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Abstract
The effect of vibronic coupling (orbit–lattice interaction), which produces a mixing between the low-lying electronic states with the emission and absorption of phonons of varying energies, is considered to explain the observed temperature dependence of Mössbauer quadrupole splitting of Fe^{2+} ions in $CsCoCl_3$ over 22 to 300 K. The various lattice dynamical parameters are estimated and then quadrupole splitting is explicitly calculated as a function of temperature. One obtains a reasonably good agreement with the experimental data, which shows that the vibrating lattice model is quite realistic and important.

1. Introduction

The Mössbauer technique has been extensively applied to study the crystal field and lattice dynamical interactions involving $^{57}Fe^{2+}$ ($3d^6$, ^5D) ions in solids. The information about the electronic charge distribution is obtained from the study of nuclear quadrupole splitting and isomer shift, while the study of the magnetic hyperfine spectra furnishes the information about the spin ordering. The temperature dependence of quadrupole splitting is effectively used to determine the symmetry and strength of crystal field interaction, the ordering of electronic state and the relative strength of vibronic coupling.

Ward *et al* [1] have measured the Mössbauer quadrupole splitting of Fe^{2+} ions in $CsCo_{0.99}Fe_{0.01}Cl_3$ over 22 to 300 K and to explain the results theoretically they have used the second order axial crystal field parameters, ~ 2650 cm^{-1}, along with the first order axial crystal field (i.e., trigonal field) parameter, ~ 2400 cm^{-1}, to modify the energy of the electronic states, which is rather unrealistic. For a free Fe^{2+} ion the strength of the second order axial crystal field parameter, if any, should be very small in comparison to first order axial crystal field parameter. It is worth mentioning that for a free Fe^{2+} ion the strength of the first order spin–orbit coupling is ~ 100 cm^{-1} [2], whereas that of the second order spin–orbit coupling is ~ 1 cm^{-1} [3, 4]. 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 $^{57}Fe^{2+}$ quadrupole splitting in $CsCo_{0.99}Fe_{0.01}Cl_3$ by taking into account the effect of orbit–lattice interaction as a perturbation over the static crystal-field potential so that usefulness of this interaction can be investigated in a more comprehensive way in Mössbauer observables. 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. Recently, Sinha and co-workers have taken into account the effect of orbit–lattice interaction to explain the observed temperature dependence of Fe^{2+} quadrupole splitting in inorganic [5], organometallic [6] and biological [7] systems. Otherwise it could not be explained on the basis of a static crystal. This interaction is very important for Fe^{2+} in $CsCoFeCl_3$ and hence a reinterpretation of the work of Ward *et al* [1] is necessary. It is to be noted that Fe^{2+} quadrupole interaction arises mainly from the valence electrons and any lattice contribution remains small and unchanged over the temperature range considered here.

2. Electronic states of Fe^{2+}

In ^{57}Fe doped $CsCoCl_3$, the ferrous ions occupy trigonally distorted octahedral sites [1] and experience a strong crystal-field potential given by [8, 9]

$$H_{cr} = B_4^0 \left(O_4^0 - 20\sqrt{2}O_4^3 \right) + B_2^0 O_2^0 + \lambda \boldsymbol{L}\cdot\boldsymbol{S} \tag{1}$$

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 [10]. The first term refers to the strong octahedral crystal field, which splits the ^5D state of a free Fe^{2+} ion into a lower orbital triplet $^5T_{2g}$ and an upper orbital doublet ^5E_g with energy separation $|180B_4^0| = \delta$. At ordinary temperature the effect of the upper doublet ^5E_g is neglected. The trigonal crystal-field potential $B_2^0 O_2^0$ splits the triplet $^5T_{2g}$ into a ground singlet (ϕ_0) and an excited doublet ($\phi_{\pm1}$) with an energy difference $|9B_2^0| = \Delta$ as shown in figure 1. These electronic orbital states are [10]

