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JAHN-TELLER EFFECTS IN MÖSSBAUER SPECTROSCOPY

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Résumé. — Nous examinons les conséquences, sur les spectres Mössbauer, du couplage des vibrations asymétriques avec des états électroniques possédant la même énergie — l'effet de Jahn-Teller. À l'aide d'un modèle simplifié, nous discutons les modifications caractéristiques du couplage quadropolaire qui sont les résultats d'une distorsion spontanée (« l'effet statique de Jahn-Teller ») ou d'un couplage dynamique entre le mouvement des électrons et celui des vibrations (« l'effet dynamique de Jahn-Teller »). Les faibles tensions du cristal sont très importantes pour déterminer quelle sorte de spectre est observée. Nous discutons aussi le rôle des transitions thermiques en moyennant les spectres sur tous les niveaux occupés. Comme exemples des effets de Jahn-Teller nous discutons des recherches pour les spectres Mössbauer de l'ion Fe^{2+} en symétrie tétraédrique et octaédrique.

Abstract. — We examine the consequences for the Mössbauer spectrum of coupling between asymmetric vibrational modes and an electronic state having orbital degeneracy — the Jahn-Teller (JT) effect. Characteristic modifications of the quadrupole coupling by a spontaneous JT distortion (« static JT effect ») and by a dynamic coupling of electronic and vibrational motions (« dynamic JT effect ») are discussed with the aid of a simplified model. The importance of small crystal strains in determining the type of spectrum observed is discussed, as is also the role of thermally induced transitions in causing motional averaging of the spectrum. Examples are given of JT effects as observed or anticipated in the Mössbauer spectrum of Fe^{2+} in crystal sites with tetrahedral and octahedral coordination.

1. Introduction. — The properties of electronic systems having degenerate or near-degenerate orbital states can be profoundly modified by their coupling to lattice vibrations. On one hand, if this coupling is sufficiently strong a spontaneous distortion to lower symmetry can result, which lifts the electronic degeneracy. This tendency of degenerate electronic states of molecules or localized defects in crystals to induce a distortion was originally investigated by Jahn and Teller in 1936 [1]. Alternatively, under certain circumstances, instead of a spontaneous distortion a dynamic coupling of the electronic and vibrational motions occurs ⁽¹⁾, with no loss of symmetry, and the resulting *vibronic* (vibrational plus electronic) states of the coupled system have properties related to but usually different from those of the original electronic system when the vibrational motion is neglected. Such *dynamic Jahn-Teller effects* can involve either lattice zero-point motion at low temperatures or thermally activated motion at higher temperature, and they have been the subject of extensive study in the last decade [2, 3], particularly in connection with work on electron paramagnetic resonance and optical spectroscopy of impurity ions and other point defects in crystals. It is the purpose of this paper to describe how a Jahn-Teller instability can affect Mössbauer spectroscopy and to

show what considerations are important in determining what type of Jahn-Teller *effect* should be observed.

Real systems that exhibit Jahn-Teller (JT) effects in their Mössbauer spectra, such as the ferrous ion (Fe^{2+}) in cubic or tetrahedral symmetry, are too complicated to permit one to give a brief and easily understandable account of the various manifestations of the JT coupling. Accordingly, for the purposes of this paper we will consider a simplified system which is more easily treated yet which shows the characteristic features that are important in real systems. At the end of the paper we cite and discuss briefly some of the cases in which JT effects have been observed or are expected in actual systems.

We will pattern our model system on the Fe^{2+} ion in tetrahedral symmetry [4] and assume that the electronic ground state is an orbital doublet belonging to the irreducible representation Γ_3 (or E) of the cubic or tetrahedral point group. However, whereas Fe^{2+} in a weak crystal field has an electronic spin $S = 2$, we will assume for simplicity no spin degeneracy ($S = 0$) in order to avoid the complications resulting from spin-orbit, spin-spin, and hyperfine interactions. The Mössbauer transition will be taken, as in ^{57}Fe , to be a magnetic-dipole transition between an excited nuclear state with nuclear spin $I = \frac{3}{2}$ and a ground state with $I = \frac{1}{2}$. The principal structure in the Mössbauer spectrum will then be the result of the quadrupole interaction between the valence electrons and the nucleus, and

⁽¹⁾ Recent reviews of dynamic JT effects are given in references [2] and [3].

the Zeeman interaction between the nuclear moment and a magnetic field.

Our concern in this paper will be only with the JT effect of an isolated impurity in a crystal. We will not consider the cooperative JT effect [2], which involves a cooperative ordering of the distortions associated with individual JT ions in concentrated systems and results from the interaction of distortions at neighboring ions.

2. The Jahn-Teller theorem. — The fundamental theorem [1] of the JT effect may be stated as follows [3] :

If a molecule or crystal defect has orbital electronic degeneracy when the nuclei are in a symmetrical configuration, then the molecule or defect is unstable with respect to at least one asymmetric displacement of the nuclei which lifts the degeneracy. The only exception to the rule is the linear molecule.

As illustrated in figure 1, an orbital doublet electronic state that is degenerate with an energy E_0 in a sym-

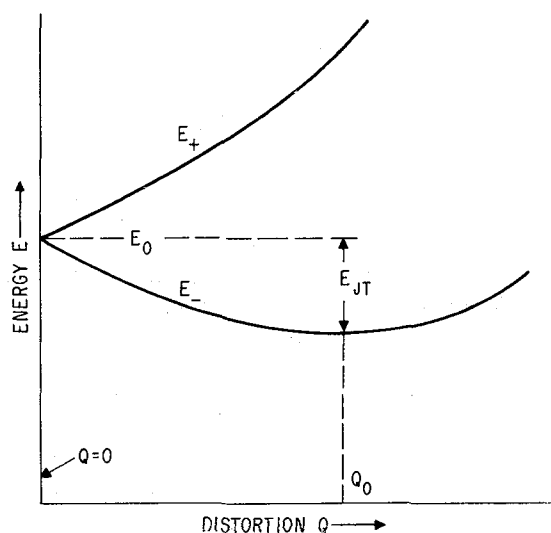


FIG. 1. — Energy splitting of a doubly degenerate electronic state under a distortion that lifts the degeneracy in first order, showing the Jahn-Teller instability of the symmetric configuration.

metrical configuration ($Q = 0$) splits linearly as a function of a suitable distortion Q and according to the JT theorem there is always at least one such distortion mode, except in the special case of a linear molecule. Because the elastic energy is positive and quadratic in Q (the symmetrical configuration is assumed to be a configuration of stable equilibrium apart from the coupling to the degenerate electronic state) the lower split-off state has a minimum at Q_0 , where the energy is E_{JT} (the JT energy) below E_0 . The symmetric configuration is unstable with respect to this distortion, since the system can thus lower its energy by spontaneously distorting to Q_0 .

