure orbitals given by

$$\langle V_{zz} \rangle_0 = \langle \phi_0 | V_{zz} | \phi_0 \rangle = (-4/7) |e| \langle r^{-3} \rangle$$

and

$$\langle V_{zz} \rangle_{\pm 1} = \langle \phi_{\pm 1} | V_{zz} | \phi_{\pm 1} \rangle = (2/7) |e| \langle r^{-3} \rangle \quad (7)$$

Similarly the vibronically perturbed excited states may be expressed as :

$$\begin{aligned} \psi_{-1} = A_{-1} [&| \phi_{-1}, 2, n_k \rangle + \alpha_3 | \phi_0, 2, n_k + 1 \rangle + \beta_3 | \phi_0, 2, n_k - 1 \rangle + \\ &+ \alpha_4 | \phi_1, 2, n_k + 1 \rangle + \beta_4 | \phi_1, 2, n_k - 1 \rangle] \end{aligned} \quad (8)$$

and

$$\begin{aligned} \psi_1 = A_1 [&| \phi_1, 2, n_k \rangle + \alpha_5 | \phi_0, 2, n_k + 1 \rangle + \beta_5 | \phi_0, 2, n_k - 1 \rangle + \\ &+ \alpha_6 | \phi_{-1}, 2, n_k + 1 \rangle + \beta_6 | \phi_{-1}, 2, n_k - 1 \rangle] \end{aligned} \quad (9)$$

where

$$A_{-1}^2 = [1 + (\alpha_3^2 + \beta_3^2) + (\alpha_4^2 + \beta_4^2)]^{-1} \quad (10)$$

and

$$A_1^2 = [1 + (\alpha_5^2 + \beta_5^2) + (\alpha_6^2 + \beta_6^2)]^{-1}. \quad (11)$$

It can be seen that

$$\alpha_1^2 + \beta_1^2 = \alpha_3^2 + \beta_3^2, \quad \alpha_2^2 + \beta_2^2 = \alpha_5^2 + \beta_5^2 \quad \text{and} \quad \alpha_4^2 + \beta_4^2 = \alpha_6^2 + \beta_6^2 \quad (12)$$

where

$$\alpha_4 = \frac{\langle \phi_{-1}, 2, n_k | H_{01} | \phi_1, 2, n_k + 1 \rangle}{(\Delta_2 - \Delta_1) + \hbar \omega_k}$$

and

$$\beta_4 = \frac{\langle \phi_{-1}, 2, n_k | H_{01} | \phi_1, 2, n_k - 1 \rangle}{(\Delta_2 - \Delta_1) - \hbar \omega_k}. \quad (13)$$

For these wavefunctions one similarly obtains that

$$\begin{aligned} \langle V_{zz} \rangle_{\psi_{-1}} &= \langle \psi_{-1} | V_{zz} | \psi_{-1} \rangle \\ &= A_{-1}^2 (-4/7) |e| \langle r^{-3} \rangle \left[-\frac{1}{2} + (\alpha_1^2 + \beta_1^2) - \frac{1}{2} (\alpha_4^2 + \beta_4^2) \right] \end{aligned} \quad (14)$$

$$= (-4/7) |e| \langle r^{-3} \rangle X_{-1} \quad (14a)$$

and

$$\begin{aligned} \langle V_{zz} \rangle_{\psi_1} &= \langle \psi_1 | V_{zz} | \psi_1 \rangle \\ &= A_1^2 (-4/7) |e| \langle r^{-3} \rangle \left[-\frac{1}{2} + (\alpha_2^2 + \beta_2^2) - \frac{1}{2} (\alpha_4^2 + \beta_4^2) \right] \end{aligned} \quad (15)$$

$$= (-4/7) |e| \langle r^{-3} \rangle X_1 \quad (15a)$$

where X_0, X_{-1} and X_1 are the factors used in expressions (6), (14) and (15) respectively. The e.f.g. 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 e.f.g., the thermal average of the e.f.g. will remain the same as can be obtained by considering only three states with $M_s = 2$ or -2 . The thermal average of the e.f.g. is finally obtained as :

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

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

$$(\Delta E_Q)_T = (\Delta E_Q)_0 \frac{X_0 + X_{-1} e^{-\Delta_1/k_B T} + X_1 e^{-\Delta_2/k_B T}}{1 + e^{-\Delta_1/k_B T} + e^{-\Delta_2/k_B T}} \quad (17)$$

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.