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

The spin–orbit coupling $\lambda\boldsymbol{L}\cdot\boldsymbol{S}$ removes the orbital degeneracy of the doublet ($\phi_{\pm1}$) and also produces a substantial mixing with the singlet ϕ_0. The 15 basis spin orbital states are the product functions $|\phi, M_s\rangle$ where, $\phi = \phi_0, \phi_{-1}, \phi_1$ and $M_s = \pm2, \pm1, 0$ and, in general, the resulting 15 electronic eigenfuntions 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 [12] and Sinha and co-workers [5–7] the essential features of the problem can be retained by assuming the spin degeneracy to be equal to two, say $M_s = \pm2$ 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 $|\phi_0, \pm2\rangle$, $|\phi_{\mp1}, \pm2\rangle$ and $|\phi_{\pm1}, \pm2\rangle$ in order of increasing energy as shown in figure 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 the same spin quantum number will be vibronically mixed. The component of the electric-field gradient (EFG) obtained from these vibronically perturbed states will be used to calculate the net quadrupole splitting (ΔE_Q).
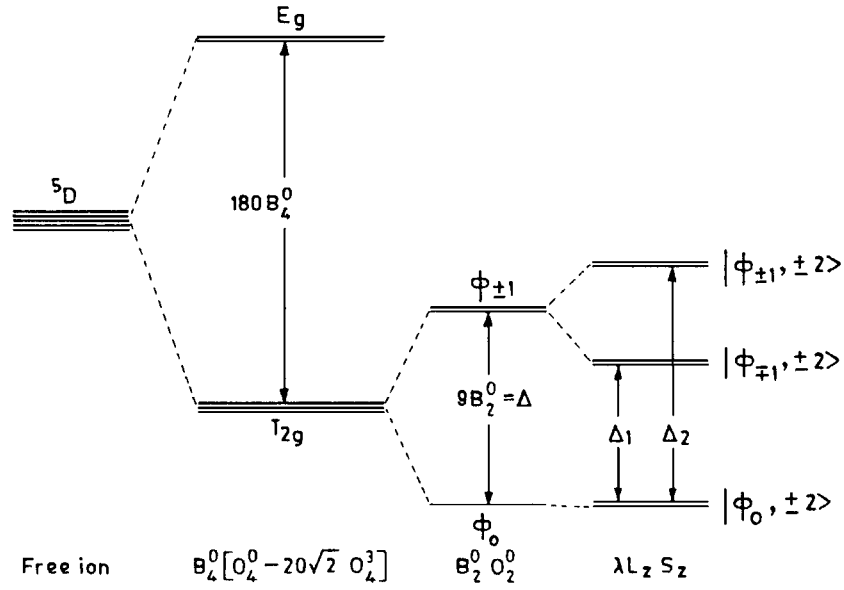
Figure 1. The electronic energy level scheme of Fe^{2+} in $CsCo_{0.99}Fe_{0.01}Cl_3$.

3. Orbit–lattice interaction

The orbit–lattice interaction accounts for the thermal modulation of the electronic charge cloud of Fe^{2+} due to vibration of the surrounding ligands, which in fact perturbs the nuclear energy states. In the long-phonon-wavelength approximation this interaction is given by

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

where the terms have their usual meaning [13].

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 and the energy of the electron–phonon system will be the sum of the electronic and vibrational energies. Assuming that the orbit–lattice interaction acts as a small perturbation, the vibronically perturbed ground state may be written as

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

where

$$\alpha_1 = \frac{\langle\phi_0, 2, n_k|H_{ol}|\phi_{-1}, 2, n_k + 1\rangle}{\Delta_1 + \hbar\omega_k}$$

$$\beta_1 = \frac{\langle\phi_0, 2, n_k|H_{ol}|\phi_{-1}, 2, n_k - 1\rangle}{\Delta_1 - \hbar\omega_k}$$

$$\alpha_2 = \frac{\langle\phi_0, 2, n_k|H_{ol}|\phi_1, 2, n_k + 1\rangle}{\Delta_2 + \hbar\omega_k}$$

and

$$\beta_2 = \frac{\langle\phi_0, 2, n_k|H_{ol}|\phi_1, 2, n_k - 1\rangle}{\Delta_2 - \hbar\omega_k}.$$

The normalization constant A_0 satisfies the relation

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

Similarly, the vibronically perturbed excited states may be expressed as

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

and

$$\psi_1 = A_1[|\phi_1, 2, n_k\rangle + \alpha_5|\phi_0, 2, n_k + 1\rangle + \beta_5|\phi_0, 2, n_k - 1\rangle$$
$$+ \alpha_6|\phi_{-1}, 2, n_k + 1\rangle + \beta_6|\phi_{-1}, 2, n_k - 1\rangle] \tag{6}$$

where

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

and

$$A_1^2 = \left[1 + \left(\alpha_5^2 + \beta_5^2\right) + \left(\alpha_6^2 + \beta_6^2\right)\right]^{-1}. \tag{7}$$

