

Vibronic Effects in Mössbauer Spectra: The ^{57}Fe Quadrupole Splitting in FeCO_3

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Abstract

The methods developed by Orbach and coworkers for calculating spin-lattice relaxation rates have been generalized to enable calculation of the effects of vibronic admixture between low-lying electronic states on observables, such as the Mössbauer quadrupole splitting, associated with magnetic ions in crystals. Emphasis is placed on the need to take proper account of the symmetry properties of the phonons until a late stage in the calculation. Application is made to the temperature dependence of the ^{57}Fe quadrupole splitting in FeCO_3 , and it is concluded that, in general, vibronic coupling effects must be considered before static splitting parameters are extracted from experimental data relating to the temperature-dependent populations of electronic levels. The superposition model of the crystal field is employed to estimate the vibronic coupling parameters.

1. Introduction

In this paper the effects of vibronic coupling on the temperature dependence of the electronic observables associated with a magnetic ion in a molecule or crystal will be considered. A formalism enabling at least semiquantitative calculation of these effects will be developed as a generalization of the work of Orbach and coworkers (Orbach 1961; Blume and Orbach 1962; Orbach and Stapleton 1972), and this will be applied to the quadrupole interaction at ^{57}Fe nuclei in FeCO_3 . Mössbauer effect measurements of this interaction have been reported by Ok (1969), Price *et al.* (1973), Nagy *et al.* (1975) and Spiering *et al.* (1976).

This particular effect of the orbit-lattice interaction has not received a great deal of attention in the past, possibly because of a paucity of reliable information on the strength of the interaction, but some investigations have been made, particularly in relation to EPR experiments because of their high sensitivity. For example, Walsh *et al.* (1965) considered the temperature dependence introduced into spin-hamiltonian parameters by vibronic effects, and their work has provided the basis for the explanation of several subsequent EPR investigations (e.g. Serway 1971; Holuj *et al.* 1972). Later, Šimánek and Orbach (1966) calculated the effect of vibronic admixture of excited electronic configurations on the magnetic hyperfine coupling constants of S-state ions. Pilbrow and Spaeth (1967*a*, 1967*b*) found evidence of vibronic admixture within the lowest term of the ground configuration of Cu^{2+} ions in NH_4Cl , and it is this sort of admixture that will be considered here. More recently, Shrivastava (1975) has reviewed orbit-lattice interaction effects in EPR spectra. Some NQR measurements (see e.g. Das and Hahn 1958; Armstrong *et al.* 1970) have also involved consideration of these effects but, in general, calculations have been done only for rather specific cases of localized molecular rotational and torsional oscillations.

Only very rarely have Mössbauer spectroscopists taken any account of the admixture effects produced by the orbit–lattice interaction on their spectra. Lang (1970) and subsequently Cianchi *et al.* (1976) interpreted the strong temperature dependence of the ^{57}Fe quadrupole splitting in oxyhaemoglobin in terms of rotations of an oxygen molecule, and Gibb *et al.* (1972) looked at the possibility that vibronic admixture within the cubic ^5E ground states of the tetrahedrally coordinated $^{57}\text{Fe}^{2+}$ ions in tetragonally distorted sites in $(\text{NMe}_4)_2\text{FeCl}_4$ was a contributing factor to the almost linear dependence of the quadrupole splitting on temperature. This latter work will be seen to be a specific case of the more general formalism to be described here.

On the other hand there has been a great deal of published Mössbauer work in which crystal field parameters, and in some cases their temperature variations, have been extracted from quadrupole splitting data without, apparently, any consideration being given to the possible role of vibronic admixture. It will be shown that such considerations can be important, at least in some cases, and consequently that these effects should only be ignored in the presence of evidence that they are negligible.

The example that will be considered in some detail here, namely the temperature dependence of the ^{57}Fe quadrupole splitting in FeCO_3 , has two main points of interest. Firstly, above the Néel temperature ($\sim 38\text{ K}$) the quadrupole splitting decreases almost linearly with temperature up to over 500 K (Price *et al.* 1973; Nagy *et al.* 1975) and cannot be reconciled with a temperature-independent crystal field model nor with any reasonable temperature dependence of the crystal field (Price *et al.* 1973, and results to be published). Secondly, when the temperature approaches the Néel temperature from below there is a sharp increase in the quadrupole splitting of $\sim 0.07\text{ mm s}^{-1}$ (Ok 1969) that has been speculatively attributed to the effects of magnetostriction on the static crystal field (Nagy *et al.* 1975; Spiering *et al.* 1976). As a result of this work it is believed that the effects of vibronic admixture within the ground term of Fe^{2+} will make at least some contribution to, and possibly even be primarily responsible for, both of these features of interest.

In this work the orbit–lattice interaction is treated as a perturbation on Born–Oppenheimer product states, the electronic parts of which are derived from the static crystal field interaction. This approach is probably not strictly valid in many systems because of the magnitude of the orbit–lattice coupling. In principle this coupling should be included in a perturbation calculation at an earlier stage than some of the smaller crystal field terms and the spin–orbit (and spin–spin) coupling, so that Jahn–Teller effects are taken into account. However, such a procedure appears to be unnecessary at least in some cases, although for reasons that are not clear: it will be argued that the present approach is valid for FeCO_3 . In any case, qualitative conclusions of the importance of accounting for vibronic effects will be unaltered.

In the next section the general framework for the calculations will be outlined. It is based largely on the work of Orbach (1961) on spin–lattice relaxation. In subsequent sections the quadrupole interactions in FeCO_3 will be discussed.

2. Formalism for Calculation of Vibronic Admixtures

(a) Orbit–Lattice Interaction

The orbit–lattice hamiltonian has been discussed by a number of authors, including the recent detailed reviews of Orbach and Stapleton (1972) and Shrivastava (1975), so it will be considered only very briefly here.

If, for the sake of simplicity, a 'quasi-molecular' cluster of a central magnetic ion and its ligands is considered, then the potential acting on an electron in the system can be expanded in powers of the normal coordinates Q_k of the cluster:

$$\mathcal{H} = \mathcal{H}^0 + \sum_k (\partial \mathcal{H}^0 / \partial Q_k) Q_k + \frac{1}{2} \sum_{k,l} (\partial^2 \mathcal{H}^0 / \partial Q_k \partial Q_l) Q_k Q_l + \dots, \quad (1)$$

where \mathcal{H}^0 is the static part that depends on the mean positions of the nuclei. The remainder of \mathcal{H} is a dynamic part, called the orbit-lattice interaction \mathcal{H}_{OL} , that depends on the displacements of the nuclei from their mean positions. Consideration here will only be given to the lowest order effects of this interaction on the value of an electronic observable, and consequently only the term in equation (1) that is linear in the normal coordinates is required.

Equivalently, distortions of the cluster may be described in terms of components of the lattice strain tensor ϵ , and Orbach (1961) wrote the (linear) orbit-lattice interaction in the form

$$\mathcal{H}_{OL} = \sum_{n,m} v_n^m \epsilon_n^m, \quad (2)$$

which is the scalar product of tensor operators v and ϵ whose components v_n^m and ϵ_n^m transform under rotation as tesseral harmonics. The matrix elements of equation (2) are strictly equivalent to those of the linear term in equation (1) only when the cluster has octahedral symmetry. For noncubic complexes an arbitrary distortion contains other terms (e.g. Curtis *et al.* 1969), even for static distortions (e.g. Ivanenko and Malkin 1970). However, for crystals in which both anions and cations are in sites of inversion symmetry, the form (2) is obtained for \mathcal{H}_{OL} in the limit of long wavelength acoustic phonons (or externally applied stress).

Since the strain is a symmetric cartesian tensor of rank 2, there are only six harmonic components given by $n = 0, 2$ and $m = -n, \dots, n$. Consequently, for an ion in a site of O_h symmetry, only the strains produced by even-parity modes contribute to matrix elements of the linear term in the orbit-lattice interaction and only electronic states with the same parity are mixed by it.

Levy's (1970) analysis of the adiabatic aspects of spin-lattice relaxation indicates that rotational modes are important but, for simplicity, they will be ignored here. In any case his work indicates that their importance arises principally from the relative motion of an applied field, which is fixed relative to laboratory axes, and the modulated crystalline potential. In this paper the effect of an applied field on the orbit-lattice interaction is not being considered.

The operators v_n^m in equation (2) act only on the electronic coordinates and may be written in terms of tesseral (or spherical) harmonics. The general form of v_n^m is

$$v_n^m = \sum_{l,m'} b_{lm'}(n, m) Z_l^{m'}, \quad (3)$$

where the $Z_l^{m'}$ are tesseral harmonics and the $b_{lm'}(n, m)$ are coupling coefficients. The summation over m' is from $-l$ to l , and for 3d ions only $l = 2, 4$ need be considered. The number of independent coupling parameters can be limited by consideration of the symmetry properties of the cluster (or of the point symmetry of the magnetic ion in the lattice). The orbit-lattice hamiltonian (2) can then be re-expressed in the form

$$\mathcal{H}_{OL} = \sum_{\Gamma, p} \sum_l b_l(\Gamma) B_l(\Gamma, p) \epsilon(\Gamma, p), \quad (4)$$

where the $\varepsilon(\Gamma, p)$ are those linear combinations of components of the strain tensor that transform as the p th subvector of the representation Γ of the relevant point group and the $B_i(\Gamma, p)$ are appropriately transforming linear combinations of the tesseral harmonics Z_i^m . The $b_i(\Gamma)$ are the coupling coefficients, which will be estimated here using the superposition model of the crystal field (Newman 1971, 1978). A brief summary of this procedure is given in subsection (d) below, but first the strain operator and its matrix elements are discussed.

(b) Strain Operator

It will become apparent that the symmetry properties of the lattice strain operator are important and must be taken into account throughout the initial stages of the calculation of vibronic admixture, in contrast to the common practice in calculating spin-lattice relaxation rates (Orbach 1961; Scott and Jeffries 1962) of using an average strain from the outset. For this reason the operator and its matrix elements will be described in some detail.