The old view of the JT effect, which prevailed until a few years ago, was that at a sufficiently low temperature such a spontaneous distortion would always occur, and experiments would then measure the properties of the distorted system. We will adopt this view in Section 3, where we will derive the quadrupole splitting of the Mössbauer spectrum that results from such a distortion (the static JT effect). Later we will discuss the circumstances in which this view is the correct one.

3. Quadrupole splitting by a spontaneous distortion.

— Starting with the orbital doublet (Γ_3) electronic ground state for our model system at a site of cubic or tetrahedral symmetry, we suppose that a spontaneous distortion takes place as in figure 1 and that the lower split-off electronic state ψ_- at the equilibrium position Q_0 is given by the linear combination

$$\psi_- = \psi_\theta \cos \theta/2 - \psi_\epsilon \sin \theta/2. \quad (1)$$

Here the two orthonormal states ψ_θ and ψ_ϵ of the Γ_3 doublet are selected to transform as

$$\begin{aligned} \psi_\theta &\sim (3z^2 - r^2), \\ \psi_\epsilon &\sim \sqrt{3}(x^2 - y^2), \end{aligned} \quad (2)$$

where x , y and z are coordinates with respect to the cubic axes of the crystal.

We consider for simplicity that the quadrupole coupling is due solely to the interaction of the electric field gradient produced at the nucleus by the valence electrons of the ion with the nuclear quadrupole moment Q . This interaction in general has the form

$$\mathcal{H}_Q = \frac{e^2 Q}{2 I(2I-1)} \sum_k \left[\frac{I(I+1)}{r_k^3} - \frac{3(\mathbf{r}_k \cdot \mathbf{I})^2}{r_k^5} \right] \quad (3)$$

where \mathbf{I} is the nuclear spin operator and the sum is over all valence electrons. With respect to the electronic doublet states ψ_θ and ψ_ϵ , \mathcal{H}_Q may be represented in the form

$$\mathcal{H}_Q = C_E \{ U_\theta [3I_z^2 - I(I+1)] + U_\epsilon \sqrt{3}[I_x^2 - I_y^2] \}, \quad (4)$$

where U_θ and U_ϵ are the operators

$$\begin{aligned} U_\theta &= -|\psi_\theta\rangle\langle\psi_\theta| + |\psi_\epsilon\rangle\langle\psi_\epsilon| \\ U_\epsilon &= +|\psi_\theta\rangle\langle\psi_\epsilon| + |\psi_\epsilon\rangle\langle\psi_\theta|. \end{aligned} \quad (5)$$

For the orbital doublet (${}^5\Gamma_3$) state of the ion Fe^{2+} C_E has the value [4]

$$C_E = (1/7) \langle r^{-3} \rangle [e^2 Q / I(2I-1)], \quad (6)$$

where $\langle r^{-3} \rangle$ denotes the one-electron average of r^{-3} , and we will suppose C_E to have a similar value in our model system.

In the distorted configuration, when the electronic state is given by ψ_- as in eq. (1), the electric field

gradient seen by the nucleus is obtained by taking the diagonal matrix element of \mathcal{H}_Q with respect to ψ_- [5]:

$$\langle \psi_- | \mathcal{H}_Q | \psi_- \rangle = -C_E \{ \cos \theta [3 I_z^2 - I(I+1)] + \sqrt{3} \sin \theta [I_x^2 - I_y^2] \}. \quad (7)$$

It is readily shown [5] that the $I = \frac{3}{2}$ excited nuclear state is split in this field into two Kramers doublets as in figure 2, the energy separation

$$\Delta E_Q = 6 |C_E| \quad (8)$$

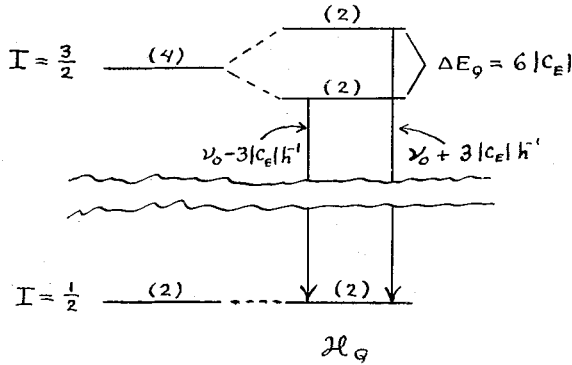


FIG. 2. — Nuclear energy levels and Mössbauer spectrum of model system, showing the splitting caused by the quadrupole coupling in the electric field gradient resulting from the valence electrons in their electronic ground state for a distorted configuration.

being independent of θ . As seen from figure 2 the resulting Mössbauer spectrum is a simple quadrupole doublet with a splitting $6 |C_E|$. Clearly, this same spectrum results at a sufficiently low temperature (so that only the electronic ground state is populated) both when the distortion is spontaneous as a result of the JT coupling and when it results from a low-symmetry component of the crystal field produced, say, by an associated defect or a large macroscopic strain.

It is of interest to ask what form of spontaneous distortion should result from the JT coupling and thus to determine what values for θ should be expected in eq. (1) to correspond to configurations of stable equilibrium. For a Γ_3 electronic state in cubic symmetry the modes of distortion that produce a linear splitting as in figure 1 are the pairs of modes that also transform as Γ_3 and the linear coupling to such a pair Q_θ, Q_ϵ can be written as

$$\mathcal{H}_{JT} = V[Q_\theta U_\theta + Q_\epsilon U_\epsilon] \quad (9)$$

Adding \mathcal{H}_{JT} to the elastic energy

$$\mathcal{H}_{el} = (\frac{1}{2}) K[Q_\theta^2 + Q_\epsilon^2] \quad (10)$$

one finds the electronic energies as functions of the Q 's to be given by

$$E_\pm(Q_\theta, Q_\epsilon) = E_0 \pm V\rho + (\frac{1}{2}) K\rho^2 \quad (11)$$

where we have made the substitution

$$Q_\theta = \rho \cos \theta, \quad Q_\epsilon = \rho \sin \theta. \quad (12)$$

The state ψ_- given in eq. (1) is the electronic eigenstate for the lower root in eq. (11) at the point in Q -space given by eq. (12) (assuming $V > 0$). As seen from eq. (11) and figure 3, these energy surfaces are independent of θ , and the energy minimum on the lower surface is attained for all values of θ on the circle with radius

