

Effect of the orbit-lattice interaction in Mössbauer studies: Quadrupole splitting of ^{57}Fe (II) in MgCO_3

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The Mössbauer quadrupole splitting of substitutional $^{57}\text{Fe}^{2+}(3d^6, ^5D)$ ions in MgCO_3 decreases linearly with temperature from 77 to 300 K. This temperature dependence cannot be explained on the basis of a static crystal-field interaction only, which usually gives the electronic eigenstates and the resulting quadrupole splitting of the ferrous ion. In this paper the effect of the orbit-lattice interaction (or vibronic coupling) on electronic states has been included, and then it is found that the observed temperature dependence of quadrupole splitting can be explained quite satisfactorily. It leads to the conclusion that the orbit-lattice interaction might be an important factor which affects the temperature variation of other Mössbauer parameters as well and hence its effect should be duly considered in Mössbauer studies.

I. INTRODUCTION

The orbit-lattice interaction (or vibronic coupling) is considered to be an important factor in producing the temperature dependence of electronic observables of magnetic ions. It is especially important in ESR studies, where small energy changes in electronic states can be accurately measured. For example, the orbit-lattice interaction has been utilized to explain the temperature dependence of spin-Hamiltonian parameters measured from ESR experiments.¹ Similarly the vibronic coupling with excited states has been considered important while determining the magnetic hyperfine coupling constant of S -state ions.² This interaction is also 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. In fact Shrivastava³ has shown that the Mössbauer isomer shift can change significantly in the presence of orbit-lattice interaction. The importance of vibronic interaction in Mössbauer studies has been qualitatively underlined by Gibb, Greenwood, and Sastry⁴ while interpreting the temperature dependence of the quadrupole splitting of Fe^{2+} in $[\text{N}(\text{CH}_3)_4]_2(\text{FeCl}_4)$. Similarly Bacci^{5,6} has included the effects of vibronic coupling while analyzing the Mössbauer quadrupole splitting and magnetic-susceptibility data of Fe^{2+} in deoxyhemoglobin and deoxymyoglobin. The strength of this interaction has been considered extremely important for the observation and interpretation of Mössbauer spin-relaxation spectra of Fe^{2+} ions in various systems.^{7,8} Recently, Price⁹ has also exploited the concept of vibronic coupling to explain the observed temperature dependence of Fe^{2+} quadrupole splitting in FeCO_3 because the experimental results cannot be explained on the basis of a static lattice. His theoretically calculated values do not show a reasonable agreement with experimental data and hence the problem needs a fresh investigation. In the following sections the vibronically perturbed electronic states of Fe^{2+} in carbonates

will be obtained and then the value of quadrupole splitting as a function of temperature will be explicitly calculated and compared with the experimental data. Such a study is expected to elucidate the importance of orbit-lattice interaction in Mössbauer studies.

II. ELECTRONIC STATES AND QUADRUPOLE SPLITTING

In a carbonate crystal the substitutional Fe^{2+} ions occupy trigonally distorted cubic sites and experience a strong crystal-field potential given by^{7,10}

$$H_{\text{cr}} = B_4^0(O_4^0 - 20\sqrt{2}O_4^{\pm 3}) + B_2^0O_2^0, \quad (1)$$

where B_n^m and O_n^m ($n=2, 4$, and $m=0, \pm 3$) are the static crystal-field parameters and Steven's equivalent operators¹⁰ compiled by Orbach.¹¹ The strong cubic field splits the 5D state of a free Fe^{2+} ion into a ground triplet $^5T_{2g}$ and an excited doublet 5E_g with energy separation $|180B_4^0| \simeq 10^4 \text{ cm}^{-1,12,13}$. At ordinary temperatures the Boltzmann population of the doublet E_g is almost negligible and hence its effect is neglected. A small trigonal-distortion potential $B_2^0O_2^0$ splits the T_{2g} states further into a lower doublet 5E_g and an upper singlet $^5A_{1g}$ with energy separation $\Delta = |9B_2^0| \simeq 1000 \text{ cm}^{-1,10-14}$. The appropriate electronic eigenstates are,^{10,15} for $^5A_{1g}$,

$$\phi_0 = Y_2^0,$$

and for 5E_g

$$\phi_1 = -(\frac{2}{3})^{1/2}Y_2^{-2} - (\frac{1}{3})^{1/2}Y_2^1,$$

$$\phi_{-1} = (\frac{2}{3})^{1/2}Y_2^2 - (\frac{1}{3})^{1/2}Y_2^{-1}. \quad (2)$$