Standard texts (e.g. Kittel 1956, 1963) show that a cartesian component of the strain induced by long wavelength acoustic phonons of frequency $\omega(\mathbf{k}, s)$ at an ion of mass M situated at the origin may be written as

$$\varepsilon_{\mu\nu} = i \sum_{\mathbf{k}, s} \{ \hbar/2M \omega(\mathbf{k}, s) \}^{\frac{1}{2}} (a_{\mathbf{k}, s} - a_{\mathbf{k}, s}^\dagger) R(\mathbf{k}, s, \mu, \nu), \quad (5)$$

where

$$R(\mathbf{k}, s, \mu, \nu) = \frac{1}{2} \{ k_\mu e_\nu(\mathbf{k}, s) + k_\nu e_\mu(\mathbf{k}, s) \},$$

with $e(\mathbf{k}, s)$ a unit vector in the direction of the polarization s of the phonon of wave vector \mathbf{k} , and $a_{\mathbf{k}, s}^\dagger$ and $a_{\mathbf{k}, s}$ are creation and annihilation operators for such a phonon. When these cartesian components are regrouped to transform under rotation in a particular way it is only the form of the factor R that is modified (Orbach and Tachiki 1967; Orbach and Stapleton 1972). Thus components of the strain operator that transform as spherical tensor components as in equation (2) may be written as

$$\varepsilon_n^m = i \sum_{\mathbf{k}, s} \{ \hbar/2M \omega(\mathbf{k}, s) \}^{\frac{1}{2}} (a_{\mathbf{k}, s} - a_{\mathbf{k}, s}^\dagger) R(\mathbf{k}, s, n, m), \quad (6)$$

with the R factor appropriately defined. For a particular set of \mathbf{k}, s values the $R(\mathbf{k}, s, n, m)$ transform under rotation like the tesseral harmonic functions Z_n^m and can therefore form a basis for a $(2n+1)$ dimensional representation of the full rotation group. They are clearly orthogonal:

$$\sum_{\mathbf{k}} R^*(\mathbf{k}, s, n, m) R(\mathbf{k}, s, n', m') \propto \delta_{nn'} \delta_{mm'}, \quad (7)$$

with the summation over the directions of \mathbf{k} only.

The component of ε that transforms as the p th subvector of the irreducible representation Γ of the point group of the central ion can similarly be written

$$\varepsilon(\Gamma, p) = i \sum_{\mathbf{k}, s} \{ \hbar/2M \omega(\mathbf{k}, s) \}^{\frac{1}{2}} (a_{\mathbf{k}, s} - a_{\mathbf{k}, s}^\dagger) R(\mathbf{k}, s, \Gamma, p) \quad (8)$$

and, for a particular set of \mathbf{k}, s , the R functions form a basis for the representation

Γ . The orthogonality relation for the R functions that is equivalent to (7) can be derived from the orthogonality theorem of group representations (e.g. Tinkham 1964). If A_γ ($\gamma = 1, \dots, h$) are the symmetry elements of the point group, then

$$\sum_{\gamma=1}^h \{A_\gamma R(\mathbf{k}, s, \Gamma, p)\}^* A_\gamma R(\mathbf{k}, s, \Gamma', p') = (h/l_i) \delta_{\Gamma\Gamma'} \delta_{pp'} \sum_{p=1}^{l_i} |R(\mathbf{k}, s, \Gamma, p)|^2, \quad (9)$$

where l_i is the dimensionality of Γ . Hence, if \mathbf{k}_γ are a set of \mathbf{k} vectors that are related by symmetry elements of the point group, then

$$\sum_{\mathbf{k}_\gamma} R^*(\mathbf{k}, s, \Gamma, p) R(\mathbf{k}, s, \Gamma', p') = (h/l_i) \delta_{\Gamma\Gamma'} \delta_{pp'} \sum_{p=1}^{l_i} |R(\mathbf{k}, s, \Gamma, p)|^2. \quad (10)$$

Baker (1971) previously drew attention to the orthogonality of these R functions, but his paper appears to contain an error (in the derivation of his equation 21) that would be overcome by use of the above relation. However, his qualitative conclusions are unaffected.

From equation (8) it can be seen that the only nonzero matrix elements of $\varepsilon(\Gamma, p)$ are

$$\langle N(\mathbf{k}, s) + 1 | \varepsilon(\Gamma, p) | N(\mathbf{k}, s) \rangle = -i[\hbar\{N(\mathbf{k}, s) + 1\}/2M\omega(\mathbf{k}, s)]^{\frac{1}{2}} R(\mathbf{k}, s, \Gamma, p), \quad (11a)$$

$$\langle N(\mathbf{k}, s) - 1 | \varepsilon(\Gamma, p) | N(\mathbf{k}, s) \rangle = i[\hbar N(\mathbf{k}, s)/2M\omega(\mathbf{k}, s)]^{\frac{1}{2}} R(\mathbf{k}, s, \Gamma, p), \quad (11b)$$

where $N(\mathbf{k}, s)$ is the number of phonons with wave vector \mathbf{k} and polarization index s .

(c) Calculation of Vibronic Admixture Effects

The basis states for the calculation will be taken to be Born–Oppenheimer products of the form

$$\Phi_{i\alpha}^0 = \psi_i \left| \prod_{\mathbf{k}, s} N_\alpha(\mathbf{k}, s) \right\rangle \quad (12)$$

where ψ_i is a solution, corresponding to the eigenvalue E_i , of the Schrödinger equation for an electron on the central ion with all nuclei fixed at their mean positions. (Possible difficulties inherent in this approach have been mentioned in the Introduction and will be discussed in more detail below. For the moment it will be assumed to be valid.) The $N_\alpha(\mathbf{k}, s)$ are the occupation numbers of the phonon states of wave vector \mathbf{k} and polarization index s ; the index α relates the particular set of occupation numbers to the product state $\Phi_{i\alpha}^0$. The energy of this state is

$$E_{i\alpha}^0 = E_i + \sum_{\mathbf{k}, s} \{N_\alpha(\mathbf{k}, s) + \frac{1}{2}\} \hbar\omega(\mathbf{k}, s). \quad (13)$$

Perturbed states are calculated by the usual first-order method, i.e.

$$\Phi_{i\alpha} = A_{i\alpha} \left\{ \Phi_{i\alpha}^0 + \sum_{j, \beta}' \left(\frac{\langle \Phi_{j\beta}^0 | \mathcal{H}_{OL} | \Phi_{i\alpha}^0 \rangle}{E_{i\alpha}^0 - E_{j\beta}^0} \Phi_{j\beta}^0 \right) \right\}, \quad (14)$$

where $A_{i\alpha}$ is the normalization constant and the summation is over all pairs of indices

(j, β) that differ from the pair (i, α) . The matrix elements of \mathcal{H}_{OL} that appear in equation (14) can be written as a sum of products of electronic and phonon matrix elements from equations (4) and (12) as

$$\langle \Phi_{j\beta}^0 | \mathcal{H}_{\text{OL}} | \Phi_{i\alpha}^0 \rangle = \sum_{\Gamma, p} \sum_{l'} b_l(\Gamma) \langle \psi_j | B_l(\Gamma, p) | \psi_i \rangle \times \left\langle \prod_{k,s} N_{\beta}(\mathbf{k}, s) \left| \varepsilon(\Gamma, p) \right| \prod_{k,s} N_{\alpha}(\mathbf{k}, s) \right\rangle. \quad (15)$$

Equation (14) shows that the perturbed wavefunctions $\Phi_{i\alpha}$ are linear combinations of Born–Oppenheimer products and consequently that the Born–Oppenheimer approximation is no longer valid. The values of observables, and in particular those that depend only on the electronic coordinates, can now be calculated from these wavefunctions. Specific reference will be made below to the electric field gradient produced by the central ion at its nucleus (to be referred to as the e.f.g., and denoted by the cartesian tensor operator \mathbf{V}), but the method is equally applicable to other measurable quantities such as g values and magnetic susceptibility.

Since the typical sampling time for a Mössbauer effect measurement, the nuclear excited state lifetime, is much longer than a typical phonon vibrational period, the time average of the e.f.g. produced by the perturbed states $\Phi_{i\alpha}$ is required. This means that the expectation value of the e.f.g. operator \mathbf{V} for the perturbed states must be calculated (e.g. Kramers 1957). Since \mathbf{V} acts only on the electronic part of a Born–Oppenheimer product, and since \mathcal{H}_{OL} , through the matrix elements of the strain operator (11), must change the set of phonon occupation numbers of a state on which it operates, products of the form $\langle \Phi_{j\beta}^0 | \mathcal{H}_{\text{OL}} | \Phi_{i\alpha}^0 \rangle \langle \Phi_{i\alpha}^0 | \mathbf{V} | \Phi_{j\beta}^0 \rangle$ must be zero. Consequently, the expectation value of \mathbf{V} contains no terms that are first order in \mathcal{H}_{OL} , and to lowest order in \mathcal{H}_{OL} it is given by

$$\langle \Phi_{i\alpha} | \mathbf{V} | \Phi_{i\alpha} \rangle = |A_{i\alpha}|^2 \left(\langle \Phi_{i\alpha}^0 | \mathbf{V} | \Phi_{i\alpha}^0 \rangle + \sum_{\substack{j,\beta \\ j',\beta'}} \frac{\langle \Phi_{i\alpha}^0 | \mathcal{H}_{\text{OL}} | \Phi_{j'\beta'}^0 \rangle \langle \Phi_{j'\beta'}^0 | \mathbf{V} | \Phi_{j\beta}^0 \rangle \langle \Phi_{j\beta}^0 | \mathcal{H}_{\text{OL}} | \Phi_{i\alpha}^0 \rangle}{(E_{i\alpha}^0 - E_{j'\beta'}^0)^* (E_{i\alpha}^0 - E_{j\beta}^0)} \right). \quad (16)$$

It will be seen that, since \mathbf{V} is an electronic operator, the only nonzero contributions to the second term in equation (16) arise when $\beta' = \beta$.