$$\rho_0 = |V|/K. \quad (13)$$

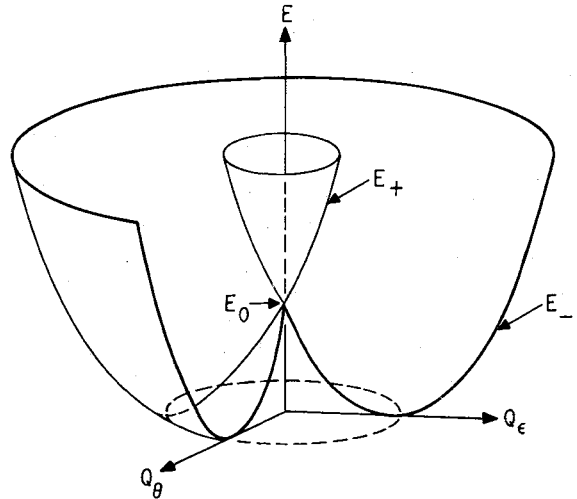


FIG. 3. — Energy surfaces $E_\pm(Q_\theta, Q_\epsilon)$ for the vibronic problem of the orbital doublet electronic state with linear Jahn-Teller coupling in cubic symmetry. The surfaces have rotational symmetry about the energy axis.

So long as we consider only linear coupling to the distortion modes, therefore, we find on the basis of energy considerations that all values of θ are equally likely [6]. In this approximation there are therefore no unique, discrete configurations of stable equilibrium and when we consider the dynamic behavior of the system (see Section 4) we must expect to find that the system undergoes some sort of motion around the trough in figure 3.

However, when we go beyond linear coupling to include the *quadratic JT coupling* [7], which changes the splitting of the electronic states by an amount quadratic in the Q 's, and a cubic anisotropy [8] of third order in the Q 's, given by adding the terms

$$V_q[U_\theta(Q_\epsilon^2 - Q_\theta^2) + 2 U_\epsilon Q_\epsilon Q_\theta] + V_c Q_\theta(Q_\theta^2 - 3 Q_\epsilon^2) \quad (14)$$

to eq. (9), we find the energy surfaces to be given, in place of eq. (11), by

$$E_\pm(Q_\theta, Q_\epsilon) = E_0 + (\frac{1}{2}) K\rho^2 + V_c \rho^3 \cos 3\theta \pm [V^2 \rho^2 + V_q^2 \rho^4 - 2 V V_q \rho^3 \cos 3\theta]^{1/2}. \quad (15)$$

The lower energy surface in figure 3 now has minima at values of θ given either by 0, $2\pi/3$ and $4\pi/3$ or $\pi/3$, π and $5\pi/3$, so that now there are three distinct configurations of stable equilibrium which correspond to tetragonal distortions (either elongations or contractions) along the three cubic axes. In general, then, these

are the distorted configurations to be expected when a spontaneous JT distortion occurs, and this expectation has been amply confirmed by paramagnetic resonance studies of ions (such as Cu^{2+}) having orbital doublet ground states in cubic symmetry [3]. In each of these configurations the electric field gradient obtained by substituting these values of θ into eq. (7) has axial symmetry about one of the cubic axes.

4. Quadrupole splitting in perfect cubic symmetry with a dynamic JT effect due to lattice zero-point motion. — In Section 3 we have seen that three energy minima may in general be expected to occur in the lower surface of figure 3, corresponding to the configurations of stable equilibrium resulting from the JT coupling. In the absence of permanent local distortions, resulting, say, from strains in the lattice, these three minima are energetically equivalent, and if the barriers between them are not too high we must expect that the system will be able to tunnel from one well to another as a result of lattice zero-point motion [9, 10]. We can study the role of tunneling theoretically by adding to eq. (9), (10), and (14) the kinetic energy terms associated with the lattice modes Q_θ and Q_ϵ .

$$\mathcal{H}_{\text{KE}} = (1/2 \mu) (P_\theta^2 + P_\epsilon^2) \quad (16)$$

where μ is the effective mass of the mode. The eigenstates of the resulting vibronic Hamiltonian have been studied extensively [10-12]. The lowest state is a degenerate doublet (Fig. 4) which, like the electronic

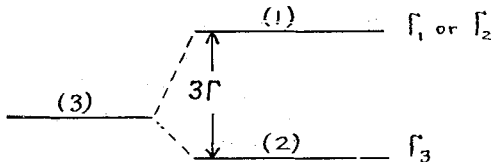


FIG. 4. — Vibronic energy levels showing the splitting of the vibronic ground state by tunneling between the three stable configurations resulting from JT coupling in an orbital doublet electronic state, including nonlinear coupling.

ground state in perfect cubic symmetry, belongs to the representation Γ_3 of the cubic group. The first excited state is a singlet belonging to Γ_1 or Γ_2 , provided the coefficients of the « warping » terms in eq. (14) are not both zero (in which case, for pure linear coupling, this state is a doublet comprising both the lowest Γ_1 and Γ_2 states). The energy difference between this singlet and the ground doublet, conventionally labeled 3Γ , is the splitting resulting from the tunneling between the lowest energy level of each of the three wells. The value of this splitting has been shown from experiment to vary from values $\gtrsim 10^{-2}$ eV for ions such as La^{2+} , Y^{2+} and Sc^{2+} in SrCl_2 [13] to a value $\sim 3 \times 10^{-4}$ eV (4 cm^{-1}) for Cu^{2+} in CaO [14], and it may be appreciably smaller than this latter value for ions showing a static JT effect in their resonance spectrum.

The effect of the quadrupole interaction \mathcal{H}_Q on the vibronic states is now quite easy to obtain if the magnitude of this interaction is small compared to the separation of the vibronic levels, so that one can ignore coupling of different levels. This condition should be satisfied in most cases for the quadrupole interaction, for which ΔE_Q as given by eq. (8) has a value $\sim 1 \times 10^{-7}$ eV, using the parameters for ^{57}Fe in eq. (6). The effect of \mathcal{H}_Q on the vibronic Γ_3 ground state, which comprises the two states $\Psi_{g\theta}$ and $\Psi_{g\epsilon}$, must, for reasons of symmetry, take a similar form to eq. (4) [15],

$$\mathcal{H}'_Q = q C_E \{ U_{g\theta} [3 I_z^2 - I(I+1)] + U_{g\epsilon} \sqrt{3} [I_x^2 - I_y^2] \} \quad (17)$$

if we introduce the vibronic operators

$$\begin{aligned} U_{g\theta} &= - | \Psi_{g\theta} \rangle \langle \Psi_{g\theta} | + | \Psi_{g\epsilon} \rangle \langle \Psi_{g\epsilon} | \\ U_{g\epsilon} &= + | \Psi_{g\theta} \rangle \langle \Psi_{g\epsilon} | + | \Psi_{g\epsilon} \rangle \langle \Psi_{g\theta} | \end{aligned} \quad (18)$$

analogous to U_θ and U_ϵ in eq. (5). Eq. (17) is obtained simply by evaluating matrix elements of \mathcal{H}_Q as given in eq. (4) with respect to $\Psi_{g\theta}$ and $\Psi_{g\epsilon}$, and the reduction factor q [15] is given simply by the matrix element

$$q = - \langle \Psi_{g\theta} | U_\theta | \Psi_{g\theta} \rangle = \langle \Psi_{g\epsilon} | U_\theta | \Psi_{g\epsilon} \rangle = \langle \Psi_{g\theta} | U_\epsilon | \Psi_{g\epsilon} \rangle. \quad (19)$$