Each of these electronic states (or crystal-field states) produces its own electric field gradient (EFG) at the Fe nucleus giving rise to a quadrupole splitting. Since this is a case of axial symmetry the quadrupole splitting is produced by the thermal average of the z component of the EFG only, which is given by^{16,17}

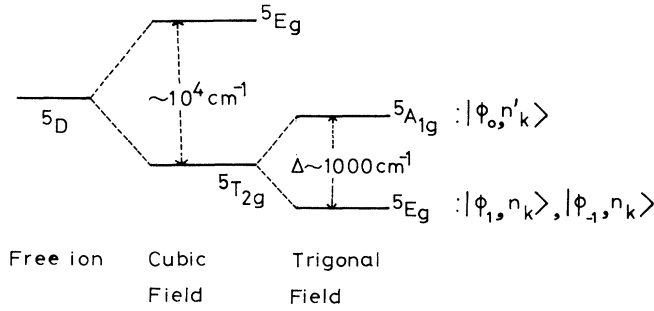


FIG. 1. Energy-level scheme of Fe^{2+} in MgCO_3 .

$$\langle V_{zz} \rangle_T = \frac{\langle V_{zz} \rangle_1 + \langle V_{zz} \rangle_{-1} + \langle V_{zz} \rangle_0 e^{-\Delta/k_B T}}{1 + 1 + e^{-\Delta/k_B T}}, \quad (3)$$

where

$$\begin{aligned} V_{zz} &= \left(\frac{2}{7}\right) |e\rangle \langle r^{-3} [L_z^2 - \frac{1}{3} L(L+1)] |e\rangle, \\ \langle V_{zz} \rangle_{\pm 1} &= \langle \phi_{\pm 1} | V_{zz} | \phi_{\pm 1} \rangle = \left(\frac{2}{7}\right) |e\rangle \langle r^{-3} |, \\ \langle V_{zz} \rangle_0 &= \langle \phi_0 | V_{zz} | \phi_0 \rangle = -\left(\frac{4}{7}\right) |e\rangle \langle r^{-3} |. \end{aligned} \quad (4)$$

Since the sign of $\langle V_{zz} \rangle_0$ is opposite to that of $\langle V_{zz} \rangle_{\pm 1}$ the thermal average of the EFG should decrease with increasing temperature. However, for $\Delta \approx 10^3 \text{ cm}^{-1}$ (which is very high) the value of $\langle V_{zz} \rangle_T$, and hence the quadrupole splitting, remains almost unchanged from 4.2 to 300 K. This is quite contrary to experimental data for Fe^{2+} in MgCO_3 (Ref. 18) and FeCO_3 .¹⁵ In paramagnetic $\text{Fe}^{2+}:\text{MgCO}_3$ the quadrupole splitting decreases very slightly from 2.02 to 2.01 mm/sec as the temperature increases from 4.2 to 77 K; but it shows a considerable linear decrease over the temperature range 77–300 K. In FeCO_3 , which is antiferromagnetic at low temperatures, the quadrupole splitting initially increases from 2.02 to 2.09 mm/sec as the temperature increases from 4.2 to 43.8 K (which is close to its Néel temperature 38.3 K), but in the paramagnetic state the quadrupole splitting again shows a linear decrease over the temperature range 60 to 200 K. It is this observed linear and substantial decrease of quadrupole splitting that cannot be explained by the existing concept of static lattice.

