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MAGNETICALLY PERTURBED MÖSSBAUER SPECTRA OF IRON AND TIN COORDINATION COMPOUNDS

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CONTENTS

A. INTRODUCTION

The utility of Mössbauer spectroscopy in the study of iron[1,2] and tin[3] coordination compounds is well established. In addition to a number of other important parameters, it is the isomer shift (δ) and quadrupole splitting (ΔE) that are most often determined from unperturbed Mössbauer spectra. The first of these parameters is related to the *s* electron density at the Mössbauer nucleus. The quadrupole splitting, if present, is a measure of distortion from spherical symmetry of the electronic charge about the nucleus and results from the interaction of the corresponding electric field gradient with a nuclear quadrupole moment. The *magnitude* of the quadrupole splitting is of chemical importance in that it is often diagnostic of oxidation and spin state, and coordination number as well as degree of distortion from regular symmetry. However, much more information is obtained from Mössbauer spectra in which the sign as well as magnitude of the quadrupole interaction is determined. In principle, it is possible to ascertain the sign by simple inspection of powder spectra for compounds of Mössbauer isotopes involving transitions among nuclear levels for which the nuclear spin quantum number (I) is greater than 3/2. Unfortunately, in the cases of iron-57 and tin-119, whose Mössbauer transitions are between $I = 1/2$ and $I = 3/2$

states, symmetric quadrupole doublet spectra are usually observed for isotropic, polycrystalline absorbers. Thus it is not possible to determine the sign of the quadrupole interaction from unperturbed powder spectra. Orientation methods have been applied successfully to the determination of the sign of quadrupole interaction in single crystals of iron[4] compounds and partially oriented tin-containing powders[5]. These methods suffer from the usual problem of obtaining good samples.

It is the purpose of this article to review the *magnetic perturbation method*, a simple technique for determining the sign of the quadrupole interaction from powder spectra through the application of an external magnetic field and the resultant removal of any remaining nuclear spin degeneracy. Essentially all of the literature concerning the application of this technique is surveyed up to the present. This is possible since the perturbation method was first applied[6] only in 1965.

In the magnetic perturbation experiment, the sign of the quadrupole coupling constant is measured directly and from this may be derived the sign of the principal component (V_{zz}) of the electric field gradient tensor. The latter parameter can in turn be related to, inter alia, the nature of the metal–ligand bond, the type of coordination of polyhedron and the form of the orbital ground-state wave function. The various magnetically perturbed Mössbauer studies reviewed will be examined in relation to the foregoing applications.

B. THEORY

(i) Unperturbed Mössbauer spectra

(a) Quadrupole interaction

The nuclear quadrupole interaction results from the quantized interaction of a nonspherical electron charge distribution about the nucleus (electric field gradient) with a nonspherical nuclear charge distribution or nuclear quadrupole moment. The Hamiltonian describing the interaction[7] is

$$\mathcal{H} = [eQ/2I(2I-1)]\ (V_{zz}I_z^2 + V_{yy}I_y^2 + V_{xx}I_x^2) \qquad (1)$$

where $-e$ is the charge on the electron, I is the nuclear spin, Q is the nuclear quadrupole moment and $-V_{zz}$ etc. are the components of the electric field gradient tensor. The electric field is the negative gradient of a scalar potential V and thus a vector quantity. The electric field gradient is the gradient of the foregoing vector quantity and is thus a complex second-rank tensor.

$$\text{Electric field gradient} = -\ \nabla\nabla V = -\begin{vmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{vmatrix} \qquad (2)$$

where, for instance, $V_{zz} = \mathrm{d}^2V/\mathrm{d}z^2$ and $V_{xy} = V_{yx}$ etc., i.e. the electric field gradient is a symmetric tensor. Owing to the symmetry, only three of the off-diagonal elements are independent. Furthermore, a special form of Poisson's equation, Laplace's equation, applies and thus the tensor is traceless, therefore

$$\nabla^2 V = V_{xx} + V_{yy} + V_{zz} = 0 \tag{3}$$

It is then always possible to choose a principal axis system for the tensor such that the off-diagonal elements of eqn. (2) vanish. In choosing this axis system it is conventional[8] to have