Now the second term in equation (16), which shall be called $\langle \Delta \mathbf{V} \rangle_{i\alpha}$, can be written using equations (4) and (12) as

$$\langle \Delta \mathbf{V} \rangle_{i\alpha} = \sum_{jj'} \langle \psi_{j'} | \mathbf{V} | \psi_j \rangle \sum_{\substack{\Gamma, p \\ \Gamma', p'}} \sum_{l'} \langle \psi_i | b_l(\Gamma) B_l(\Gamma, p) | \psi_{j'} \rangle \langle \psi_j | b_{l'}(\Gamma') B_{l'}(\Gamma', p') | \psi_i \rangle \times \left\{ \sum_{\beta} \frac{\left\langle \prod_{ks} N_{\alpha}(\mathbf{k}, s) \left| \varepsilon(\Gamma, p) \right| \prod_{ks} N_{\beta}(\mathbf{k}, s) \right\rangle \left\langle \prod_{ks} N_{\beta}(\mathbf{k}, s) \left| \varepsilon(\Gamma', p') \right| \prod_{ks} N_{\alpha}(\mathbf{k}, s) \right\rangle}{(E_{i\alpha}^0 - E_{j'\beta}^0)^* (E_{i\alpha}^0 - E_{j\beta}^0)} \right\}. \quad (17)$$

Expansion of the term inside the braces (which involves the phonon states only and which will be denoted $C_{jj'}^i$), using the matrix elements (11) of the strain operator

and equation (13), gives

$$C_{jj'}^i = \sum_{\mathbf{k}, s} \left(\frac{\hbar}{2M \omega(\mathbf{k}, s)} \right) R^*(\mathbf{k}, s, \Gamma, p) R(\mathbf{k}, s, \Gamma', p') \times \left(\frac{N_\alpha(\mathbf{k}, s) + 1}{\{E_i - E_{j'} - \hbar\omega(\mathbf{k}, s)\}^* \{E_i - E_j - \hbar\omega(\mathbf{k}, s)\}} + \frac{N_\alpha(\mathbf{k}, s)}{\{E_i - E_{j'} + \hbar\omega(\mathbf{k}, s)\}^* \{E_i - E_j + \hbar\omega(\mathbf{k}, s)\}} \right). \quad (18)$$

The importance of properly accounting for the symmetry properties of the strain operator up to this point in the calculation now becomes clear. The phonon frequencies $\omega(\mathbf{k}, s)$ and the population factors $N_\alpha(\mathbf{k}, s)$ will be invariant for \mathbf{k} vectors that are related by symmetry elements of the space group of the crystal. Furthermore, at least for the simple, or symmorphic, space groups, the point group is a subgroup of the space group, so that these quantities will be independent of \mathbf{k} for \mathbf{k} vectors that are related by symmetry elements of the point group, i.e. for \mathbf{k} vectors that belong to a set \mathbf{k}_γ , as introduced above. Therefore, using the orthogonality relation (10), the expression (18) becomes

$$C_{jj'}^i = \sum_{\mathbf{k}', s} \left(\frac{\hbar}{2M \omega(\mathbf{k}', s)} \right) \left(\frac{N_\alpha(\mathbf{k}', s) + 1}{\{E_i - E_{j'} - \hbar\omega(\mathbf{k}', s)\}^* \{E_i - E_j - \hbar\omega(\mathbf{k}', s)\}} + \frac{N_\alpha(\mathbf{k}', s)}{\{E_i - E_{j'} + \hbar\omega(\mathbf{k}', s)\}^* \{E_i - E_j + \hbar\omega(\mathbf{k}', s)\}} \right) \times (h/l_i) \delta_{\Gamma\Gamma'} \delta_{pp'} \sum_{p=1}^{l_i} |R(\mathbf{k}', s, \Gamma, p)|^2, \quad (19)$$

where the summation is over vectors \mathbf{k}' that are not related by symmetry elements of the point group, that is, \mathbf{k} vectors that lie in the irreducible segment of the Brillouin zone. The effect of the δ functions in equation (19) is to eliminate the summations over Γ' and p' in equation (17) so that the electronic contribution to $\langle \Delta \mathbf{V} \rangle_{ia}$ becomes

$$\sum_{jj'} \langle \psi_{j'} | \mathbf{V} | \psi_j \rangle \sum_{\Gamma, p} \sum_{\Gamma', p'} \langle \psi_i | b_i(\Gamma) B_i(\Gamma, p) | \psi_{j'} \rangle \langle \psi_j | b_i(\Gamma') B_i(\Gamma', p') | \psi_i \rangle. \quad (20)$$

Failure to include these δ functions in this way may result not only in incorrect numerical results but, for a tensor operator such as the e.f.g. \mathbf{V} , in expectation values that have a lower symmetry than that of the point group of the ion concerned. For example, the time-averaged e.f.g. at the nucleus of an ion in an axially symmetric environment must have axial symmetry (the symmetry of the e.f.g. may be higher but cannot be lower than that of the ion), but neglect of the symmetry properties of the strain operator may result in the appearance of non-axial e.f.g. components. Baker (1971) has previously drawn attention to the necessity of properly accounting for the symmetry of the strain in some computations of relaxation effects that involve the orbit-lattice interaction to second order. The present case gives an even clearer illustration of this necessity, involving as it does the overall symmetry of the result as well as the magnitude.

Considerations similar to those above apply also to the calculation of the normalization constant $|A_{ix}|^2$ in equation (16), which is

$$|A_{ix}|^2 = \left(1 + \sum_{j,\beta} \left| \frac{\langle \Phi_{j\beta}^0 | \mathcal{H}_{OL} | \Phi_{ix}^0 \rangle}{E_{ix}^0 - E_{j\beta}^0} \right|^2 \right)^{-1}. \quad (21)$$

Both $\langle \Delta \mathbf{V} \rangle_{ix}$ and $|A_{ix}|^2$ will therefore be temperature dependent through the populations of the phonon states. Consequently, if these quantities are large enough they will introduce a temperature dependence in the quadrupole interaction observed in a Mössbauer spectrum over and above that produced by the normal electronic state repopulation effects (e.g. Ingalls 1964).

At this point in the calculation an average may, if necessary, be performed over the directional properties of the phonon states. The simplest approximation (Orbach 1961) is to assume that the phonon spectrum is isotropic, i.e. that the phonon states depend only on k ($= |\mathbf{k}|$) and s , and to average over the directional properties of the strain. The three mutually orthogonal polarization directions are taken to be equivalent. The following approximate substitutions can then be made:

$$\omega(\mathbf{k}, s) \rightarrow \omega(k), \quad N_\alpha(\mathbf{k}, s) \rightarrow N_\alpha(k), \quad R(\mathbf{k}, s, \Gamma, p) \rightarrow k,$$

and the phonon term $C_{jj'}^i$ in equation (19) becomes

$$C_{jj'}^i = 3 \sum_k \left(\frac{\hbar k^2}{2M \omega(k)} \right) \left(\frac{N_\alpha(k) + 1}{\{E_i - E_{j'} - \hbar \omega(k)\}^* \{E_i - E_j - \hbar \omega(k)\}} + \frac{N_\alpha(k)}{\{E_i - E_{j'} + \hbar \omega(k)\}^* \{E_i - E_j + \hbar \omega(k)\}} \right) \delta_{\Gamma\Gamma'} \delta_{pp'}. \quad (22)$$

The e.f.g. is then

$$\langle \mathbf{V} \rangle_{ix} = \langle \Phi_{ix} | \mathbf{V} | \Phi_{ix} \rangle = |A_{ix}|^2 (\langle \Phi_{ix}^0 | \mathbf{V} | \Phi_{ix}^0 \rangle + \langle \Delta \mathbf{V} \rangle_{ix}), \quad (23)$$

with

$$\langle \Delta \mathbf{V} \rangle_{ix} = \sum_{jj'} \langle \psi_{j'} | \mathbf{V} | \psi_j \rangle \sum_{\Gamma, p} \sum_{l, l'} \langle \psi_i | b_l(\Gamma) B_l(\Gamma, p) | \psi_j \rangle \times \langle \psi_j | b_{l'}(\Gamma) B_{l'}(\Gamma, p) | \psi_i \rangle C_{jj'}^i.$$

In order to illustrate the calculation in more detail, the specific example of Fe^{2+} ions in FeCO_3 will now be examined, but first the superposition model of the orbit-lattice interaction will be briefly summarized.

(d) Superposition Model of Orbit-Lattice Interaction

Newman (1978) has recently described the application of the superposition model of the crystal field (e.g. Newman 1971), in which it is assumed that each ligand acts independently on the open-shell electrons of a central paramagnetic ion, to the determination of orbit-lattice coupling coefficients. In the superposition model the static crystal field is expressed as a sum of axially symmetric contributions from the

individual ligands, and so can be thought of as a generalization of the point charge model, albeit one with much wider range of validity. If the crystal field hamiltonian is written in the form

$$\mathcal{H}^0 = \sum_{\Gamma} \sum_{\Gamma, p} A_{\Gamma}(\Gamma) B_{\Gamma}(\Gamma, p), \quad (24)$$

where the $A_{\Gamma}(\Gamma)$ are coefficients and, as before, the $B_{\Gamma}(\Gamma, p)$ are linear combinations of tesseral harmonics that transform as the p th subvector of the irreducible representation Γ of the point group of the magnetic ion, then the parameters $A_{\Gamma}(\Gamma)$ may be written

$$A_{\Gamma}(\Gamma) = \sum_i K_{\Gamma}(\Gamma, p, \theta_i, \phi_i) \bar{A}_{\Gamma}(R_i). \quad (25)$$

The sum is over ligands at $R_i = (R_i, \theta_i, \phi_i)$ and the $\bar{A}_{\Gamma}(R_i)$ are intrinsic parameters describing the axially symmetric crystal field due to a ligand at R_i . The $K_{\Gamma}(\Gamma, p, \theta_i, \phi_i)$ are known as coordination factors and are functions of the angular positions of the ligands. They are determined from the transformation properties of the $B_{\Gamma}(\Gamma, p)$. The parameters $\bar{A}_{\Gamma}(R)$ are normally assumed to follow a power-law dependence on R , at least over small ranges of R :

$$\bar{A}_{\Gamma}(R_i) = \bar{A}_{\Gamma}(R_0) (R_0/R_i)^{t_{\Gamma}}. \quad (26)$$

Using this model, the orbit-lattice interaction becomes

$$\begin{aligned} \mathcal{H}_{\text{OL}} &= \sum_{\Gamma, p} B_{\Gamma}(\Gamma, p) \sum_{\mu, \nu} \sum_i \left\{ K_{\Gamma}(\Gamma, p, \theta_i, \phi_i) \frac{\partial \bar{A}_{\Gamma}(R_i)}{\partial \mu_i} v_i + \frac{\partial K_{\Gamma}(\Gamma, p, \theta_i, \phi_i)}{\partial \mu_i} v_i \bar{A}_{\Gamma}(R_i) \right\} \varepsilon_{\mu\nu} \\ &= \sum_{\Gamma, p} B_{\Gamma}(\Gamma, p) \sum_{\mu, \nu} \sum_i \{ \gamma_{\mu\nu}(\Gamma, p, \mu, \nu, \theta, \phi) \bar{A}'_{\Gamma}(R_i) + \beta_{\mu\nu}(\Gamma, p, \mu, \nu, \theta, \phi) \bar{A}_{\Gamma}(R_i) \} \varepsilon_{\mu\nu}, \quad (27) \end{aligned}$$

where $\gamma_{\mu\nu}$ and $\beta_{\mu\nu}$ are referred to as dynamic coordination factors and are derived from the K_{Γ} . The quantity \bar{A}'_{Γ} may be treated as a distinct parameter but, if equation (26) is assumed, then

$$\bar{A}'_{\Gamma}(R_i) = R_i (\partial \bar{A}_{\Gamma}(R_i) / \partial R_i) = -t_{\Gamma} \bar{A}_{\Gamma}(R_i). \quad (28)$$

The expression (27) has the form (4) since

$$b_{\Gamma}(\Gamma) \varepsilon(\Gamma, p) = \sum_{\mu, \nu} \varepsilon_{\mu\nu} \sum_i \{ \gamma_{\mu\nu} \bar{A}'_{\Gamma}(R_i) + \beta_{\mu\nu} \bar{A}_{\Gamma}(R_i) \}. \quad (29)$$

Newman (1978) has discussed the methods by which values may be obtained for the parameters \bar{A}_{Γ} and t_{Γ} .