$$\Psi_1 = A \left[| \phi_{1, n_k} \rangle + \frac{\langle \phi_{1, n_k} | H_{ol} | \phi_{0, n'_k} \rangle}{[\Delta + \hbar\omega_k(n'_k + \frac{1}{2})] - [\hbar\omega_k(n_k + \frac{1}{2})]} | \phi_{0, n'_k} \rangle \right], \quad (7)$$

where A is the normalization constant. The operator H_{ol} contains a linear combination of a_k and a_k^* , and hence the matrix can have a nonzero values only when $n'_k - n_k = \pm 1$. Then it may be explicitly written that

$$\begin{aligned} \Psi_1 = A \left[| \phi_{1, n_k} \rangle + \frac{\langle \phi_{1, n_k} | H_{ol} | \phi_{0, n_k+1} \rangle}{\Delta + \hbar\omega_k} | \phi_{0, n_k+1} \rangle \right. \\ \left. + \frac{\langle \phi_{1, n_k} | H_{ol} | \phi_{0, n_k-1} \rangle}{\Delta - \hbar\omega_k} | \phi_{0, n_k-1} \rangle \right], \quad (8) \end{aligned}$$

III. EFFECT OF ORBIT-LATTICE INTERACTION

Since A_{1g} and E_g group theoretical irreducible representations correspond to symmetric electronic wave functions they can be coupled only through some symmetric vibrational mode as required from parity considerations.^{9,19} It is known that the symmetric modes of vibration of an octahedral complex (or molecule) are A_{1g} , E_g , and T_{2g} . Now it can be seen that the electronic states E_g and A_{1g} are coupled through the E_g vibrational mode only because the product $\langle A_{1g} | E_g | E_g \rangle$ contains A_{1g} and hence it is nonzero.¹⁹ It is easy to see that

$$\langle A_{1g} | A_{1g} | E_g \rangle = \langle A_{1g} | T_{2g} | E_g \rangle = 0$$

because these products do not contain A_{1g} . Therefore, the Fe^{2+} quadrupole splitting may show a significant temperature variation if the coupling to the E_g vibrational mode is strong.

The orbit-lattice interaction (which represents the vibrational coupling) under long-phonon-wavelength approximation is given by^{11,20}

$$H_{ol} = \sum_k \sum_{n,m} \left[\frac{\hbar}{2M\omega_k} \right]^{1/2} k V_n^m(L) (a_k + a_k^*), \quad (5)$$

where a_k and a_k^* are phonon annihilation and creation operators,²¹ ω_k is the frequency of phonons with wave vector k , $V_n^m(L)$ is the crystal-field potential with dynamic parameters, and M is the mass of the crystal. As one must consider both electronic and lattice vibrational interactions, the basis states may be represented in the form of a Born-Oppenheimer product of electron and phonon states, such as $|\phi_e, n_k\rangle$. A phonon state of the lattice is expressed in terms of a phonon occupation number n_k , which is given by the Bose-Einstein distribution function. The energy of a noninteracting electron-phonon state is given by

$$E = E_e + \sum_k \hbar\omega_k (n_k + \frac{1}{2}), \quad (6)$$

which is equal to the sum of the electronic and vibrational energies (see Fig. 1).

Now the vibronically perturbed states may be obtained by using the first-order perturbation method. This immediately yields

or

$$\Psi_1 = A (| \phi_{1, n_k} \rangle + \alpha | \phi_{0, n_k+1} \rangle + \beta | \phi_{0, n_k-1} \rangle), \quad (9)$$

where

$$\alpha = \frac{\langle \phi_{1, n_k} | H_{ol} | \phi_{0, n_k+1} \rangle}{\Delta + \hbar\omega_k}, \quad (10a)$$

$$\beta = \frac{\langle \phi_{1, n_k} | H_{ol} | \phi_{0, n_k-1} \rangle}{\Delta - \hbar\omega_k}, \quad (10b)$$

and

$$A^2 = (1 + \alpha^2 + \beta^2)^{-1}. \quad (10c)$$

For the vibronically perturbed eigenstate Ψ_1 , the expectation value of the EFG operator V_{zz} is now given as

$$\langle V_{zz} \rangle_1 = A^2 [\langle \phi_1 | V_{zz} | \phi_1 \rangle + (\alpha^2 + \beta^2) \langle \phi_0 | V_{zz} | \phi_0 \rangle] \quad (11a)$$