$$V_{zz} \geqslant V_{yy} \geqslant V_{xx} \tag{4}$$

and to define the asymmetry parameter η such that

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \tag{5}$$

Thus $0 \leqslant \eta \leqslant 1$ and while the quadrupole splitting measures the extent of distortion from spherical symmetry, η measures the departure from cylindrical symmetry about the principal "Z" axis. The "Z" or *principal component* of the electric field gradient is defined as

$$-V_{zz} = -eq \tag{6}$$

Hence in the principal axis system, one has the two independent parameters q and η such that eqn. (1) simplifies to

$$\mathcal{H} = \left\{\frac{e^2qQ}{4I(2I-1)}\right\} \{3I_z^2 - I(I+1) + \eta\,(I_x^2 - I_y^2)\} \tag{7}$$

The nuclear ground spin states of iron-57 and tin-119 have $I = 1/2$ and $Q = 0$. On the other hand, the first excited levels of the preceding nuclei correspond to transitions to $I = 3/2$ for $Q \neq 0$. The eigenvalues[9] of their quadrupole interaction, using the principal axis Hamiltonian (eqn. (7)) are

$$E_Q(m_I) = \left\{\frac{e^2qQ}{4I(2I-1)}\right\} \left\{3I_z^2 - I(I+1)\left(1 + \frac{\eta^2}{3}\right)\right\}^{1/2} \tag{8}$$

or for the | 3/2, ± 3/2 > and | 3/2, ± 1/2 > states of tin-119 and iron-57,

$$E_Q(\pm 3/2) = \frac{1}{4} e^2qQ \left(1 + \frac{\eta^2}{3}\right)^{1/2} \tag{9}$$

$$E_Q(\pm 1/2) = \frac{1}{4} e^2qQ \left(1 + \frac{\eta^2}{3}\right)^{1/2} \tag{10}$$

Thus the quadrupole interaction (ΔE) determined in a typical unperturbed Mössbauer experiment is

$$\Delta E = |E_Q(\pm 3/2) - E_Q(\pm 1/2)| = \frac{1}{2}e^2qQ \left(1 + \frac{\eta^2}{3}\right)^{1/2} \tag{11}$$

or

$$\Delta E = \frac{1}{2}eQ[\tfrac{2}{3}(V_{xx}^2 + V_{yy}^2 + V_{zz}^2)]^{1/2} \tag{12}$$

It is seen that the quadrupole interaction lifts the degeneracy of only those states differing in I_z and thus an unperturbed powder spectrum will not yield the sign of interaction.

The discussion up to this point has dealt with the left and center of Fig. 1. (H is an applied magnetic field.) Corresponding to these is an experimentally observed unperturbed spectrum[6] as in Fig. 2(a). As stated previously, it is the sign of the quadrupole coupling constant, (e^2qQ), that is of interest chemically and is determined directly by the magnetic perturbation technique. For $e^2qQ > 0$, the $I_z = \pm 3/2$ states are at higher energy than $I_z = \pm 1/2$. Thus, if $Q > 0$ as in the case[10] of iron-57, $q = V_{zz}/e > 0$. For tin-119m, $Q < 0$ and hence $e^2qQ > 0$ implies $V_{zz}/e < 0$ in tin compounds[5].

(b) Nature of the electric field gradient tensor

In order to have a useful interpretation of a positive or negative sign for V_{zz}, it is now necessary to consider in rather more detail the individual elements of eqn. (2) and also the factors contributing to the total electric field gradient felt by the nucleus.

The total electric field gradient can be thought of as due to a valence orbital occupation contribution (q_v) and the so-called "lattice" contribution (q_l) owing to a non-cubic distribution of charges or dipoles of coordinated ligands as well as those on more distant uncoordinated species in the lattice. A non-zero q_v might arise from covalence anisotropy as exemplified in certain low-spin iron(II) and also tin(IV) compounds. For paramagnetic iron systems such as high-spin iron(II) and low-spin iron(III), a non-zero valence electric field gradient will result from low-symmetry ligand field components[11] which serve to remove the degeneracy of an electron or hole in the t_{2g} manifold. In consideration of the preceding, the total electric field gradient is written as

$$eq = V_{zz} = eq_l(1 - \gamma_{00}) + eq_v(1 - R) \tag{13}$$

where γ_{00} and R are the appropriate Sternheimer[12] factors. That is, lattice and valence charge distributions can cause polarization of the otherwise spherically symmetric core electrons. This results in an additional electric field gradient whose magnitude is proportional to the valence and lattice contributions and is accounted for by the Sternheimer factors.