3. Model Calculation for Fe^{2+} in Trigonal Symmetry: FeCO_3

(a) Crystal Structure and Static Crystal Field Theory

FeCO_3 and the isomorphous compounds MgCO_3 , ZnCO_3 , CaCO_3 etc. have a rhombohedral structure in which the cation is coordinated to six oxygen ions that form an octahedron with an elongational distortion along a [111] axis. This axis coincides with the crystallographic c axis. The point group of the cation site is S_6 .

The group $S_6 (= C_3 \times i)$ contains six one-dimensional irreducible representations of which three are even under inversion. One of these is the totally symmetric A_{1g} representation, for which the spherical harmonics Y_n^0 (n even) form bases. The other two even representations are related by time reversal, so states that transform according to them are degenerate; the two representations are therefore grouped together and labelled E_g . The spherical harmonics Y_2^2 and Y_2^{-1} transform according to one of these representations and Y_2^{-2} and Y_2^1 transform according to the other. Table 1 is a character table for the even representations of S_6 and gives the spherical harmonics Y_n^m for $n = 2, 4$ that transform according to each of these representations. The transformation properties of the tesseral harmonics Z_n^m can therefore be deduced readily from Table 1.

Table 1. Character table for even-parity representations of group S_6

The spherical harmonic functions Y_n^m ($n = 2, 4$) that transform according to various irreducible representations are listed. Here $\omega = \exp(\frac{2}{3}\pi i)$

Y_n^m for S_6 ($\bar{3}$)					Representation	E	C_3	C_3^2	i	iC_3	iC_3^2
Y_2^0	Y_4^0	Y_4^3	Y_4^{-3}		A_{1g}	1	1	1	1	1	1
Y_2^1	Y_2^{-2}	Y_4^1	Y_4^{-2}	Y_4^4	E_g	$\left\{ \begin{array}{l} 1 \\ 1 \end{array} \right.$	ω	ω^2	1	ω	ω^2
Y_2^{-1}	Y_2^2	Y_4^{-1}	Y_4^2	Y_4^{-4}							

The crystal field acting on the 3d electrons of Fe^{2+} in $FeCO_3$ has been discussed recently by Spiering *et al.* (1976) and by Price *et al.* (1977), and reference should be made to these papers for details of the spectroscopic work involved. The 5D ground electronic term of Fe^{2+} is split by a field of O_h symmetry into an orbital triplet ($^5T_{2g}$) and a doublet (5E_g), with the triplet lying below the doublet (by $\sim 10^4$ cm^{-1}). When the symmetry is lowered to S_6 , the $^5T_{2g}$ multiplet is split into an orbital singlet ($^5A_{1g}$) and a time-reversed doublet (5E_g). The doublet is lower in $FeCO_3$ (Ono and Ito 1964) by $\gtrsim 1000$ cm^{-1} (Spiering *et al.* 1976). Unfortunately, however, insufficient electronic transitions have been unambiguously identified to enable a unique set of values to be determined for the parameters of the crystal field, and the situation is complicated somewhat by the fact that $FeCO_3$ is antiferromagnetically ordered at low temperatures ($\lesssim 38$ K) where, of necessity, much of the spectroscopic work has been done. The hamiltonian that describes the splitting of the free ion 5D term may be written in terms of the Stevens operator equivalents O_n^m (whose form is given by Orbach 1961) as

$$\mathcal{H} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^3 O_4^3 + \lambda L \cdot S + JS_2. \quad (30)$$

A set of parameter values (given by Price *et al.* 1977) that satisfies the observations of electronic transitions to levels at 112.5, 160 and 438 cm^{-1} , describes the applied magnetic field dependence of the 112.5 cm^{-1} transition (Prinz *et al.* 1973) and gives a reasonable value for the ionic magnetic moment (as measured by Jacobs (1963) in a crystal of unknown purity) is: $B_2^0 = -125$ cm^{-1} , $B_4^0 = -55.56$ cm^{-1} , $B_4^3 = -20\sqrt{2}B_4^0 = 1571$ cm^{-1} , $\lambda = -94.4$ cm^{-1} and $J = -17.0$ cm^{-1} . For this parameter set the cubic field $^5T_{2g} \rightarrow ^5E_g$ splitting is $180|B_4^0| = 10000$ cm^{-1} and the trigonal distortion is given entirely by the term $B_2^0 O_2^0$ in equation (30); the $^5A_{1g}$ level is $9|B_2^0| = 1125$ cm^{-1} above the 5E_g ground multiplet in the absence of spin-orbit

coupling and exchange. While these parameter values are not unambiguous, they are expected to be of the correct order of magnitude: the experimental data clearly require the trigonal ${}^5A_{1g}$ - 5E_g splitting to be much larger than λ , and that λ be not reduced greatly in magnitude from its free ion value of -103 cm^{-1} . This is the basis for the argument, referred to in the Introduction above, that Jahn-Teller effects are small and that, consequently, the perturbation approach to vibronic admixture effects described in Section 2c is valid for FeCO_3 (and presumably for other Fe^{2+} compounds as well).

Effects of a large Jahn-Teller coupling of the electronic and vibrational wavefunctions include partial quenching of the orbital moment and of the spin-orbit coupling (Ham 1965) and significant reduction in the trigonal splitting of the cubic ${}^5T_{2g}$ level (Stephens 1969; Abou-Ghantous *et al.* 1974). While the values of the ionic magnetic moment (~ 5 Bohr magnetons) and the spin-orbit splitting of the 5E_g ground multiplet indicate that the Ham reduction must be quite small, perhaps the strongest evidence of minimal Jahn-Teller effects can be drawn from the crystal field parameters. If the superposition model (see Section 2d above and Newman 1971) is applied to the Fe^{2+} ion in FeCO_3 then, considering only the effects of the six coordinated oxygen ions and using the X-ray data of Graf (1961), we find that the crystal field parameters in equation (30) are given by

$$B_2^0 = -\frac{2}{21}(0.216)\bar{A}_2(R), \quad B_4^0 = \frac{2}{63}(-2.438)\bar{A}_4(R), \quad B_4^3 = \frac{2}{63}(64.677)\bar{A}_4(R), \quad (31)$$

with $R = 2.14 \text{ \AA}$. Estimates of the intrinsic parameters \bar{A}_2 and \bar{A}_4 may be obtained from the following.

- (i) Manson *et al.* (1976) measured a value $\bar{A}_4 = 701 \text{ cm}^{-1}$ for $\text{Fe}^{2+}:\text{MgO}$ that scales to 642 cm^{-1} in FeCO_3 with $t_4 = 5$, for which there is some theoretical and experimental evidence (e.g. Stedman 1969);
- (ii) Newman *et al.* (1978) found $\bar{A}_4 = 596 \text{ cm}^{-1}$ (with $t_4 = 5$) and $\bar{A}_2 = 6300 \pm 800 \text{ cm}^{-1}$ (with $t_2 = 3.5 \pm 0.5$) for Fe^{2+} in D_2 sites in pyrope garnets. Scaling these values to $R = 2.14 \text{ \AA}$, appropriate to the oxygen ligands in FeCO_3 , gives $\bar{A}_4 = 680 \text{ cm}^{-1}$ and $\bar{A}_2 = 6900 \pm 800 \text{ cm}^{-1}$.

If the values $\bar{A}_2 = 6900 \pm 800 \text{ cm}^{-1}$ and $\bar{A}_4 = 660 \pm 20 \text{ cm}^{-1}$ are assumed for Fe^{2+} in FeCO_3 , then the expressions (31) give

$$B_2^0 = -142 \pm 16 \text{ cm}^{-1}, \quad B_4^0 = -51.1 \pm 1.6 \text{ cm}^{-1}, \quad B_4^3 = 1355 \pm 41 \text{ cm}^{-1}.$$

These values, when compared with those listed above, would indicate very small, if any, reduction of the trigonal splitting due to Jahn-Teller effects. Consequently, it will be assumed that the perturbation approach to the treatment of vibronic effects described in this paper has some justification, at least for Fe^{2+} in FeCO_3 .

(b) Orbit-Lattice Interaction in FeCO_3

The orbit-lattice interaction can now be written in the form (4) of Section 2. Two of the harmonic components of the strain tensor (ϵ_0^0 and ϵ_2^0) transform as A_{1g} and the other four as two different E_g representations. For simplification, the small effect of the trigonal distortion on the orbit-lattice coupling will be ignored, and the expressions given below correspond strictly only to cubic symmetry. In terms of

both the cartesian components of the strain tensor and those that transform as tesseral harmonics, the $\varepsilon(\Gamma, p)$ are given by

$$\varepsilon(A_{1g}^{(1)}, 1) = \varepsilon_0^0 = \sqrt{\frac{1}{5}}(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}), \quad (32a)$$

$$\varepsilon(A_{1g}^{(2)}, 1) = \varepsilon_2^0 = \frac{1}{2}(2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy}), \quad (32b)$$

$$\varepsilon(E_g^{(1)}, 1) = \sqrt{\frac{1}{3}}\varepsilon_2^1 - \sqrt{\frac{2}{3}}\varepsilon_2^2 = \varepsilon_{xz} - \sqrt{\frac{1}{2}}(\varepsilon_{xx} - \varepsilon_{yy}), \quad (32c)$$

$$\varepsilon(E_g^{(1)}, 2) = \sqrt{\frac{1}{3}}\varepsilon_2^{-1} + \sqrt{\frac{2}{3}}\varepsilon_2^{-2} = \varepsilon_{yz} + \sqrt{2}\varepsilon_{xy}, \quad (32d)$$

$$\varepsilon(E_g^{(2)}, 1) = \sqrt{\frac{2}{3}}\varepsilon_2^1 + \sqrt{\frac{1}{3}}\varepsilon_2^2 = \sqrt{2}\varepsilon_{xz} + \frac{1}{2}(\varepsilon_{xx} - \varepsilon_{yy}), \quad (32e)$$

$$\varepsilon(E_g^{(2)}, 2) = \sqrt{\frac{2}{3}}\varepsilon_2^{-1} - \sqrt{\frac{1}{3}}\varepsilon_2^{-2} = \sqrt{2}\varepsilon_{yz} - \varepsilon_{xy}. \quad (32f)$$