Now we need the evaluation of $(\alpha_1^2 + \beta_1^2)$, $(\alpha_2^2 + \beta_2^2)$ and $(\alpha_4^2 + \beta_4^2)$. In an earlier paper [4] 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 :

$$\begin{aligned} \alpha_1^2 + \beta_1^2 &= aI(T) T^4 \\ \alpha_2^2 + \beta_2^2 &= bI(T) T^4 \\ \alpha_4^2 + \beta_4^2 &= cI(T) T^4 \end{aligned} \quad (18)$$

where

$$\begin{aligned} a &= \left[\frac{\hbar}{4 \pi^2 \rho v^5} \right] \frac{\left| \left\langle \phi_0 \left| \sum_{n,m} V_n^m \right| \phi_{-1} \right\rangle \right|^2}{\Delta_1^2} \left[\frac{k_B}{\hbar} \right]^4 \\ b &= \left[\frac{\hbar}{4 \pi^2 \rho v^5} \right] \frac{\left| \left\langle \phi_0 \left| \sum_{n,m} V_n^m \right| \phi_1 \right\rangle \right|^2}{\Delta_2^2} \left[\frac{k_B}{\hbar} \right]^4 \\ c &= \left[\frac{\hbar}{4 \pi^2 \rho v^5} \right] \frac{\left| \left\langle \phi_{-1} \left| \sum_{n,m} V_n^m \right| \phi_1 \right\rangle \right|^2}{(\Delta_2 - \Delta_1)^2} \left[\frac{k_B}{\hbar} \right]^4 \\ I(T) &= \int_0^{\theta_D/T} \frac{x^3 (e^x + 1)}{(e^x - 1)} dx \end{aligned} \quad (19)$$

ρ = density, v = velocity of sound and θ_D = Debye temperature of the crystal. It has been assumed that $\Delta_1, \Delta_2 \gg \hbar \omega_D$ where $\hbar \omega_D$ is the Debye energy and the phonon spectrum is isotropic.

4. Calculation of $(\Delta E_Q)_T$

The calculation of $(\Delta E_Q)_T$ requires an estimation of various parameters. We take $(\Delta E_Q)_0 = -3.61$ mm/s

which is the measured value at 4.2 K assuming that the vibrational effect will be negligible at this temperature. The static parameter B_4^0 is obtained from the cubic splitting $180 B_4^0 = 10^4$ cm⁻¹. There is ample evidence that for Fe(II) in trigonally distorted sites in various compounds (like chlorides, carbonates, ferrites etc.) the axial field splitting $\Delta = 1000$ cm⁻¹ [7, 8]. In the case of FeSiF₆·6 H₂O the trigonal splitting (Δ) has been reported of the order of 760 cm⁻¹ from the study of the temperature variation of quadrupole splitting [10, 11] and 1200 cm⁻¹ from the study of the magnetic susceptibility at low temperature [1]. These values are widely different and hence we have taken it as a variable parameter within this range, and we have always kept $\Delta_1 = \Delta - |2\lambda|$ and $\Delta_2 = \Delta + |2\lambda|$ where $\lambda = -100$ cm⁻¹. The static trigonal field parameter B_2^0 is each time derived from the relation $9 B_2^0 = \Delta$. The matrix elements over dynamic crystal field potential are obtained as :