(after dropping the identical phonon state assignments). Similarly,

$$\langle V_{zz} \rangle_{-1} = A^2 [\langle \phi_{-1} | V_{zz} | \phi_{-1} \rangle + (\alpha^2 + \beta^2) \langle \phi_0 | V_{zz} | \phi_0 \rangle], \quad (11b)$$

and

$$\langle V_{zz} \rangle_0 = A^2 [\langle \phi_0 | V_{zz} | \phi_0 \rangle + (\alpha^2 + \beta^2) \langle \phi_{\pm 1} | V_{zz} | \phi_{\pm 1} \rangle]. \quad (11c)$$

The EFG remains axially symmetric even after vibronic coupling. The temperature dependence of the EFG (or quadrupole splitting) arises due to the variation of $(\alpha^2 + \beta^2)$ and A^2 with temperature.

Now with the use of the properties of phonon annihilation and creation operators²¹ one obtains that

$$\alpha^2 + \beta^2 = \sum_k \left[\frac{\hbar}{2M\omega_k} \right] \left| \left\langle \phi_1 \left| \sum_{n,m} V_n^m \right| \phi_0 \right\rangle \right|^2 \times \left[\frac{k^2(n_k+1)}{(\Delta + \hbar\omega_k)^2} + \frac{k^2n_k}{(\Delta - \hbar\omega_k)^2} \right]. \quad (12)$$

It may be assumed that the phonon spectrum of the crystal is Debye-type and isotropic so that

$$\alpha^2 + \beta^2 = \int \left[\frac{\hbar}{2M\omega_k} \right] \left| \left\langle \phi_1 \left| \sum_{n,m} V_n^m \right| \phi_0 \right\rangle \right|^2 \times \left[\frac{k^2(n_k+1)}{(\Delta + \hbar\omega_k)^2} + \frac{k^2n_k}{(\Delta - \hbar\omega_k)^2} \right] g(k) dk, \quad (13)$$

where the density of phonon states for a crystal of volume V is given by

$$g(k) dk = (V/2\pi^2) k^2 dk. \quad (14)$$

$$\langle V_{zz} \rangle_T = \left(\frac{2}{7} \right) |e| \langle r^{-3} \rangle \left[\frac{2[1 - 2aI(T)T^4] + [-2 + aI(T)T^4]e^{-\Delta/k_B T}}{2 + e^{-\Delta/k_B T}} \right]. \quad (18)$$

The quadrupole splitting is proportional to $\langle V_{zz} \rangle_T$. At $T=0$ there is no vibronic coupling and the EFG is produced by the electronic states ($\phi_{\pm 1}$) only. Therefore, one finds that

$$(\Delta E_Q)_T = \frac{(\Delta E_Q)_0}{1 + aI(T)T^4} \left[\frac{2[1 - 2aI(T)T^4] + [-2 + aI(T)T^4]e^{-\Delta/k_B T}}{2 + e^{-\Delta/k_B T}} \right], \quad (19)$$

where $(\Delta E_Q)_T$ and $(\Delta E_Q)_0$ are the quadrupole splitting at temperature T and absolute zero, respectively. This is the general expression for the variation of quadrupole splitting with temperature.