Here

$$\alpha_1^2 + \beta_1^2 = \alpha_3^2 + \beta_3^2,$$
$$\alpha_2^2 + \beta_2^2 = \alpha_5^2 + \beta_5^2$$

and

$$\alpha_4^2 + \beta_4^2 = \alpha_6^2 + \beta_6^2 \tag{8}$$

where

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

and

$$\beta_4 = \frac{\langle\phi_{-1}, 2, n_k|H_{ol}|\phi_1, 2, n_k - 1\rangle}{\Delta_2 - \Delta_1 - \hbar\omega_k}.$$

In an earlier paper [6] 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 can obtain the values of $\alpha_1^2 + \beta_1^2$, $\alpha_2^2 + \beta_2^2$ and $\alpha_4^2 + \beta_4^2$. The expectation values of the EFG operators are 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

$$\langle V_{zz}\rangle_{\psi_0} = \langle\psi_0|V_{zz}|\psi_0\rangle$$
$$= A_0^2\left[\langle\phi_0|V_{zz}|\phi_0\rangle + \left(\alpha_1^2 + \beta_1^2\right)\langle\phi_{-1}|V_{zz}|\phi_{-1}\rangle + \left(\alpha_2^2 + \beta_2^2\right)\langle\phi_1|V_{zz}|\phi_1\rangle\right]$$
$$= A_0^2\tfrac{4}{7}|e|\langle r^{-3}\rangle\left[1 - \tfrac{1}{2}\left(\alpha_1^2 + \beta_1^2\right) - \tfrac{1}{2}\left(\alpha_2^2 + \beta_2^2\right)\right]$$
$$= \tfrac{4}{7}|e|\langle r^{-3}\rangle F_0(\alpha, \beta). \tag{9}$$

Similarly,

$$\langle V_{zz}\rangle_{\psi_{-1}} = \langle\psi_{-1}|V_{zz}|\psi_{-1}\rangle$$
$$= A_{-1}^2\tfrac{4}{7}|e|\langle r^{-3}\rangle\left[-\tfrac{1}{2} + \left(\alpha_1^2 + \beta_1^2\right) - \left(\alpha_4^2 + \beta_4^2\right)\right]$$
$$= \tfrac{4}{7}|e|\langle r^{-3}\rangle F_{-1}(\alpha, \beta) \tag{10}$$

and

$$\langle V_{zz}\rangle_{\psi_1} = \langle\psi_1|V_{zz}|\psi_1\rangle = A_1^2 \tfrac{4}{7}|e|\langle r^{-3}\rangle \left[-\tfrac{1}{2} + \left(\alpha_2^2 + \beta_2^2\right) - \left(\alpha_4^2 + \beta_4^2\right)\right] = \tfrac{4}{7}|e|\langle r^{-3}\rangle F_1(\alpha, \beta) \tag{11}$$

where we have used the standard values of the EFG [2] produced by the pure orbitals.

The EFG remains axially symmetric even after vibronic coupling. The Boltzmann thermal average of the EFG is finally obtained as

$$\langle V_{zz}\rangle_T = \frac{\langle V_{zz}\rangle_{\psi_0} + \langle V_{zz}\rangle_{\psi_{-1}}\mathrm{e}^{-\Delta_1/k_B T} + \langle V_{zz}\rangle_{\psi_1}\mathrm{e}^{-\Delta_2/k_B T}}{1 + \mathrm{e}^{-\Delta_1/k_B T} + \mathrm{e}^{-\Delta_2/k_B T}}. \tag{12}$$

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

$$(\Delta E_Q)_T = (\Delta E_Q)_0 \frac{F_0(\alpha, \beta) + F_{-1}(\alpha, \beta)\mathrm{e}^{-\Delta_1/k_B T} + F_1(\alpha, \beta)\mathrm{e}^{-\Delta_2/k_B T}}{1 + \mathrm{e}^{-\Delta_1/k_B T} + \mathrm{e}^{-\Delta_2/k_B T}} \tag{13}$$

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.