The value of q depends on the strength of the JT coupling and is shown in figure 5 [3, 15, 16] for pure linear coupling as a function of the ratio of the JT energy

$$E_{\text{JT}} = V^2/2K \quad (20)$$

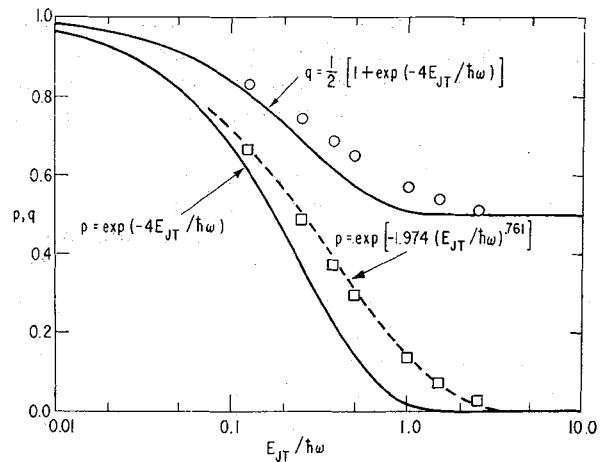


FIG. 5. — Reduction factors for the vibronic ground state in the case of an orbital doublet electronic state with linear JT coupling. The points are exact values from calculations of Child and Longuet-Higgins (1962) and the curves represent the approximate expressions indicated.

to the vibrational energy quantum

$$\hbar\omega = \hbar(K/\mu)^{1/2}. \quad (21)$$

The range of q in the ground state extends in general from unity for zero JT coupling ($E_{\text{JT}} = 0$) to $\sim \frac{1}{2}$ for strong coupling ($E_{\text{JT}}/\hbar\omega \gtrsim 2$), so that the effect of this

coupling is to reduce the effective strength of the quadrupole interaction as compared with the pure electronic states in a static lattice. This appearance of a reduction factor in the coupling to the vibronic ground state, with no change in the form or symmetry of the perturbing interaction, is a characteristic feature of the dynamic JT effect [2, 3, 15].

The splitting of the $I = \frac{3}{2}$ nuclear state (which belongs to the Γ_8 representation of the cubic double group) by the quadrupole interaction in the vibronic Γ_3 ground state, as given by eq. (17), is easily obtained when we note that the combined nuclear-vibronic system then comprises the states given by the direct product

$$\Gamma_3 \times \Gamma_8 = \Gamma_6 + \Gamma_7 + \Gamma_8. \quad (22)$$

Writing down the proper linear combination of product wave functions for any of these combined states, using tables [17] of coupling coefficients, we can then evaluate the matrix element of \mathcal{H}'_Q from eq. (17) for each such state. As shown in figure 6 the relative energy of these states is found to be

$$\begin{aligned} E(\Gamma_7) &= -6qC_E \\ E(\Gamma_8) &= 0 \\ E(\Gamma_6) &= +6qC_E. \end{aligned} \quad (23)$$

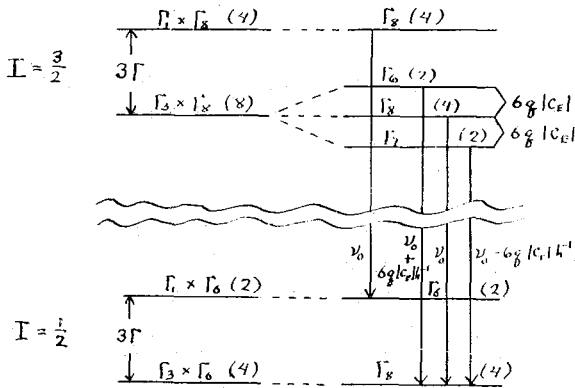


FIG. 6. — Nuclear-vibronic energy levels and Mössbauer spectrum (slow relaxation spectrum) of model system in perfect cubic symmetry (zero strain), showing the splitting of the tunneling levels (Γ_1 singlet and Γ_3 doublet) by the electric field gradient due to the valence electrons.

The $I = \frac{1}{2}$ nuclear ground state, on the other hand, is unaffected by \mathcal{H}'_Q . The Mössbauer spectrum expected in perfect cubic symmetry when the vibronic system is in its ground state (and we assume temperature sufficiently low to suppress all thermally induced transitions) is then, as shown in figure 6, a three-line spectrum. The relative line intensity is found from the appropriate matrix elements, assuming a magnetic-dipole transition and equal population of all the substates of the excited $I = \frac{3}{2}$ level, to be 1 : 2 : 1.

The excited tunneling singlet state Γ_1 or Γ_2 , on the other hand, is completely unaffected by the quadrupole interaction, since the matrix element of eq. (4) with

respect to a Γ_1 or Γ_2 state (or between such states) vanishes. As shown in figure 6, if this state were thermally populated its Mössbauer spectrum would simply add to the intensity of the unshifted central line from the doublet ground state.

5. The dynamic JT effect in the presence of random strain. — The treatment of Section 4 for an ion in perfect cubic symmetry is not realistic, however, because it ignores the effect of strains which are always present in a crystal and which, as we will now show, play a crucial role in determining the Mössbauer spectrum that is observed experimentally. Random strains in the best available crystals typically cause splittings of order 10^{-4} eV (1 cm^{-1}) in the orbitally degenerate states of impurity ions and other defects. Compared with this typical strain splitting the quadrupole interaction \mathcal{H}_Q is weak and must be treated as a perturbation on the strain-split states.