Case I: Low temperatures ($T < \Theta_D$). For $T < \Theta_D$ (or $x > 1$) the integral $I(T)$ must be evaluated numerically at any given temperature. As T increases, the value of the integral decreases. At low temperatures the term containing the fac-

In terms of phonon frequency the expression (13) takes the form

$$\alpha^2 + \beta^2 = \left[\frac{\hbar}{4\pi^2\rho v^5} \right] \left| \left\langle \phi_1 \left| \sum_{n,m} V_n^m \right| \phi_0 \right\rangle \right|^2 \times \int_0^{\omega_D} \left[\frac{\omega_k^3(n_k+1)}{(\Delta + \hbar\omega_k)^2} + \frac{\omega_k^3n_k}{(\Delta - \hbar\omega_k)^2} \right] d\omega_k, \quad (15)$$

where ρ is the density of the crystal, $v (= \omega/k)$ is the velocity of acoustic phonons in the crystal, and ω_D is the Debye frequency.

For FeCO_3 , MgCO_3 , and ZnCO_3 crystals, the Debye temperature^{7,18} $\Theta_D \simeq 300$ K, and hence $\Delta \gg \hbar\omega_k$ for all possible phonons. Therefore, in the denominator of expression (15) $\hbar\omega_k$ may be neglected compared to Δ and then the expression reduces to

$$\alpha^2 + \beta^2 = \left[\frac{\hbar}{4\pi^2\rho v^5} \right] \frac{\left| \left\langle \phi_1 \left| \sum_{n,m} V_n^m \right| \phi_0 \right\rangle \right|^2}{\Delta^2} \times \int_0^{\omega_D} \frac{\omega^3 [\exp(\hbar\omega/k_B T) + 1]}{\exp(\hbar\omega/k_B T) - 1} d\omega, \quad (16)$$

where the phonon occupation number $n = [\exp(\hbar\omega/k_B T) - 1]^{-1}$. With the use of the substitution $x = \hbar\omega/k_B T$, the expression (16) may be expressed in a convenient form such as

$$\alpha^2 + \beta^2 = aI(T)T^4, \quad (17a)$$

where

$$a = \left[\frac{\hbar}{4\pi^2\rho v^5} \right] \frac{\left| \left\langle \phi_1 \left| \sum_{n,m} V_n^m \right| \phi_0 \right\rangle \right|^2}{\Delta^2} \left[\frac{k_B}{\hbar} \right]^4, \quad (17b)$$

and

$$I(T) = \int_0^{\Theta_D/T} \frac{x^3(e^x + 1)dx}{(e^x - 1)}. \quad (17c)$$

Finally with the help of expression (17), (11), and (3) it can easily be seen that in the presence of vibronic coupling the thermal average of the EFG at the nucleus is given by

tor $\exp(-\Delta/k_B T)$ can be neglected. It is easy to see that the quadrupole splitting is a maximum at $T=0$ and it decreases for higher values of T .

Case II: High temperatures ($T > \Theta_D$). In the limit of the high temperatures $T > \Theta_D$ (or $x < 1$) the integral $I(T)$ approximates to

$$I(T) \simeq \frac{2}{3} \left[\frac{\Theta_D}{T} \right]^3 + \frac{1}{4} \left[\frac{\Theta_D}{T} \right]^4. \quad (20)$$

With the use of this result in expression (17a) one finds that

$$\alpha^2 + \beta^2 = bT + c, \quad (21a)$$

where

$$b = \frac{2}{3} a \Theta_D^3, \quad c = \frac{1}{4} a \Theta_D^4. \quad (21b)$$

Finally expression (19) yields that

$$(\Delta E_Q)_T = \frac{(\Delta E_Q)_0}{(1+bT+c)} \left[\frac{2(1-2bT-2c) + (-2+bT+c)e^{-\Delta/k_B T}}{2+e^{-\Delta/k_B T}} \right]. \quad (22)$$

Although the variation of ΔE_Q with T is represented by a complicated formula it is apparent that ΔE_Q decreases with increasing temperature.