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

The calculation of Fe^{2+} quadrupole splitting in CsCoCl₃ needs a good estimate of various parameters. We have taken $(\Delta E_Q)_0 = 2.63$ mm s⁻¹, which is the measured value at 22 K assuming that the vibrational effect will be negligible at low temperatures. The spin–orbit coupling parameter $\lambda = 103$ cm⁻¹ for a free Fe^{2+} ion, but its magnitude decreases significantly due to covalency in various compounds. In order to match the theoretical and experimental values of the quadrupole splitting, an approximate value of $\lambda \simeq 65$ cm⁻¹ has already been estimated by Ward et al [1]. We have done the calculation for $\lambda = 60$ cm⁻¹.

An experimental value of the Debye temperature (Θ_D) in this compound is not available; however, it has been estimated to be $\simeq$260 K [1]. We have done the calculation for $\Theta_D = 250$ K and the velocity of sound v has been estimated from the standard phonon density-of-states relation

$$v^3 = \frac{V E_D^3}{6\pi^2 \hbar^3 N}$$

where N is the number of molecules in volume V and E_D the Debye energy. The molecular weight of this compound is 298 g mol⁻¹ and the density $\rho = 2.8$ g cm⁻³, which corresponds to the molar volume $V = 106.4$ cm³. This gives $v = 4.7 \times 10^5$ cm s⁻¹. The calculations have also been performed for different values of Θ_D ranging from 150 K to 350 K keeping the other parameters fixed ($\delta = 5500$ cm⁻¹ and $\Delta = 410$ cm⁻¹) and the results are shown in figure 2. It appears that a change of the order of ± 100 K in the value of Θ_D does not affect the results significantly.

The static parameter B_4^0 is obtained from the octahedral field splitting $180 B_4^0 = \delta$. In an earlier calculation, δ has been estimated to be $\simeq$6000 cm⁻¹ [11, 1]. We have done the calculations for δ ranging from 4500 cm⁻¹ to 7000 cm⁻¹ (taking $\Theta_D = 250$ K and $\Delta = 410$ cm⁻¹) and the results are plotted in figure 3.

In order to get a better agreement between the theoretical and experimental values of the quadrupole splitting, we have generated several sets of theoretical values of ΔE_Q as a function of temperature by taking different values of Δ between 350 and 550 cm⁻¹. The static parameter B_0^2 $(9 B_0^2 = \Delta)$ and Δ_1 $(=\Delta - 2\lambda)$ and Δ_2 $(=\Delta + 2\lambda)$ are each time derived for a
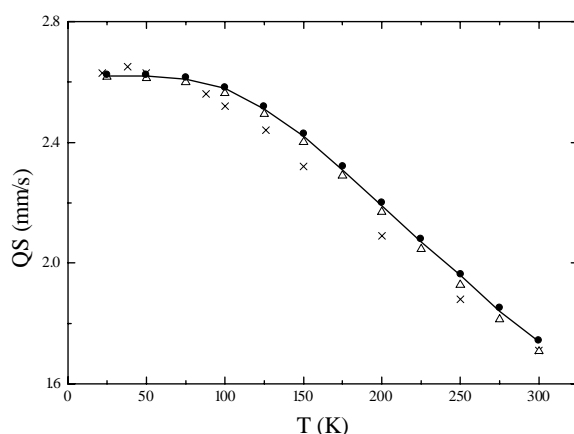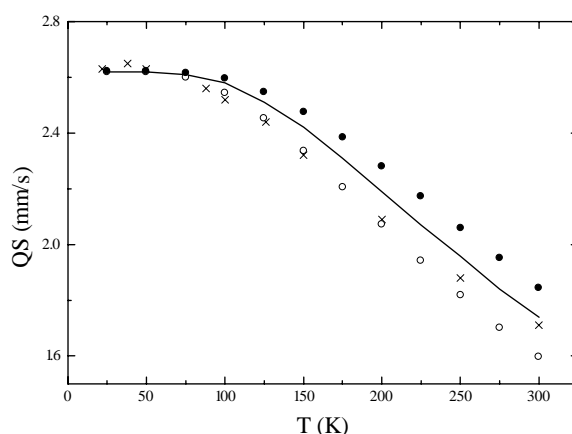
Figure 2. Comparison of observed and calculated quadrupole splitting of Fe^{2+} in $CsCo_{0.99}Fe_{0.01}Cl_3$ as a function of temperature for different values of Θ_D. $\times$, experimental; solid line, $\triangle$ and $\bullet$, calculated for $\Theta_D = 250$, 150 and 350 K respectively. Here $\delta = 5500$ cm^{-1} and $\Delta = 410$ cm^{-1}.
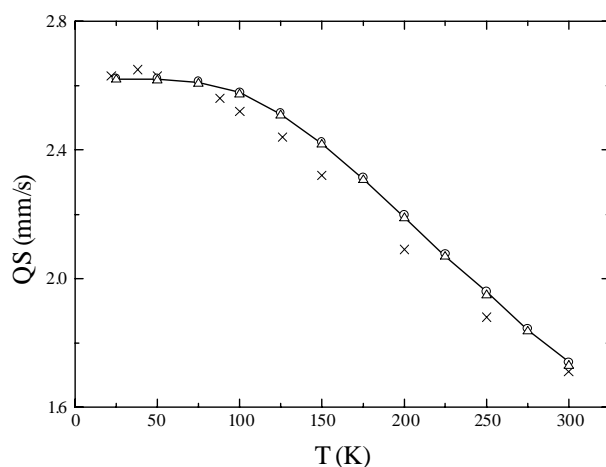
Figure 3. Comparison of observed and calculated quadrupole splitting of Fe^{2+} in $CsCo_{0.99}Fe_{0.01}Cl_3$ as a function of temperature for different values of δ. $\times$, experimental; solid line, $\triangle$ and $\circ$, calculated for $\delta = 5500$, 7000 and 4500 cm^{-1} respectively. Here $\Theta_D = 250$ K and $\Delta = 410$ cm^{-1}.