The coupling of the Γ_3 vibronic ground state of our model system to strains characterized by the components

$$\begin{aligned} e_\theta &= e_{zz} - \frac{1}{2}(e_{xx} + e_{yy}) \\ e_s &= \frac{1}{2}\sqrt{3}(e_{xx} - e_{yy}) \end{aligned} \quad (24)$$

of the strain tensor has the form

$$\mathcal{H}_s = qV_s(U_{g\theta}e_\theta + U_{gs}e_s) \quad (25)$$

in terms of the operators of eq. (18). Defining a strain magnitude $e = (e_\theta^2 + e_s^2)^{1/2}$ and an angle φ such that

$$e_\theta = e \cos \varphi, \quad e_s = e \sin \varphi \quad (26)$$

we find that as long as we ignore coupling with higher vibronic states the eigenstates of eq. (25) are

$$\begin{aligned} \Psi_{g+} &= \sin(\varphi/2) \Psi_{g\theta} + \cos(\varphi/2) \Psi_{gs} \\ \Psi_{g-} &= \cos(\varphi/2) \Psi_{g\theta} - \sin(\varphi/2) \Psi_{gs} \end{aligned} \quad (27)$$

separated by an energy difference

$$\delta = 2qV_s e. \quad (28)$$

Diagonal matrix elements of \mathcal{H}'_Q , as given by eq. (17), with respect to these states (27) are given by

$$\begin{aligned} &\langle \Psi_{g\pm} | \mathcal{H}'_Q | \Psi_{g\pm} \rangle = \\ &= \pm qC_E \{ \cos \varphi [3I_z^2 - I(I+1)] + \sqrt{3} \sin \varphi [I_x^2 - I_y^2] \}. \end{aligned} \quad (29)$$

Just as in eq. (7) and (8), for each of the states Ψ_{g+} and Ψ_{g-} this coupling splits the $I = \frac{3}{2}$ nuclear state into two doublets with a separation

$$\Delta E_Q = 6q|C_E| \quad (30)$$

independent of φ . The Mössbauer spectrum for each of these two strain-split vibronic states is therefore a single quadrupole doublet, independent of φ and the strain magnitude e , and these two spectra coincide. Compared with the quadrupole doublet obtained in Section 3 for the electronic state split by a fixed distortion or a static

JT distortion, however, the doublet given by eq. (30) for the vibronic ground state with a dynamic JT effect is reduced by the reduction factor q .

A strain broadening of the Mössbauer spectrum analogous to that found in the paramagnetic resonance spectrum of a $^2\Gamma_3$ state [3] occurs if we consider the simultaneous effect of the quadrupole coupling and a magnetic field on the nuclear states. Assuming for simplicity that the nuclear Zeeman splitting of the $I = \frac{3}{2}$ state is large compared to the quadrupole coupling, and taking the magnetic field to be oriented in the direction of the unit vector \mathbf{n} , which has components n_x, n_y, n_z , we find that the diagonal matrix elements of eq. (29) with respect to the nuclear Zeeman eigenstates $|I_n\rangle$ are the same as those of the diagonal operator

$$\mathcal{H}'_Q(\pm, I_n) = \pm (qC_E/2) [3I_n^2 - I(I+1)] \times \\ \times [\cos \varphi (3n_z^2 - 1) + \sin \varphi \sqrt{3}(n_x^2 - n_y^2)]. \quad (31)$$

Defining an angle α by

$$\cos \alpha = \frac{1}{2} (3n_z^2 - 1) [1 - 3(n_x^2 n_y^2 + n_y^2 n_z^2 + n_z^2 n_x^2)]^{-1/2} \quad (32)$$

$$\sin \alpha = \frac{1}{2} (\sqrt{3})(n_x^2 - n_y^2) [1 - 3(n_x^2 n_y^2 + n_y^2 n_z^2 + n_z^2 n_x^2)]^{-1/2}$$

we see that eq. (31) can be rewritten as

$$\mathcal{H}'_Q(\pm, I_n) = \\ = \pm qC_E \cos(\varphi - \alpha) [3I_n^2 - I(I+1)] \times \\ \times [1 - 3(n_x^2 n_y^2 + n_y^2 n_z^2 + n_z^2 n_x^2)]^{1/2}. \quad (33)$$

If the strain distribution is random, the angle φ defined by eq. (26) will vary at random in the range $(0, 2\pi)$

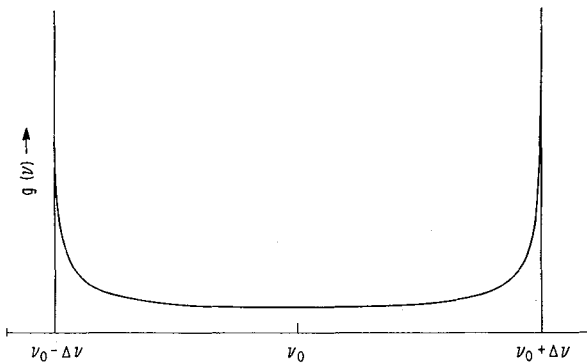


FIG. 7. — Line shape $g(\nu)$ of individual Zeeman components of Mössbauer spectrum of model system in a strong magnetic field. The line shape results from broadening by random strain as described by eq. (33).

among different sites in the crystal. Accordingly, each Zeeman component of the Mössbauer spectrum is broadened by eq. (33) between the limits obtained by setting $\cos(\varphi - \alpha) = \pm 1$. The line shape has the form shown in figure 7. This broadening has its maximum for H along $[100]$ and vanishes for H along $[111]$.

6. Transition from dynamic to static JT effect. —

When the strain splitting δ of the Γ_3 vibronic ground state as given by eq. (28) approaches the tunneling splitting 3Γ , we can no longer ignore the strain coupling to the excited singlet. Assuming this singlet Ψ_1 has Γ_1 symmetry (a similar analysis holds if the singlet is Γ_2), we define [3] in analogy with eq. (19) a parameter r from the matrix elements

$$r = \langle \Psi_1 | U_\theta | \Psi_{g\theta} \rangle = \langle \Psi_1 | U_\varepsilon | \Psi_{g\varepsilon} \rangle. \quad (34)$$

Treating the strain mixing with the singlet by perturbation theory, we find to first order in $\delta/3\Gamma$ that the quadrupole splitting of the $I = \frac{3}{2}$ state into two Kramers doublets (with no magnetic field) has the value

$$(\Delta E_Q)_+ = 6q |C_E| [1 - (\delta/3\Gamma) (r^2/q^2) \sin^2(3\varphi/2)] \quad (35a)$$

for the vibronic state derived from Ψ_{g+} in eq. (27) and

$$(\Delta E_Q)_- = 6q |C_E| [1 + (\delta/3\Gamma) (r^2/q^2) \cos^2(3\varphi/2)] \quad (35b)$$

for Ψ_{g-} . The quadrupole doublets in the Mössbauer spectra for these two states therefore are now broadened by the strain and no longer coincide, the splitting of one being increased and that of the other diminished as compared with eq. (30).