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

Any explicit calculation of $(\Delta E_Q)_T$ needs a good estimate of various parameters. From the study of the Mössbauer recoilless fraction in Fe:ZnCO₃ (Ref. 7) and the zero-point energy in Fe:MgCO₃ (Ref. 18) the Debye temperature of these systems has been estimated as 290 ± 20 K. For FeCO₃ the value of the Debye temperature will also be very similar in view of a similar structure, density, and binding forces. Therefore, it is reasonable to assume that for these carbonates $\Theta_D \simeq 300$ K. This is supported by the low-energy (or acoustic) E_g -mode phonon spectrum of various carbonate crystals.²²

For this Debye temperature the velocity of sound is $v \simeq 3.8 \times 10^5$ cm/sec. This may change to some extent from system to system because their densities are somewhat different. However, it will be quite appropriate to take a representative value of $v \simeq 4 \times 10^5$ cm/sec. It will be assumed to be isotropic and independent of phonon frequency and polarization effects if any. It may be noted that the velocity of ultrasonic pulses in CaCO₃ crystals

along various directions of propagation has been found to lie between 2.6×10^5 and 7.2×10^5 cm/sec²³ and the same may be applicable (with slight modifications) for other isomorphous carbonates. Therefore, a mean value of $v \simeq 4 \times 10^5$ cm/sec appears quite reasonable. The value of quadrupole splitting at $T=0$ K will be assumed to be equal to that at $T=4.2$ K because at such low temperatures there are almost no vibrational effects.

Now one has to calculate the matrix elements involved in expression (17b). In a general case when both symmetric and antisymmetric vibrational modes are taken into consideration the matrix element assumes the form^{9,11}

$$\langle \phi_1 \left| \sum_{n,m} V_n^m \right| \phi_0 \rangle = \langle \phi_1 \left| (C_2^1 O_2^{\pm 1} + C_2^2 O_2^{\pm 2} + C_4^1 O_4^{\pm 1} + C_4^2 O_4^{\pm 2}) \right| \phi_0 \rangle, \quad (23)$$

where O_n^m are the Orbach operators,¹¹ and C_n^m are the dynamic crystal-field interaction parameters. However, as the vibronic coupling between $\phi_{\pm 1}(E_g)$ and $\phi_0(A_{1g})$ states is made possible by a symmetric mode of vibration, only those components of the interaction should be retained in

TABLE I. $(\Delta E_Q)_0 = 2.02$ mm/sec, $a = 5.2 \times 10^{-12}$, and ΔE_Q is in mm/sec.

$T(K)$	$I(T)$	ΔE_Q (calculated)	ΔE_Q (observed in Fe:MgCO ₃) Ref. 18	ΔE_Q (observed in FeCO ₃) Ref. 15
77	67.60	1.95	2.01	2.05
100	26.76	1.94	1.99	2.03
150	6.83	1.91	1.95	1.97
200	2.74	1.88	1.90	1.92
250	1.26	1.86	1.85	
300	0.75	1.82	1.80	

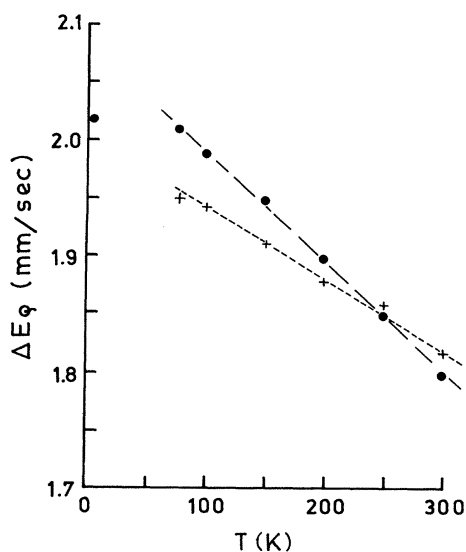


FIG. 2. Mössbauer quadrupole splitting of $\text{Fe}^{2+}:\text{MgCO}_3$ as a function of temperature. ● are the experimental values; + are the calculated values.