(c) Point charge approximation

If one considers the electric field gradient and hence quadrupole splitting as due to the ligand charge distribution or covalence anisotropy induced by this distribution, then the total electric field gradient can be calculated by evaluation of the elements of eqn. (2) over all ligand coordinates[13]. In this approach the charges on ligands as well as the charge distributions resulting from ligand electron donation or withdrawal are treated as points. The expressions convenient for evaluation of the elements of eqn. (2) are given in Table 1.

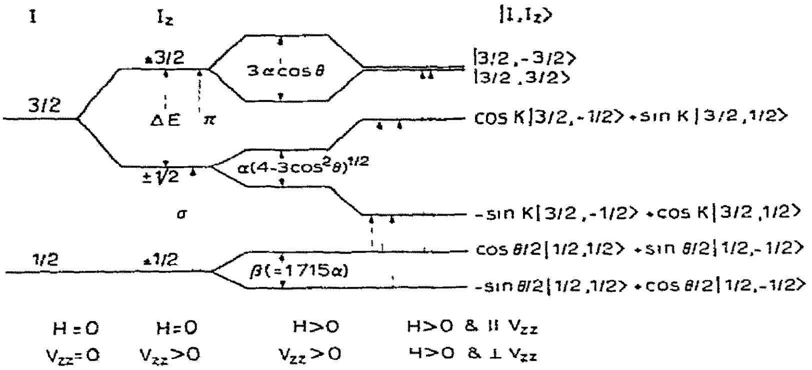


Fig. 1. Energy level diagram for Fe^{57} (reproduced with permission from ref. 6).

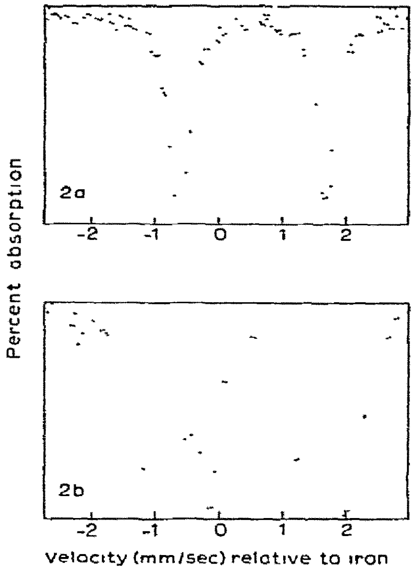
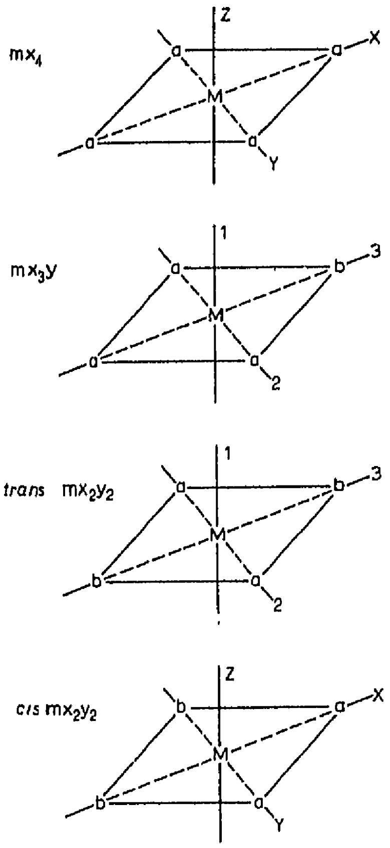


Fig. 2. Mössbauer spectrum of ferrocene at 4.2°K, $H = 0$, $H = 26$ kgauss (reproduced with permission from ref. 6).