In the *intermediate coupling* regime where $\delta \sim 3\Gamma$, the complicated shape of the Mössbauer spectrum due to random strain would have to be calculated by numerical analysis, as in the corresponding paramagnetic resonance lineshape problem [18, 19]. There seems to be no simple description that is appropriate to this regime.

The transition to the case of a static JT effect treated in Section 3 occurs as δ becomes larger than 3Γ , and we can analyse this situation by introducing a unitary transformation [3] of the vibronic states $\Psi_1, \Psi_{g\theta}$ and $\Psi_{g\varepsilon}$ given by

$$\begin{aligned} \Psi_x &= (1/\sqrt{3}) \Psi_1 - (1/\sqrt{6}) \Psi_{g\theta} + (1/\sqrt{2}) \Psi_{g\varepsilon} \\ \Psi_y &= (1/\sqrt{3}) \Psi_1 - (1/\sqrt{6}) \Psi_{g\theta} - (1/\sqrt{2}) \Psi_{g\varepsilon} \\ \Psi_z &= (1/\sqrt{3}) \Psi_1 + (2/\sqrt{6}) \Psi_{g\theta}. \end{aligned} \quad (36)$$

In this new basis the energy matrix comprising the tunneling splitting and the strain coupling takes the form

Ψ_x	Ψ_y	Ψ_z	
$\Psi_x: qV_s(e_\theta - \sqrt{3}e_\varepsilon)(1 - 2\varepsilon)$	$-2qV_s e_\theta \varepsilon + \Gamma$	$qV_s(e_\theta + \sqrt{3}e_\varepsilon)\varepsilon + \Gamma$	(37)
$\Psi_y: -2qV_s e_\theta \varepsilon + \Gamma$	$qV_s(e_\theta + \sqrt{3}e_\varepsilon)(1 - 2\varepsilon)$	$qV_s(e_\theta - \sqrt{3}e_\varepsilon)\varepsilon + \Gamma$	
$\Psi_z: qV_s(e_\theta + \sqrt{3}e_\varepsilon)\varepsilon + \Gamma$	$qV_s(e_\theta - \sqrt{3}e_\varepsilon)\varepsilon + \Gamma$	$-2qV_s e_\theta(1 - 2\varepsilon)$	

where we have introduced the parameter ε defined by the relation

$$r/q = -\sqrt{2}(1 - 3\varepsilon). \quad (38)$$

Numerical analysis [20] of the vibronic states shows that ε is always small: for pure linear coupling we have $\varepsilon \sim 0.10$, and ε becomes rapidly smaller as the size of the *warping* terms in eq. (14) increases. Thus it is usually a good approximation to set $\varepsilon = 0$ in the matrix (37):

$$\begin{array}{ccc} & \Psi_x & \Psi_y & \Psi_z \\ \Psi_x: & -2qV_s[e_{xx} - (\frac{1}{2})(e_{yy} + e_{zz})] & \Gamma & \Gamma \\ \Psi_y: & \Gamma & -2qV_s[e_{yy} - (\frac{1}{2})(e_{zz} + e_{xx})] & \Gamma \\ \Psi_z: & \Gamma & \Gamma & -2qV_s[e_{zz} - (\frac{1}{2})(e_{xx} + e_{yy})] \end{array} \quad (39)$$

Clearly the states Ψ_x , Ψ_y and Ψ_z represent good approximations to the energy eigenstates when the differences in the strain matrix elements on the diagonal of the matrix (39) are larger than the tunneling matrix element Γ . In this same basis, again setting $\varepsilon = 0$, we have for the quadrupole interaction \mathcal{H}_Q in eq. (4)

$$\begin{array}{ccc} & \Psi_x & \Psi_y & \Psi_z \\ \Psi_x: & -2qC_E[3I_x^2 - I(I+1)] & 0 & 0 \\ \Psi_y: & 0 & -2qC_E[3I_y^2 - I(I+1)] & 0 \\ \Psi_z: & 0 & 0 & -2qC_E[3I_z^2 - I(I+1)] \end{array} \quad (40)$$

Since, as we have seen, Ψ_x , Ψ_y and Ψ_z are the energy eigenstates when the strain splitting suppresses the tunneling, we see from eq. (40) that the quadrupole splitting of $I = \frac{3}{2}$ for each of these states is

$$\Delta E_Q = 12q|C_E|. \quad (41)$$

Since we have $q \sim \frac{1}{2}$ when the JT coupling is at least moderately strong, as in figure 5, this result (41) is identical with the quadrupole splitting $6|C_E|$ obtained for the spontaneous JT distortion in eq. (8). Moreover, the diagonal entries in eq. (40) are identical with the quadrupole coupling we obtained from eq. (7) on setting $\theta = 0, 2\pi/3, 4\pi/3$ (or $\pi/3, \pi, 5\pi/3$), which according to Section 3 are the values of θ corresponding to the equilibrium configurations for the spontaneous JT distortion.

We see therefore from this discussion how the effect of a small random strain, in suppressing the tunneling, leads to a *static JT effect* in which the Mössbauer spectrum is the same as that of the electronic ground state in a strongly distorted tetragonal crystal field [3]. A static JT effect could appear in other ways, for sufficiently strong JT coupling, without strain playing the crucial role, but in practice in all the cases examined to date [3] it is always the random crystal strain that dominates other anisotropic interactions in being responsible for the transition to a static JT effect.

7. Motional effects of thermally induced transitions.

— Our consideration up to this point has been with the individual vibronic eigenstates of the coupled electron-lattice system, and with the Mössbauer spectrum that results from having the system in one of these states, without worrying about motional effects resulting from thermally induced transitions. As is well known, however, such transitions are important in determining

experimental spectra because the spectrum is motionally averaged [5, 21] if the relaxation time τ for the establishment of thermal equilibrium between the vibronic states is shorter than the reciprocal of the angular frequency difference ($2\pi\Delta\nu$) between the spectra of the individual states

$$\tau \ll (2\pi\Delta\nu)^{-1}. \quad (42)$$

On the other hand, when the inequality (42) is reversed and the relaxation time is long, the Mössbauer spectrum should be the superposition of these spectra of the different states, each weighted in intensity with its Boltzmann population factor. The transition between these two types of spectra, which occurs when $\tau \sim (2\pi\Delta\nu)^{-1}$, is described by the standard theory of the motional averaging of resonance spectra [21].