The corresponding combinations of tesseral harmonics Z_l^m (normalized to $4\pi/(2l+1)$) that comprise the $B_l(\Gamma, p)$ are

$$B_2(A_{1g}^{(1)}, 1) = 0, \quad B_4(A_{1g}^{(1)}, 1) = -\frac{1}{3}\sqrt{\frac{1}{3}}(\sqrt{7}Z_4^0 - 2\sqrt{5}Z_4^3); \quad (33a)$$

$$B_2(A_{1g}^{(2)}, 1) = Z_2^0, \quad B_4(A_{1g}^{(2)}, 1) = -\frac{1}{3}\sqrt{\frac{1}{3}}(2\sqrt{5}Z_4^0 + \sqrt{7}Z_4^3); \quad (33b)$$

$$B_2(E_g^{(1)}, 1) = \sqrt{\frac{1}{3}}(Z_2^1 - \sqrt{2}Z_2^2), \quad B_4(E_g^{(1)}, 1) = \frac{1}{3}\sqrt{\frac{1}{6}}(5Z_4^1 - Z_4^2 + 2\sqrt{7}Z_4^4); \quad (33c)$$

$$B_2(E_g^{(1)}, 2) = \sqrt{\frac{1}{3}}(Z_2^{-1} + \sqrt{2}Z_2^{-2}), \quad B_4(E_g^{(1)}, 2) = \frac{1}{3}\sqrt{\frac{1}{6}}(5Z_4^{-1} + Z_4^{-2} + 2\sqrt{7}Z_4^{-4}); \quad (33d)$$

$$B_2(E_g^{(2)}, 1) = \sqrt{\frac{1}{3}}(\sqrt{2}Z_2^1 + Z_2^2), \quad B_4(E_g^{(2)}, 1) = \frac{1}{3}\sqrt{\frac{1}{3}}(2Z_4^1 - 4Z_4^2 - \sqrt{7}Z_4^4); \quad (33e)$$

$$B_2(E_g^{(2)}, 2) = \sqrt{\frac{1}{3}}(\sqrt{2}Z_2^{-1} - Z_2^{-2}), \quad B_4(E_g^{(2)}, 2) = \frac{1}{3}\sqrt{\frac{1}{3}}(-2Z_4^{-1} - 4Z_4^{-2} + \sqrt{7}Z_4^{-4}). \quad (33f)$$

Estimates of the coupling coefficients $b_l(\Gamma)$ are available from two independent sources. Firstly, Price *et al.* (1977) measured the spin-lattice relaxation of Fe^{2+} in the isomorphous compound ZnCO_3 . A different but equivalent formulation of the orbit-lattice interaction was used in that work and only $l = 2$ terms were included. According to their interpretation of their data, the coupling parameters appropriate to the present formulation of \mathcal{H}_{OL} (equation 4) would lie in the range

$$3 \times 10^3 \lesssim |b_2(\Gamma)| \lesssim 3 \times 10^4 \text{ cm}^{-1}.$$

Secondly, a superposition model calculation (Section 2*d*) can be employed. Considering only the six coordinated oxygen ligands and using the X-ray data of Graf (1961), such a calculation yields

$$b_2(A_{1g}^{(1)}) = 0, \quad b_4(A_{1g}^{(1)}) = \frac{1}{3}\sqrt{\left(\frac{3}{5}\pi\right)}\bar{A}'_4(R); \quad (34a)$$

$$b_2(A_{1g}^{(2)}) = 16\sqrt{\left(\frac{1}{3}\pi\right)}\bar{A}_2(R), \quad b_4(A_{1g}^{(2)}) = \frac{3}{3}\sqrt{\left(\frac{5}{3}\pi\right)}\bar{A}_4(R); \quad (34b)$$

$$b_2(E_g^{(1)}) = 16\sqrt{\left(\frac{1}{3}\pi\right)}\bar{A}_2(R), \quad b_4(E_g^{(1)}) = \frac{3}{3}\sqrt{\left(\frac{5}{3}\pi\right)}\bar{A}_4(R); \quad (34c)$$

$$b_2(E_g^{(2)}) = 8\sqrt{\left(\frac{1}{3}\pi\right)}\bar{A}'_2(R), \quad b_4(E_g^{(2)}) = \frac{1}{3}\sqrt{\left(\frac{5}{3}\pi\right)}\bar{A}'_4(R). \quad (34d)$$

These expressions are identical with those given by Orbach and Tachiki (1967) if the point charge values of the \bar{A}_l and t_l are substituted in them. If the values of

$\bar{A}_l(R)$ and t_l given in Section 3a are used, the coefficient values (in units of cm^{-1}) are

$$b_2(A_{1g}^{(1)}) = 0, \quad b_4(A_{1g}^{(1)}) \approx -10 \times 10^4; \quad (35a)$$

$$b_2(A_{1g}^{(2)}) = b_2(E_g^{(1)}) \approx (8.7 \pm 1.0) \times 10^4, \quad b_4(A_{1g}^{(2)}) = b_4(E_g^{(1)}) \approx 1.6 \times 10^4; \quad (35b)$$

$$b_2(E_g^{(2)}) \approx -(15.0 \pm 0.5) \times 10^4, \quad b_4(E_g^{(2)}) \approx -4.0 \times 10^4. \quad (35c)$$

(c) Electronic States and Phonon Spectrum

Appropriate $L = 2$ functions for the A_{1g} and E_g states derived from the octahedral ${}^5T_{2g}$ multiplet are (e.g. Bleaney and Stevens 1953)

$$A_{1g}: \quad \psi_0 = Y_2^0; \quad (36a)$$

$$E_g: \quad \psi_1 = -\sin \theta Y_2^{-2} - \cos \theta Y_2^1, \quad \psi_{-1} = \sin \theta Y_2^2 - \cos \theta Y_2^{-1}; \quad (36b)$$

with $\cos \theta = \sqrt{1/3}$, $\sin \theta = \sqrt{2/3}$ for cubic symmetry. For the sake of simplicity only these electronic states will be included in the calculation, i.e. consideration will only be given to vibronic admixtures between these low-lying states. The matrices of the operators $B_l(\Gamma, p)$ of equations (33) in the basis $\psi_1, \psi_0, \psi_{-1}$ are given in Appendix 1. Because (in cubic symmetry) these states transform under rotation like a $P(L = 1)$ state (Abragam and Pryce 1951), the $B_4(\Gamma, p)$ matrices are proportional to those of the $B_2(\Gamma, p)$ operators, and all of the effects of the orbit-lattice interaction can be obtained if only the $l = 2$ terms in the \mathcal{H}_{OL} of equation (4) are included. Consequently the $l = 4$ terms will be ignored for the purposes of the present qualitative discussion.

It will be assumed henceforth that the acoustic phonon states can be adequately described by the Debye model. While this may not be a particularly good quantitative approximation, it should serve to illustrate the qualitative effects of the vibronic coupling. In any case, the measured phonon spectrum of the isomorphous compound CaCO_3 (Plihal 1973) appears to be reasonably Debye-like at low frequencies (Price *et al.* 1977). The characteristic temperature will be taken as ~ 300 K, which is roughly what is derived from Mössbauer relative area data (Price *et al.* 1973, and results to be published).

(d) Case of No Spin-Orbit Coupling

The expression (23) will now be evaluated. As an initial simplification the spin-orbit coupling will be ignored, so that no account need be taken of the five-fold spin degeneracy of the electronic states (36). The justification for such a simplification being made at this stage is that, in the absence of vibronic effects, the dominant temperature dependence of the quadrupole interaction in the temperature range up to several hundred kelvins is expected to be due to temperature-dependent repopulation of the three orbital states (Ingalls 1964).

In evaluating equation (23) it will be seen that only three different phonon factors $C_{jj'}^i$ (equation 22) are required. This is because (i) $C_{jj'}^i = C_{j'j}^i$ and (ii) all sums of electronic matrix elements of the form

$$\sum_p \langle \psi_i | B_l(\Gamma, p) | \psi_{j'} \rangle \langle \psi_j | B_l(\Gamma, p) | \psi_i \rangle$$

are zero for $j \neq j'$, as can be verified by inspection of the matrices given in Appendix 1. Consequently, if the electronic energies E_i are taken to be $E_1 = E_{-1} = 0$, $E_0 = \Delta$ (see Fig. 1 inset) then the only $C_{jj'}$ factors required are (see equation 22)

$$C_{0,0}^1 = C_{0,0}^{-1} = 3 \sum_k \left(\frac{\hbar k^2}{2M \omega(k)} \right) \left(\frac{N_\alpha(k)+1}{\{\Delta + \hbar \omega(k)\}^2} + \frac{N_\alpha(k)}{\{\Delta - \hbar \omega(k)\}^2} \right), \quad (37a)$$

$$C_{1,1}^0 = C_{-1,-1}^0 = 3 \sum_k \left(\frac{\hbar k^2}{2M \omega(k)} \right) \left(\frac{N_\alpha(k)+1}{\{\Delta - \hbar \omega(k)\}^2} + \frac{N_\alpha(k)}{\{\Delta + \hbar \omega(k)\}^2} \right), \quad (37b)$$

$$C_{0,0}^0 = C_{1,1}^1 = C_{-1,-1}^{-1} = C_{-1,-1}^1 = C_{1,1}^{-1} = 3 \sum_k \left(\frac{\hbar k^2}{2M \omega(k)} \right) \left(\frac{2N_\alpha(k)+1}{\hbar^2 \omega^2(k)} \right). \quad (37c)$$

These same terms also appear in the expressions for the normalization constants $|A_{iz}|^2$. They are evaluated within the Debye model by replacing the k summations by integrals over a uniform distribution of points in k space. The set of phonon state occupation numbers α is taken to be the thermal equilibrium set at temperature T , that is,

$$N_\alpha(k) = \{\exp(\hbar \omega(k)/k_B T) - 1\}^{-1}, \quad (38)$$

where k_B is the Boltzmann constant.