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

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

where C_n^m are the dynamic crystal field parameters. In the light of earlier calculations [4] these dynamic parameters are estimated as :

$$\begin{aligned} C_2^1 &\approx C_2^2 \approx (n+1) B_2^0 = 3 B_2^0 = 316.6 \text{ cm}^{-1} \\ C_4^1 &\approx C_4^2 \approx (n+1) B_4^0 = 5 B_4^0 = 277.8 \text{ cm}^{-1}. \end{aligned}$$

The Debye temperature of FeSiF₆·6 H₂O has been estimated as 180 ± 13 K by the Mössbauer method which has also shown that the anisotropy of the recoilless fraction is very small [12]. This also implies that the phonon spectrum is fairly isotropic. Using $\theta_D = 180$ K the integral $I(T)$ has been evaluated numerically at different temperatures. An experimental value of the velocity of sound in this compound is not available. However, it can be

estimated from the standard phonon density of states relation :

$$v^3 = \frac{VE_D^3}{6\pi^2\hbar^3N} \quad (20)$$

where N is the number of molecules in volume V and E_D is the Debye energy. Using molecular weight = 306 g/mole, density $\rho = 1.96$ g/cm³ and the Debye temperature mentioned above, one obtains $v = 3.86 \times 10^5$ cm/s. which appears quite reasonable. Using all these estimated parameters the $(\Delta E_Q)_T$ has

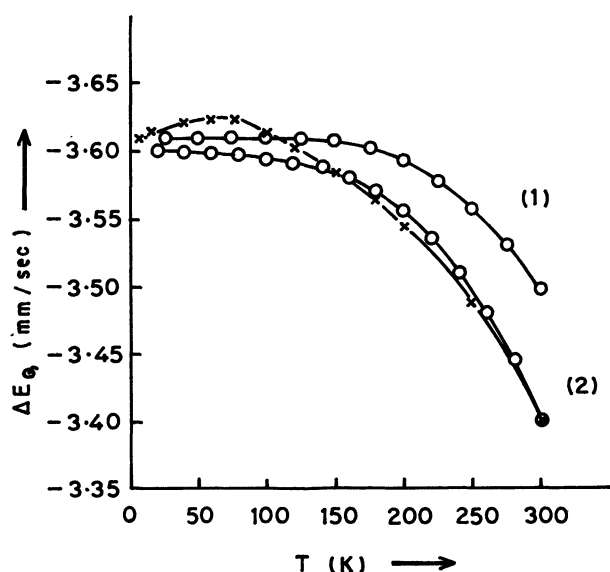


Fig. 2. — Temperature variation of quadrupole splitting of Fe(II) in $\text{FeSiF}_6 \cdot 6 \text{H}_2\text{O}$. \times experimental points. \circ theoretical points (curve 1 without vibrational effects, curve 2 with vibrational effects).

been calculated as a function of temperature and compared with the observed data. The agreement appears fairly reasonable for $\Delta = 950 \text{ cm}^{-1}$ ($\Delta_1 = 750 \text{ cm}^{-1}$, $\Delta_2 = 1150 \text{ cm}^{-1}$), as shown in figure 2.

5. Conclusions.

The agreement between theoretical and experimental data appears fairly reasonable as shown in figure 2 (curve 2) and this indicates the relevance of vibronic interaction for ferrous ions. We have also calculated the temperature variation of the quadrupole splitting in a static crystal (i.e. no vibronic interaction) for the given energy level scheme (Fig. 1) and shown the same in figure 2 (curve 1). A comparison between the two curves shows the relative success of the static and dynamic crystal approaches in explaining the experimental data. At temperatures between 77 to 300 K the vibronic coupling does appear to be significant. At lower temperatures, between 4.2 to 77 K, the observed quadrupole splitting initially increases with temperature and then decreases continuously for higher temperature ($T > 77$ K). This initial increase is well understood as arising from the orbital admixture produced by the spin-orbit coupling [1], which we have neglected. Therefore, this feature is not reproduced by the present calculations.

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