For the strain-split doublet states Ψ_{g+} and Ψ_{g-} of eq. (27), the electric field gradients obtained from eq. (29) have the same magnitude but opposite signs. Taking the splitting δ as given by eq. (28), we obtain the motionally averaged quadrupole splitting [5] by averaging the electric field gradient over the two states, giving the higher the relative weight of the Boltzmann factor $\exp(-\delta/kT)$. The resulting splitting of the Mössbauer doublet when the inequality (42) is satisfied is then

$$\Delta E_Q = 6q|C_E| \tanh(\delta/2kT) \quad (43)$$

in place of eq. (30). The relaxation time at liquid helium temperature in this case, when the direct absorption or emission of a single phonon dominates the transition process, is given [3] by

$$\tau^{-1} = [3\delta^3(qV_s)^2/20\pi\hbar^4\rho s_T^5] \times [1 + (\frac{2}{3})(s_T/s_L)^5] \coth(\delta/2kT) \quad (44)$$

where qV_s is the strain-coupling coefficient from eq. (25), s_T and s_L are the transverse and longitudinal sound velocities in the crystal, and ρ is the crystal density. Taking as representative values [3] $\delta = 1 \text{ cm}^{-1}$, $qV_s = 1 \text{ eV}$, and the other parameters appropriate to CaF_2 and MgO , we find for τ at 0 K (the lifetime of the higher of the strain-split states) the values $1.5 \times 10^{-8} \text{ s}$ for CaF_2 and $5 \times 10^{-7} \text{ s}$ for MgO . Comparing with $\hbar/\Delta E_Q = (2\pi\Delta\nu)^{-1} = 1 \times 10^{-8} \text{ s}$ from eq. (30), using the parameters of ^{57}Fe , we would expect from the inequality (42) that our model system would show a motionally averaged spectrum above $\sim 1.5 \text{ K}$ for CaF_2 and $\sim 35 \text{ K}$ for MgO . The quadrupole splitting of this averaged spectrum vanishes, of course, according to eq. (43), for temperatures such that $2kT \gg \delta$.

By contrast with eq. (43), if, with a spontaneous JT (*static*) distortion, we had no thermally induced reorientation but only a Boltzmann distribution between the split *electronic* states, or if we had a permanent distortion due to some associated defect, we would obtain on averaging [5] from eq. (8) or (41)

$$E_Q = 6 |C_E| \tanh(\Delta E/2kT) \quad (45)$$

where ΔE is the splitting of the *electronic* states [given by $\Delta E = 4E_{JT}$ from eq. (11), (13) and (20) for the spontaneous distortion]. However, with a spontaneous JT distortion we must expect that reorientation occurs as the temperature rises, since as we have seen in eq. (39) the energies of the vibronic states Ψ_x, Ψ_y, Ψ_z corresponding to the spontaneously distorted tetragonal states of different orientation differ only by amounts proportional to the strength of the random strain or other local distortion. Phonons can cause transitions between these states and thus cause reorientation of the distortion, by the process of phonon-assisted tunneling [3]. This leads to a low-temperature relaxation time for a direct one-phonon process given [3] by

$$\tau^{-1} = [27 \Gamma^2(qV_s)^2 kT/5\pi\hbar^4 s_T^5] [1 + (\frac{2}{3})(s_T/s_L)^5] \quad (46)$$

which is valid if the temperature is sufficiently high so that kT is larger than the strain energy differences $\delta_{xy}, \delta_{yz}, \delta_{zx}$ between the states Ψ_x, Ψ_y, Ψ_z . The average of the electric field gradients corresponding to the individual distorted states and given by eq. (40) is isotropic if $kT \gg \delta_{xy}, \delta_{yz}, \delta_{zx}$, and the quadrupole splitting of the motionally averaged spectrum then vanishes. However, if kT is comparable with these strain energy differences the average must be taken using the appropriate Boltzmann factors, and the quadrupole splitting will be narrowed but will not vanish. Note in this case that it is the energy differences $\delta_{xy}, \delta_{yz}, \delta_{zx}$ due to strain or other local distortion that enter this averaging, not the electronic splitting ΔE as in eq. (45). The detailed form of the spectrum through the transition region in which the motionally

averaged spectrum first appears can be derived from the theory of Tjon and Blume [22].

8. JT effects in real systems : Fe^{2+} in octahedral and tetrahedral coordination. — As remarked in the introduction, real systems exhibit JT effects with characteristic features similar to those we have derived for our model system, but they are rather more complicated in detail. As two examples of such systems where JT effects in the Mössbauer spectrum have been identified or actively sought, we will discuss briefly some aspects of the spectra of the Fe^{2+} ion in octahedral and tetrahedral coordination.

The energy level diagram of the Fe^{2+} ion in cubic symmetry for octahedral coordination is given in figure 8. The 5D term of the free ion is split by the

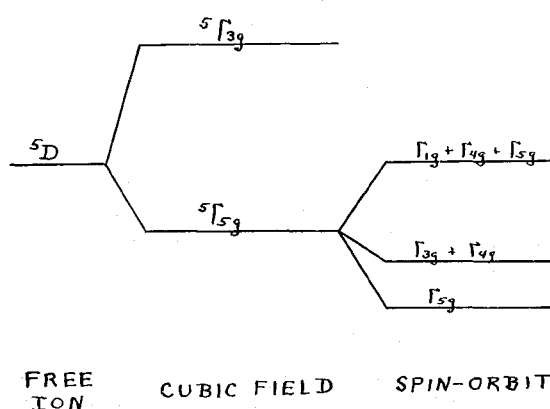


FIG. 8. — Energy level diagram of the Fe^{2+} 5D term in cubic symmetry and octahedral coordination.

cubic field into an orbital triplet, $^5\Gamma_{5g} (^5T_{2g})$ and a doublet $^5\Gamma_{3g} (^5E_g)$, of which the triplet is lower in octahedral coordination. This triplet is in turn split by the spin-orbit interaction, the lowest level being a spin-orbit Γ_{5g} triplet comprising states $\psi_\xi, \psi_\eta, \psi_\zeta$, transforming as yz, zx, xy respectively. Although the JT coupling in the $^5\Gamma_{5g}$ state is typically not sufficiently strong to cause a spontaneous distortion, it is now believed that for Fe^{2+} in MgO , CaO and KMgF_3 a dynamic JT effect significantly reduces the spin-orbit splitting and changes the parameters which describe the coupling of the ground-state triplet to various perturbations. The theory of the dynamic JT effect for this system, as applied to optical, paramagnetic resonance, and Mössbauer studies, has been given in a previous paper [23], where it has been shown how the various JT reduction factors depend on the strength of the coupling to the Γ_{3g} and Γ_{5g} vibrational modes. In the absence of a magnetic field, and at temperatures at which the electronic relaxation time is sufficiently long to avoid motional averaging (below 12 K for KMgF_3 and 14 K for MgO), it has also been shown that small random strains play a crucial role, as in Section 5, in splitting the ^{57}Fe Mössbauer spectrum into a quadru-