Since Δ is expected to be $\gtrsim 1000 \text{ cm}^{-1}$ (e.g. Spiering *et al.* 1976; Price *et al.* 1977) and the Debye temperature $\theta_D \sim 300 \text{ K}$, there will be no problem with divergence of the integrands in equations (37) for $\hbar \omega \sim \Delta$. For smaller values of Δ such divergence can be removed by inclusion of the lifetime broadening of the excited electronic state, as was done in the resonant relaxation problem (Orbach 1961; Orbach and Stapleton 1972). The integrals in equations (37) reduce to

$$C_{0,0}^1 = \frac{3}{4\pi^2 \rho v^5 \hbar} \left(\frac{2k_B T}{\hbar} \right)^2 \int_0^X \frac{1}{2} x^3 \operatorname{cosech} x \left(\frac{e^x}{(\delta+x)^2} + \frac{e^{-x}}{(\delta-x)^2} \right) dx, \quad (39a)$$

$$C_{1,1}^0 = \frac{3}{4\pi^2 \rho v^5 \hbar} \left(\frac{2k_B T}{\hbar} \right)^2 \int_0^X \frac{1}{2} x^3 \operatorname{cosech} x \left(\frac{e^x}{(\delta-x)^2} + \frac{e^{-x}}{(\delta+x)^2} \right) dx, \quad (39b)$$

$$C_{0,0}^0 = \frac{3}{4\pi^2 \rho v^5 \hbar} \left(\frac{2k_B T}{\hbar} \right)^2 \int_0^X x \coth x dx, \quad (39c)$$

where ρ is the density of the lattice, v is the (average) velocity of sound in the lattice, $x = \hbar \omega(k)/2k_B T$, $X = \hbar \omega_D/2k_B T = \theta_D/2T$ and $\delta = \Delta/2k_B T$. In the high temperature limit ($T \gg \theta_D$) the behaviour is

$$C_{0,0}^1 \propto aT - b, \quad C_{1,1}^0 \propto aT + b, \quad C_{0,0}^0 \propto T,$$

with a and b constants.

The $C_{jj'}$ could be evaluated even more readily for optical phonons or other essentially dispersionless modes (such as local molecular rotations), but the calculations done here have incorporated only the long wavelength acoustic phonons.

Because the only nonzero contributions to the sum in equation (23) come from $j = j'$ terms, only diagonal matrix elements of the e.f.g. operator \mathbf{V} are involved and consequently the e.f.g. retains its axial symmetry in the presence of the vibronic

coupling. Then, since $\langle \mathbf{V} \rangle_{ix}$ represents the thermal equilibrium expectation value at temperature T , equation (23) may be rewritten

$$\langle \mathbf{V} \rangle_{ix} = \langle \mathbf{V} \rangle_i(T) = \left(\langle \mathbf{V} \rangle_i^0 + \sum_j \langle \mathbf{V} \rangle_j^0 D_{ij}(T) \right) / \left(1 + \sum_j D_{ij}(T) \right), \quad (40)$$

where

$$\langle \mathbf{V} \rangle_i^0 = \langle \psi_i | \mathbf{V} | \psi_i \rangle = \langle \Phi_{ix}^0 | \mathbf{V} | \Phi_{ix}^0 \rangle$$

and

$$D_{ij}(T) = \left(\sum_{\Gamma, p} \sum_{l, l'} \langle \psi_i | b_l(\Gamma) B_l(\Gamma, p) | \psi_j \rangle \langle \psi_j | b_{l'}(\Gamma) B_{l'}(\Gamma, p) | \psi_i \rangle \right) C_{ij}^l(T).$$

Since all of the states derived from the cubic ${}^5T_{2g}$ orbital triplet are included, it follows that $\sum_j \langle \mathbf{V} \rangle_j^0 = 0$. Therefore at least one of the $\langle \mathbf{V} \rangle_j^0$ values will be of opposite sign to $\langle \mathbf{V} \rangle_i^0$ and so, if the corresponding coupling coefficient D_{ij} is nonzero, $|\langle \mathbf{V} \rangle_i(T)|$ will be less than $|\langle \mathbf{V} \rangle_i^0|$ and will decrease progressively as T increases owing to the temperature dependence of the $D_{ij}(T)$. The calculation of the observed e.f.g. is completed by making an ensemble average of the $\langle \mathbf{V} \rangle_i(T)$, assuming that the relaxation between the electronic states is sufficiently fast:

$$\langle \langle \mathbf{V} \rangle \rangle(T) = \frac{\langle \mathbf{V} \rangle_1(T) + \langle \mathbf{V} \rangle_{-1}(T) + \langle \mathbf{V} \rangle_0(T) \exp(-\Delta/k_B T)}{1 + 1 + \exp(-\Delta/k_B T)}. \quad (41)$$

The matrix elements of the diagonal cartesian components of \mathbf{V} , taking the z axis as the crystal c axis, are given in Appendix 2 for the basis $\psi_1, \psi_0, \psi_{-1}$. These are the only components that have nonzero diagonal matrix elements. Since $\langle V_{xx} \rangle_i = \langle V_{yy} \rangle_i = -\frac{1}{2} \langle V_{zz} \rangle_i$, only $\langle V_{zz} \rangle_i$ and its ensemble average have been calculated.

Representative results of this calculation are shown in Fig. 1. The energy difference Δ was taken to be $\sim 1000 \text{ cm}^{-1}$ (e.g. Spiering *et al.* 1976; Price *et al.* 1977), and the wavefunctions and energy levels are shown in the inset to the figure. Relative values of the coupling parameters were chosen roughly in accordance with the results of the superposition model calculation referred to above; that is, $b_2(E_g^{(2)}) = 1.5 b_2(E_g^{(1)})$. The curves in Fig. 1 show the ${}^{57}\text{Fe}$ quadrupole splitting, which is proportional to $\langle \langle V_{zz} \rangle \rangle$ and which has been normalized so that in the absence of vibronic coupling its low temperature value is 2.0 mms^{-1} . The vibronic coupling induces a change in the temperature dependence of the quadrupole splitting when it mixes the excited A_{1g} state with the ground E_g states, since the e.f.g. values associated with these states have opposite sign. For these calculations the velocity of sound v was taken to be the Debye model value of $\sim 4 \times 10^3 \text{ ms}^{-1}$ and the crystal density to be 4.0 g cm^{-3} . The three curves drawn correspond to different values for the vibronic coupling parameters, as explained in the figure caption.

Coupling to the A_{1g} vibrational modes alone does not produce any change in the temperature dependence of the quadrupole splitting, since these modes cannot mix the A_{1g} and E_g electronic states (matrix elements of the form $\langle A_{1g} | A_{1g} | E_g \rangle$ are always zero since $A_{1g} \times E_g$ does not contain A_{1g}). However, the E_g modes mix A_{1g} and E_g electronic states since $E_g \times E_g$ contains A_{1g} , and coupling to E_g modes will change the temperature dependence of $\langle \langle V_{zz} \rangle \rangle$. Therefore, observable effects may be expected if coupling to E_g modes is sufficiently strong whereas, if coupling to the A_{1g} modes is dominant, little effect should be seen. The results shown in Fig. 1 confirm this expectation.

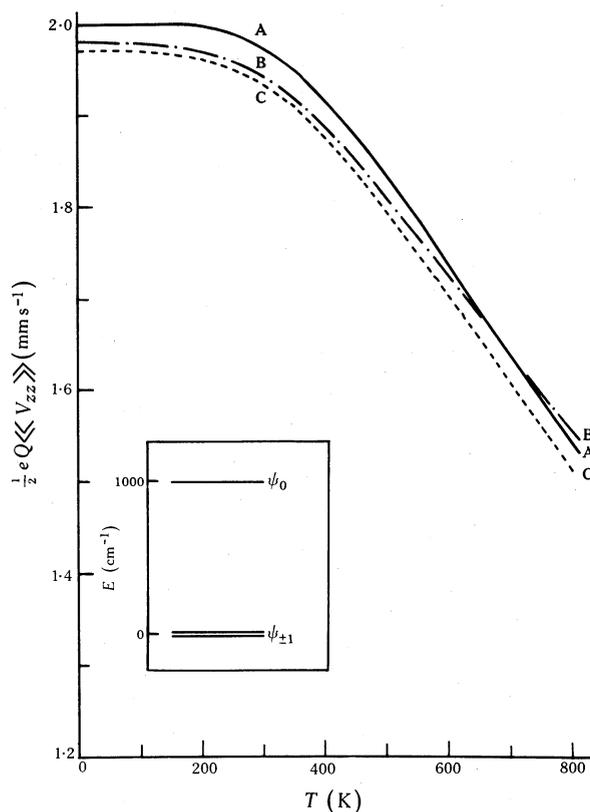


Fig. 1. ^{57}Fe quadrupole splitting $\frac{1}{2}eQ\langle\langle V_{zz}\rangle\rangle$ calculated as described in Section 3d. The inset shows the wavefunctions and energy levels assumed. The coupling parameters used in the calculations were:

- A: no vibronic coupling (or coupling to A_{1g} modes only);
 B: $b_2(A_{1g}^{(2)}) = b_2(E_g^{(1)}) = 12\,000\text{ cm}^{-1}$, $b_2(E_g^{(2)}) = 18\,000\text{ cm}^{-1}$;
 C: $b_2(A_{1g}^{(2)}) = 0$, $b_2(E_g^{(1)}) = b_2(E_g^{(2)}) = 12\,000\text{ cm}^{-1}$.

While the values of the coupling parameters used in the calculation were chosen mainly for illustrative purposes they are of the same order of magnitude as the parameters deduced by Price *et al.* (1977) from the study of the spin-lattice relaxation rates of $^{57}\text{Fe}^{2+}$ in ZnCO_3 that was referred to above. Consequently, effects of vibronic coupling might be expected to be observed in the ^{57}Fe quadrupole splitting in FeCO_3 and similar compounds. It is believed that this is a likely explanation for the 'anomalous' temperature dependence of the quadrupole splitting in these compounds (Price *et al.* 1973; Nagy *et al.* 1975). In the following subsections possible effects on the vibronic coupling of the spin-orbit splitting of the ground electronic multiplet and of the exchange interaction will be examined.