calculation, which are symmetric functions of spatial coordinates. Then the matrix element reduces to

$$\begin{aligned} \langle \phi_1 | \sum_{n,m} V_n^m | \phi_0 \rangle &= \langle \phi_1 | (C_2^1 O_2^{\pm 2} + C_4^2 O_4^{\pm 2}) | \phi_0 \rangle \\ &= 2C_2^2 + 6C_4^2 \end{aligned} \quad (24)$$

using $\langle 2 | O_2^{\pm 2} | 0 \rangle = \sqrt{6}$ and $\langle 2 | O_4^{\pm 2} | 0 \rangle = 3\sqrt{6}$, for $L=2$ and $m_L=0, \pm 2$. At this stage one must know the strength of the dynamic crystal-field parameters, which are often unknown. Orbach¹¹ has opined that for transition-metal ions the static and dynamic crystal-field parameters should be very similar. Scott and Jeffries²⁴ have also contributed to the same view. Huang²⁵ has suggested that the dynamic parameters should be about $n+1$ times greater than the static ones. It should be noted that although these approximations are very crude they provide the starting point. Price *et al.*⁷ have calculated the electronic spin-lattice relaxation rate of $^{57}\text{Fe}^{2+}$ in ZnCO_3 and compared the same with the experimental data (obtained from a Mössbauer study at low temperatures) and then they have concluded that the dynamic crystal-field parameters should be substantially higher than the static ones. In view of this evidence in a carbonate lattice, it will be fairly reasonable to start with the Huang's model. Then one can start with the following parameters:

$$|C_2^2| \simeq |3B_2^0| \simeq 3 \times 112 \quad (25)$$

and

$$|C_4^2| \simeq |5B_4^0| \simeq 5 \times 55 \quad (26)$$

in units of cm^{-1} . Utilizing all these estimated parameters in expression (17b) and using $\rho = 3.0 \text{ g/cm}^3$ for $\text{Fe}:\text{MgCO}_3$ one finds that $a \simeq 5.2 \times 10^{-12}$.

The integral $I(T)$ has been numerically evaluated at various temperatures as given in Table I. Once the values of a , $(\Delta E_Q)_0$, and $I(T)$ become available it is easy to calculate $(\Delta E_Q)_T$ at various temperatures by using expression (19). When this is done it is found that the quadrupole splitting decreases linearly with temperature, which is consistent with the experimentally observed behavior despite some discrepancies between calculated and observed data (Table I and Fig. 2).

V. CONCLUSIONS

The agreement between theoretical and experimental values of quadrupole splitting in $\text{Fe}^{2+}:\text{MgCO}_3$ is fairly reasonable as shown in Fig. 2. A significant difference towards the low-temperature side may be due to a departure of the phonon spectrum from its Debye-type nature. Perhaps at low temperatures all vibrational modes are not excited and the vibronic coupling is weak. The linear temperature variation of Fe^{2+} quadrupole splitting in FeCO_3 (for $T > 60 \text{ K}$) can also be explained provided some of the parameters are slightly changed, which will be quite expected.

It is worth mentioning that the anomalous behavior of Fe^{2+} quadrupole splitting in antiferromagnetic FeCO_3 around its Néel temperature has already drawn the attention of Price²⁶ who has shown that it might be due to an Orbach-type¹¹ resonant vibronic coupling (by phonons of energy approximately less than 70 cm^{-1}) between the exchange-split electronic ground doublet.

It might be appropriate to note that Huang's model of estimating the dynamic crystal-field parameters from the static ones appears to be reasonable in the present case and it may also be true in the case of other transition-metal ions. In the present calculation the effect of spin-orbit coupling has not been included because any additional coupling introduced between E_g and A_{1g} states by means of this interaction will be small and it will not be temperature dependent. In perspective the present study shows that the observed linear temperature dependence of the quadrupole splitting of Fe^{2+} in MgCO_3 and FeCO_3 can be quite reasonably explained in terms of a simple phenomenological model of orbit-lattice interaction. This interaction might be important in controlling the temperature dependence of other electronic observables as well.

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