pole doublet [24]. The splitting of this doublet is given by

$$\Delta E_Q = 6 C_E [K_E^2 + (K_T^2 - K_E^2) (a^2 b^2 + b^2 c^2 + c^2 a^2)]^{1/2} \quad (47)$$

for the linear combination of the electronic states

$$\psi = a\psi_g + b\psi_n + c\psi_c \quad (48)$$

where C_E is given by eq. (6). According to crystal-field theory the reduction factors K_E and K_T should both have the value $+1/10$, so that eq. (47) would then be independent of the choice of a , b , c and thus of the detailed form of the strain. However, JT coupling to Γ_{3g} modes increases K_E and diminishes K_T , while coupling to Γ_{5g} modes diminishes K_E and leaves K_T almost unchanged [23]. If the coupling to these two types of modes is of different strength, so that K_E and K_T are unequal, the Mössbauer doublet should be broadened by random strain in accord with eq. (47). Moreover, the relative values of K_E and K_T can be measured separately from the quadrupole splitting induced by a strong magnetic field if the field is oriented along [100] and [111] directions, respectively [24]. As Regnard [25] discusses in another paper at this Conference, the experimental Mössbauer data indicate that for Fe^{2+} in KMgF_3 the JT coupling to the Γ_{5g} modes is the stronger, while in CaO the coupling to the Γ_{3g} modes dominate. For Fe^{2+} in MgO , in contrast, the two types of coupling are found to have more or less equal strength [23, 26].

For Fe^{2+} in tetrahedral symmetry the cubic field splitting in figure 8 is inverted, and ${}^5\Gamma_3$ is the lower state. As shown in figure 9, the ${}^5\Gamma_3$ state is split into

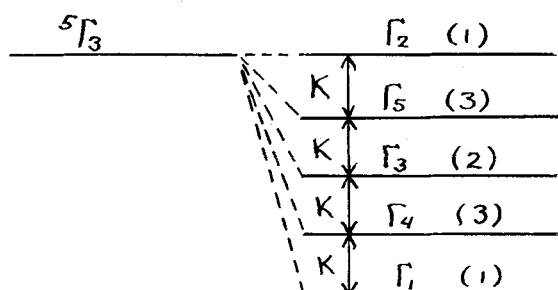


FIG. 9. — Splitting of ${}^5\Gamma_3$ ground state of Fe^{2+} ion in tetrahedral symmetry, by spin-orbit and spin-spin coupling.

five levels by the spin-orbit coupling to the ${}^5\Gamma_5$ and higher levels and by spin-spin interaction, the lowest level being a Γ_1 singlet [27]. According to crystal-field theory modified by a dynamic JT effect of weak or moderate coupling strength, these levels are equally spaced, to a good approximation, with a separation K given [28] by

$$K = 6 q [(\lambda^2/4) + \rho] \quad (49)$$

where λ is the spin-orbit parameter, 4 the cubic-field splitting, ρ the effective spin-spin parameter, and q the reduction factor of Section 4. K is found experimentally to be $15.0 \pm 0.1 \text{ cm}^{-1}$ for Fe^{2+} in ZnS [29] and to lie

typically in the range $10\text{--}20 \text{ cm}^{-1}$ for Fe^{2+} in other crystals with tetrahedral coordination [28]. With strong JT coupling, on the other hand, we have an orbital singlet vibronic state (${}^5\Gamma_1$ or ${}^5\Gamma_2$) corresponding to the excited tunneling state in Section 4 and lying an energy 3Γ above the ${}^5\Gamma_3$ ground state, and the spin-orbit splitting is more complicated [28].

If the system is in the lowest spin-orbit level of figure 9 (Γ_1) there is no electric field gradient at the nucleus, provided the effect of local strain is small compared to the spin-orbit splitting K . A single unsplit Mössbauer line corresponding to this situation has indeed been observed at 4.2 K for 0.2% Fe in ZnS (cubic and hexagonal) by Gerard *et al.* [4]. However, strain mixes the Γ_1 and Γ_3 states, and the quadrupole splitting of the $I = \frac{3}{2}$ state caused by the resulting electric field gradient is given by

$$\Delta E_Q = 6 q |C_E| [\delta/(4K^2 + \delta^2)^{1/2}] \quad (50)$$

where δ is the strain splitting given by eq. (28) for an arbitrary strain e_θ , e_ϵ . A broadening of the 4.2 K Mössbauer line into a strain-broadened doublet consistent with eq. (50) has been observed by Gerard *et al.* [4] for Fe^{2+} in ZnS and CdS at higher concentrations; in addition a well-defined doublet with a peak separation $\sim 3 \text{ mm/s}$ appears which evidently results from pairs of Fe^{2+} in nearest neighbor metal sites. The strain splitting δ for these pairs is found [4] to be $\sim 100 \text{ cm}^{-1}$ from the temperature variation of this splitting, using the same temperature dependence as in eq. (4). A similar spectrum for Fe^{2+} at the tetrahedral A sites of natural spinel (MgAl_2O_4) has been observed by Ono *et al.* [30], who concluded that there are two different groups of Fe^{2+} ions, one with $\delta \sim 20 \text{ cm}^{-1}$, the other with $\delta \sim 100 \text{ cm}^{-1}$. A somewhat larger splitting ($\delta \sim 200 \text{ cm}^{-1}$) was found in synthetic spinel crystals.

If the first excited spin-orbit level of figure 9 could be populated at a temperature low enough to avoid relaxation averaging, theory shows that a quadrupole splitting

$$E_Q = 6 q |C_E| \quad (51)$$

should be observed which, unlike eq. (50), is independent of the strain splitting δ . To the authors' knowledge, no such spectrum has ever been reported, although it might be observable in ZnS , say, at $\sim 10 \text{ K}$.

As indicated in eq. (49) and (50), both the spin-orbit and quadrupole splittings should be reduced by a dynamic JT effect through the appearance of the reduction factor q . However, the JT coupling for Fe^{2+} in tetrahedral sites is evidently weak, and compelling evidence has not so far been presented that q is much less than unity. Also, no persuasive evidence for a spontaneous JT distortion of an isolated Fe^{2+} ion at a tetrahedral site has been presented (which would of course imply strong JT coupling), such splittings as have been found evidently always being the result of crystal strain and other local distortion resulting from nearby impurities and other defects.

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