(e) Approximation to Effect of Spin-Orbit Coupling

Spin-orbit coupling affects the temperature dependence of the e.f.g. at a ^{57}Fe nucleus in a compound like FeCO_3 , particularly in the low temperature region, both by removing the spin degeneracy of the E_g ground orbital states ψ_1, ψ_{-1} and

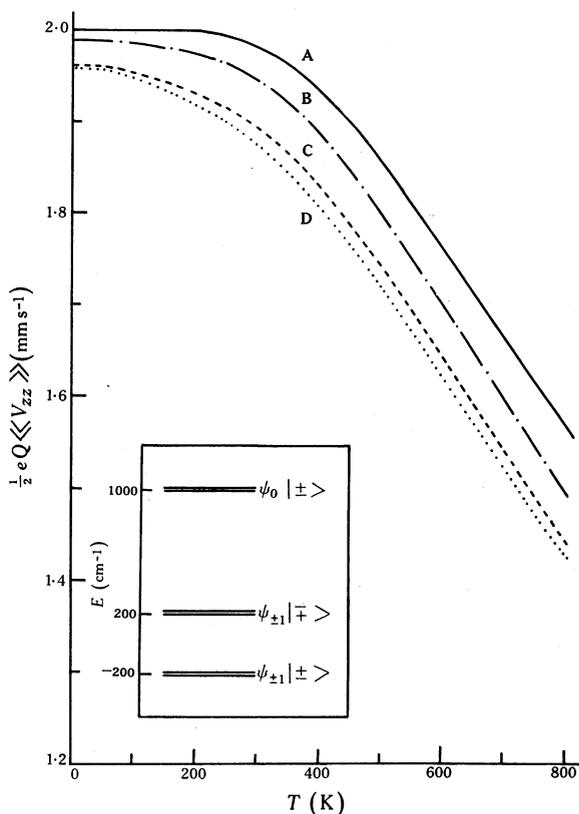


Fig. 2. ^{57}Fe quadrupole splitting $\frac{1}{2}eQ\langle\langle V_{zz}\rangle\rangle$ calculated as described in Section 3e. The inset shows the wavefunctions and energy levels assumed. The coupling parameters used in the calculations were:

- A: no vibronic coupling (or coupling to A_{1g} modes only);
 B: $b_2(A_{1g}^{(2)}) = b_2(E_g^{(1)}) = 6000 \text{ cm}^{-1}$, $b_2(E_g^{(2)}) = 9000 \text{ cm}^{-1}$;
 C: $b_2(A_{1g}^{(2)}) = b_2(E_g^{(1)}) = 12000 \text{ cm}^{-1}$, $b_2(E_g^{(2)}) = 18000 \text{ cm}^{-1}$;
 D: $b_2(A_{1g}^{(2)}) = 6000 \text{ cm}^{-1}$, $b_2(E_g^{(1)}) = 12000 \text{ cm}^{-1}$, $b_2(E_g^{(2)}) = 18000 \text{ cm}^{-1}$.

by mixing some of the excited A_{1g} state ψ_0 with them. Although this admixture can have a significant effect on the ^{57}Fe quadrupole splitting it shall be ignored initially and only the effect on the vibronic admixture of removing the spin degeneracy of ψ_1, ψ_{-1} will be considered.

The essential features of the problem can be retained whilst simplifying the calculation if the spin degeneracy is taken to be two. If the spin states are labelled $|+\rangle$ and $|-\rangle$ then the eigenstates of the static hamiltonian $\mathcal{H}^0 + \lambda \mathbf{L} \cdot \mathbf{S}$ are as shown in the inset of Fig. 2. The calculation then proceeds along the same lines as described in subsection (d) above, but, since the orbit-lattice hamiltonian does not operate on the spin functions, only states with the same spin quantum number will be vibronically admixed. Therefore, the only difference between this calculation and that of subsection (d) is that some of the energy denominators in the C_{jj}^i terms (37) are different.

Representative results are shown in Fig. 2. The $A_{1g}-E_g$ level splitting Δ was again taken to be 1000 cm^{-1} and the overall splitting of the ground spin-orbit multiplet taken as 400 cm^{-1} , which is roughly that expected for Fe^{2+} (Section 3a; Spiering *et al.* 1976). All other parameters had the values given in Section 3d.

From Fig. 2 it will be seen, again, that the effect of the vibronic coupling is only important when there is significant coupling to E modes. The effect of the spin-orbit coupling in this case is to further decrease the quadrupole splitting. This is because the splitting causes a decrease in the E_g-E_g ($\psi_1-\psi_{-1}$) admixture and consequently an enhancement of the effect of the E_g-A_{1g} admixture.

While these calculations can have at best a qualitative relationship to the situation in a real compound such as FeCO_3 , this mechanism may be at least partially responsible for the unusual temperature dependence of the quadrupole splitting at ^{57}Fe nuclei in the rhombohedral carbonate compounds and should be investigated in more detail. It also seems possible, although again only on the basis of qualitative arguments, that the rather abrupt change in the ^{57}Fe quadrupole splitting at the Néel temperature in FeCO_3 ($\sim 38\text{ K}$; Ok 1969) which has previously been assigned to static effects associated with magnetostriction may be due predominantly to changes in the vibronic coupling, and this will be considered below.

(f) Possible Effect of Exchange Interaction

As already noted in the Introduction, the ^{57}Fe quadrupole splitting in FeCO_3 increases sharply by $\sim 0.07\text{ mm s}^{-1}$ near the transition from the antiferromagnetic to the paramagnetic phase. It has been speculated (Nagy *et al.* 1975; Spiering *et al.* 1976) that this is due to the effect of magnetostriction on the (static) crystal field. Possible effects that the exchange interaction might have on the vibronic coupling described above will now be examined. In doing so it will be necessary to look more closely than above at the effects of the spin-orbit coupling on the lowest electronic multiplet.

Fig. 3 shows the energy levels derived from the 5E_g orbital doublet ground state in the presence of spin-orbit coupling and the exchange interaction (see e.g. Prinz *et al.* 1973; Price *et al.* 1974). The wavefunctions, written in terms of the $\psi_i|S_z\rangle$ basis states, for spin-orbit coupling only and including admixtures of the $^5A_{1g}$ excited states, are given in Appendix 3. The small changes in these functions that accompany the application of the exchange interaction will be neglected. It may be seen from Appendix 3 that the admixtures produced by the spin-orbit coupling give rise to small nonzero matrix elements of the orbital operators $B_l(\Gamma, p)$ involved in the orbit-lattice interaction (4) between states where they would otherwise have been spin-forbidden. Consequently, the orbit-lattice interaction couples together many of the states within this multiplet and not just the strongly spin-allowed ones, although the electronic matrix elements involved in the coupling may be reduced by an order of magnitude or more. These couplings will therefore be insignificant unless the phonon terms are correspondingly larger than those involved in spin-allowed coupling. However, inspection of Fig. 3 shows that the energy separations of the lowest level (labelled $|1\rangle$) from several excited levels, to which it may be coupled by the orbit-lattice interaction, decrease significantly when the exchange is reduced to zero. Since these states all produce approximately the same e.f.g. at the Fe nucleus the decrease

of their excitation energies as the temperature is raised through the Néel temperature (~ 38 K) and the associated increase of their vibronic admixture into the ground state $|1\rangle$ mean that the effect of coupling to the ${}^5A_{1g}$ multiplet will be decreased and hence the quadrupole splitting will increase, as is observed. It remains to be demonstrated that the change in the quadrupole splitting from this mechanism will be large enough to be observable. This will be done in a future publication.

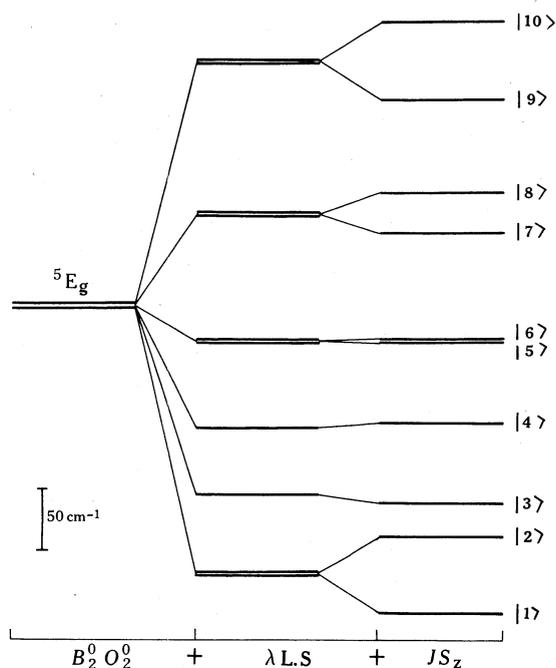


Fig. 3. Splitting of the ground 5E_g multiplet of Fe^{2+} in a trigonally elongated octahedral crystal field ($B_2^0 O_2^0$) by the spin-orbit coupling ($\lambda L.S$) and axial exchange interaction ($J S_z$). The parameters used for the purely illustrative purposes of this diagram were $B_2^0 = -100 \text{ cm}^{-1}$, $\lambda = -100 \text{ cm}^{-1}$ and $J = -16 \text{ cm}^{-1}$, which are of the correct general order of magnitude for FeCO_3 (see Section 3a). The labels $|l\rangle$ given to the states refer to the functions listed in Appendix 3.

(g) Fe^{2+} Quadrupole Splitting for Trigonal Compression

If an Fe^{2+} ion in an octahedrally coordinated site that has a compressional trigonal distortion, such as occurs in, for example, ferrous fluosilicate ($\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$) (Johnson 1967; Varret and Jehanno 1975), is considered then a similar model to that set up for Fe^{2+} in FeCO_3 , but with the orbital singlet ψ_0 lower than the doublet $\psi_{\pm 1}$, can be used. In fact there is a small non-axial distortion in $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ (Varret and Jehanno 1975; Chappert *et al.* 1977) below ~ 230 K, but this should have little influence on the results of the present calculation. The inset of Fig. 4 shows the energy level scheme used, and representative results are shown in the same figure. All parameters have been arbitrarily given the same values as for FeCO_3 . It can be seen that, particularly when coupling to the E_g vibrational modes is dominant, the results bear a qualitative similarity to the experimental quadrupole

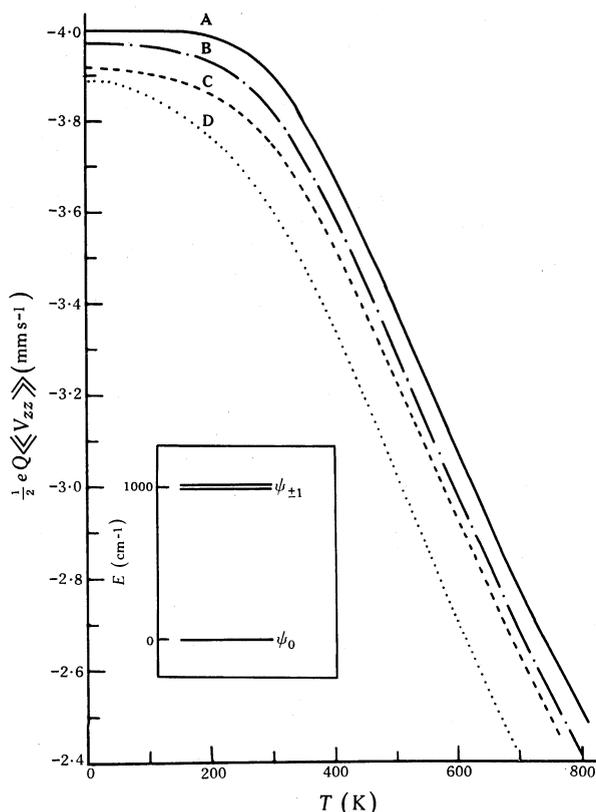


Fig. 4. ^{57}Fe quadrupole splitting $\frac{1}{2}eQ\langle\langle V_{zz}\rangle\rangle$ calculated as described in Section 3*g*. The inset shows the wavefunctions and energy levels assumed. The coupling parameters used in the calculations were:

- A: no vibronic coupling (or coupling to A_{1g} modes only);
- B: $b_2(A_{1g}^{(2)}) = b_2(E_g^{(1)}) = 6000 \text{ cm}^{-1}$, $b_2(E_g^{(2)}) = 9000 \text{ cm}^{-1}$;
- C: $b_2(A_{1g}^{(2)}) = b_2(E_g^{(1)}) = 12000 \text{ cm}^{-1}$, $b_2(E_g^{(2)}) = 18000 \text{ cm}^{-1}$;
- D: $b_2(A_{1g}^{(2)}) = 6000 \text{ cm}^{-1}$, $b_2(E_g^{(1)}) = 12000 \text{ cm}^{-1}$, $b_2(E_g^{(2)}) = 18000 \text{ cm}^{-1}$.

splitting measurements of Varret and Jehanno (1975), although, of course, no definite conclusions can be drawn as no independent information regarding the strength of the orbit–lattice coupling parameters is available.

For the cases of Fe^{2+} in nickel and zinc fluosilicates, for which measurements were also reported by Varret and Jehanno (1975), the situation is far more complex because the axial splitting is much smaller than in the ferrous compound and is only of the same order of magnitude as the spin–orbit coupling. Consequently the spin–orbit coupling will produce strong admixture between the $^5A_{1g}$ and 5E_g states and there will be many electronic states that can be coupled by the orbit–lattice interaction to the ground state and that will lie within the phonon continuum associated with the ground state. Calculation of the temperature dependence of the Fe^{2+} quadrupole interaction including vibronic coupling effects would therefore be very difficult, but it does not seem implausible that the results of Varret and Jehanno may be explained by the consideration of vibronic effects.

4. Conclusions

An approximate formalism has been outlined for the calculation of the effects of vibronic coupling on an electronic observable, and referred particularly to the calculation of the electric field gradient at the nucleus of a paramagnetic ion in a crystal or molecule. For the specific case of the temperature dependence of the ^{57}Fe quadrupole splitting in FeCO_3 it has been seen that significant effects may be expected. Further experimental evidence of this will be presented in a future publication, in which detailed measurements of the quadrupole splitting at ^{57}Fe nuclei in a series of isomorphous rhombohedral carbonates will be described.

Vibronic coupling may similarly be expected to affect other observables, such as g factors, magnetic hyperfine coupling constants and magnetic moments to some extent and can also give rise to a temperature dependence of electronic transition energies. This latter effect will be considered in a separate paper with particular reference to the observed temperature dependence of the 438 cm^{-1} Raman transition in FeCO_3 . This work emphasizes that vibronic coupling can make quite large zero-point and temperature-dependent contributions to electronic transition energies so that one must be wary when obtaining static splitting parameters.

It must be emphasized that the work reported here represents a very much simplified picture designed to examine only the qualitative features of the coupling. As may be inferred from the discussion in Section 3*f* of the effect of the spin-orbit coupling and the exchange interaction in FeCO_3 , more realistic calculations become rapidly more complex. Also, because of the strength of the vibronic coupling, at least in some cases, it is doubtful whether a perturbation approach is really satisfactory, and certainly higher order effects are likely to be significant. What is clear, however, is that great care must be exercised in the extraction of static electronic splitting parameters from data that reflect the temperature-dependent repopulation of the split levels.

Extension of these calculations to other ions and other symmetries is obvious. Tetrahedrally coordinated Fe^{2+} ions and octahedral Cu^{2+} ions both have orbital doublet E ground electronic states in cubic environments that are split by a tetragonal distortion. Vibronic admixture between the two resulting singlets has been shown to be important by Gibb *et al.* (1972) for $(\text{NMe}_4)_2\text{FeCl}_4$ and by Pilbrow and Spaeth (1967*a*, 1967*b*) for Cu^{2+} in NH_4Cl . These calculations could be readily made within the formalism presented here.

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Appendix 1

Presented here are the matrices for the orbital operators $B_l(\Gamma, \rho)$ defined by equations (33) in terms of the basis states $\psi_1, \psi_0, \psi_{-1}$ (in that order) that are in turn defined by equations (36) for cubic symmetry. The operator matrices for the $A_{1g}^{(1)}$ representations are

$$B_2(A_{1g}^{(1)}, 1) = 0, \quad B_4(A_{1g}^{(1)}, 1) = -3\sqrt{\frac{7}{5}}\rho_4 \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

For all other representations the operator matrices for $l = 4$ are proportional to those for $l = 2$. Then, for $l = 2, 4$, the required expressions are

$$B_l(A_{1g}^{(2)}, 1) = \sqrt{2}\rho_l \begin{bmatrix} 3 & 0 & 0 \\ 0 & -6 & 0 \\ 0 & 0 & 3 \end{bmatrix}$$

and

$$B_l(E_g^{(1)}, 1) = \rho_l \begin{bmatrix} 0 & 3 & -6 \\ 3 & 0 & -3 \\ -6 & -3 & 0 \end{bmatrix}, \quad B_l(E_g^{(1)}, 2) = i\rho_l \begin{bmatrix} 0 & -3 & -6 \\ 3 & 0 & 3 \\ 6 & -3 & 0 \end{bmatrix},$$

$$B_l(E_g^{(2)}, 1) = \rho_l \begin{bmatrix} 0 & -3\sqrt{2} & -3\sqrt{2} \\ -3\sqrt{2} & 0 & 3\sqrt{2} \\ -3\sqrt{2} & 3\sqrt{2} & 0 \end{bmatrix}, \quad B_l(E_g^{(2)}, 2) = i\rho_l \begin{bmatrix} 0 & 3\sqrt{2} & -3\sqrt{2} \\ -3\sqrt{2} & 0 & -3\sqrt{2} \\ 3\sqrt{2} & 3\sqrt{2} & 0 \end{bmatrix}.$$

Here

$$\rho_2 = \frac{1}{2}\sqrt{\frac{1}{2}}\langle L || \alpha || L \rangle, \quad \rho_4 = \sqrt{\frac{5}{6}}\langle L || \beta || L \rangle,$$

where the reduced matrix elements $\langle L || \alpha || L \rangle$ and $\langle L || \beta || L \rangle$ have the values $-\frac{2}{21}$ and $\frac{2}{63}$ respectively for Fe^{2+} .

Appendix 2

Matrix elements of the diagonal cartesian components of the electric field gradient operator in the basis $\psi_1, \psi_0, \psi_{-1}$ are presented here. All elements are zero except the following:

$$\langle \psi_1 | V_{zz} | \psi_1 \rangle = \langle \psi_{-1} | V_{zz} | \psi_{-1} \rangle = 3\rho,$$

$$\langle \psi_0 | V_{zz} | \psi_0 \rangle = -6\rho,$$

$$\langle \psi_1 | V_{xx} | \psi_1 \rangle = \langle \psi_{-1} | V_{xx} | \psi_{-1} \rangle = -\frac{3}{2}\rho,$$

$$\langle \psi_0 | V_{xx} | \psi_0 \rangle = 3\rho,$$

$$\langle \psi_1 | V_{yy} | \psi_1 \rangle = \langle \psi_{-1} | V_{yy} | \psi_{-1} \rangle = -\frac{3}{2}\rho,$$

$$\langle \psi_0 | V_{yy} | \psi_0 \rangle = 3\rho,$$

where

$$\rho = \langle L || \alpha || L \rangle \langle r^{-3} \rangle (1-R).$$

The reduced matrix element $\langle L || \alpha || L \rangle = -\frac{2}{21}$ for Fe^{2+} , while $\langle r^{-3} \rangle$ is an average for the valence electrons of the ion and R is the Sternheimer shielding factor.

Appendix 3

Presented here are the wavefunctions for the lowest spin-orbit multiplet of Fe^{2+} in a trigonal crystal field as described in the text. Admixtures from states within the cubic ${}^5\text{T}_{2g}$ levels only are included. Basis states are $\psi_i |S_z\rangle$ with the ψ_i defined by equations (36) and $S = 2$. Labels $|l\rangle$, $l = 1, \dots, 10$, relate to the levels in Fig. 3. The required wavefunctions are then

$$\begin{aligned} |1\rangle &= c\psi_1|0\rangle + b\psi_0|1\rangle + (1-a)\psi_{-1}|2\rangle, \\ |2\rangle &= (1-a)\psi_1|-2\rangle + b\psi_0|-1\rangle + c\psi_{-1}|0\rangle, \\ |3\rangle &= (\sqrt{\frac{1}{2}}-d)\psi_1|-1\rangle + e\psi_0|0\rangle + (\sqrt{\frac{1}{2}}-d)\psi_{-1}|1\rangle, \\ |4\rangle &= -\sqrt{\frac{1}{2}}\psi_1|-1\rangle + \sqrt{\frac{1}{2}}\psi_{-1}|1\rangle, \\ |5\rangle &= (1-f)\psi_1|0\rangle + g\psi_0|1\rangle + h\psi_{-1}|2\rangle, \\ |6\rangle &= h\psi_1|-2\rangle + g\psi_0|-1\rangle + (1-f)\psi_{-1}|0\rangle, \\ |7\rangle &= (1-p)\psi_1|1\rangle + q\psi_0|2\rangle, \\ |8\rangle &= q\psi_0|-2\rangle + (1-p)\psi_{-1}|-1\rangle, \\ |9\rangle &= \psi_1|2\rangle, \\ |10\rangle &= \psi_{-1}|-2\rangle. \end{aligned}$$

For typical values of the static splitting parameters, e.g. $A \sim 1000 \text{ cm}^{-1}$ and $\lambda \sim -100 \text{ cm}^{-1}$, and when the states are normalized, the quantities $\alpha = a, \dots, h, p, q$ are of order $|\alpha| \sim 0.01-0.2$. In general, the exchange interaction changes these admixture parameters only slightly.