given value of Δ. The matrix elements over the dynamic crystal-field potential are calculated as done previously [6]. The dynamic crystal-field parameters are calculated using Huang's approximation [14]. It has been found that for $\Delta = 410$ cm^{-1} and hence $\Delta_1 = 290$ cm^{-1} and $\Delta_2 = 530$ cm^{-1}, the agreement between calculated and observed values of $(\Delta E_Q)_T$ is fair. The results are shown in figure 4. It is seen that a small change of the order of ± 20 K in the value of Δ does not affect the results significantly but a large change does. Thus a best fit of the observed data is obtained for $\Theta_D = 250$ K, $\delta = 5500$ cm^{-1} and $\Delta = 410$ cm^{-1} as shown in figures 2, 3 and 4 by a continuous line. These values are quite reasonable and well within the expected range. It is to be mentioned here that in an octahedrally symmetric environment the three T_{2g} states are degenerate (figure 1) and hence are equally populated by the sixth

Figure 4. Comparison of observed and calculated quadrupole splitting of Fe^{2+} in CsCo$_{0.99}$Fe$_{0.01}$Cl$_3$ as a function of temperature for different values of Δ. $\times$, experimental; solid line, $\circ$ and $\bullet$, calculated for $\Delta = 410$, 440 and 390 cm^{-1} respectively. Here $\delta = 5500$ cm^{-1} and $\Theta_D = 250$ K.

electron. Such an equal mixture of the three states has cubic symmetry. So a variation in the value of δ does not affect the results as shown in figure 3. In the axial (trigonal) symmetry, the environment is distorted from octahedral symmetry and the threefold degeneracy of the T$_{2g}$ orbitals is lifted (figure 1). The population of these levels is now determined by the Boltzmann factor $\exp(-\Delta/k_B T)$. So the calculated results are highly sensitive to Δ, which is reflected in figure 4.

5. Conclusions

The overall agreement between the theoretical and the experimental data of quadrupole splitting between 25 and 300 K is fairly good, which indicates that the proposed scheme is physically consistent and satisfactory. Hence the orbit-lattice interaction (vibronic coupling) can reasonably explain the observed temperature dependence of Fe^{2+} quadrupole splitting in CsCo$_{0.99}$Fe$_{0.01}$ Cl$_3$ over 25 to 300 K. This interaction, though weak in general, may be quite important in the case of 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.

Acknowledgement

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