In Table 1, q is the ligand charge, r approximates the center charge to nucleus distance and θ and ϕ are the usual azimuthal and longitudinal angles of spherical polar coordinates. After diagonalization in a principal axis system, one need consider only the summation over all ligands of the first three terms of Table 1. The results of such calculations, including evaluation of the asymmetry parameter η, are summarized in Fig. 3 for several different coordination polyhedra[14, 15] with coordination number varying from 4 to 8. It should be noted that for the case of $\eta = 1$, the concept of a sign to the "principal component of the electric field gradient tensor" ceases to have meaning since $\eta = 1$ implies

Square planar complexes



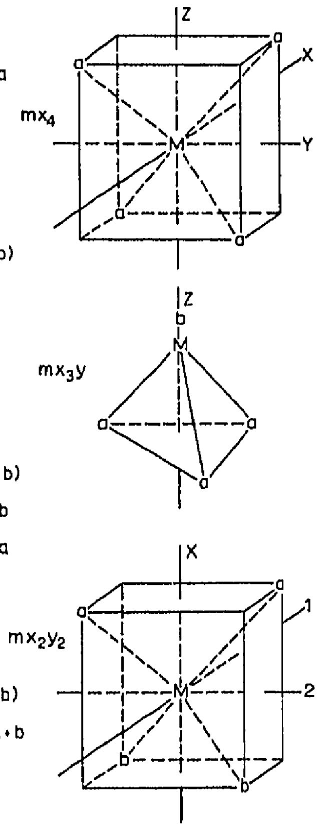
mx_4: $V_{zz} = -4a$; $V_{yy} = V_{xx} = 2a$; $\eta = 0$

mx_3y: $V_{11} = -(3a+b)$; $V_{22} = 3a-b$; $V_{33} = 2b$; $\eta = *$

trans mx_2y_2: $V_{11} = -2(a+b)$; $V_{22} = 4a-2b$; $V_{33} = 4b-2a$; $\eta = *$

cis mx_2y_2: $V_{zz} = -2(a+b)$; $V_{yy} = V_{xx} = a+b$; $\eta = 0$

Tetrahedral complexes

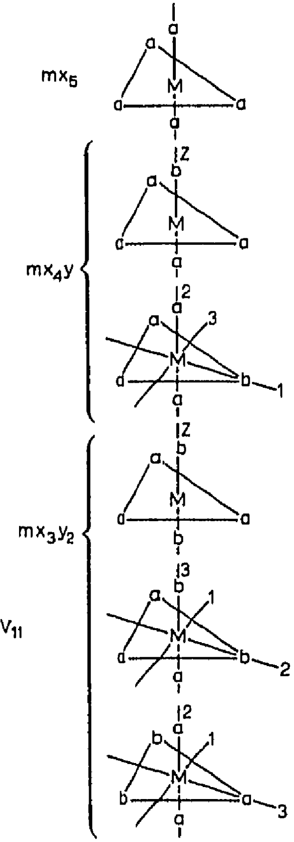


mx_4: $V_{zz} = V_{yy} = V_{xx} = 0 = \eta$

mx_3y: $V_{zz} = 2(b-a)$; $V_{yy} = V_{xx} = a-b$; $\eta = 0$

mx_2y_2: $V_{11} = 2(a-b)$; $V_{22} = 2(b-a) = -V_{11}$; $V_{xx} = 0$; $\eta = 1$

Trigonal bipyramid complexes



mx_5: $V_{zz} = a$; $V_{yy} = V_{xx} = -\frac{a}{2}$; $\eta = 0$

mx_4y:

$V_{zz} = 2b-a$; $V_{yy} = V_{xx} = \frac{a}{2} - b$; $\eta = 0$

$V_{11} = 2b - \frac{5a}{2}$; $V_{22} = 2a-b$; $V_{33} = \frac{a}{2} - b$; $\eta = *$

mx_3y_2:

$V_{zz} = 4b-3a$; $V_{yy} = V_{xx} = \frac{3a}{2} - 2b$; $\eta = 0$

$V_{11} = \frac{3a}{2} - 2b$; $V_{22} = b - \frac{3a}{2}$; $V_{33} = b$; $\eta = *$

$V_{11} = \frac{5b}{2} - 3a$; $V_{22} = 3a-2b$; $V_{33} = -\frac{b}{2}$; $\eta = *$

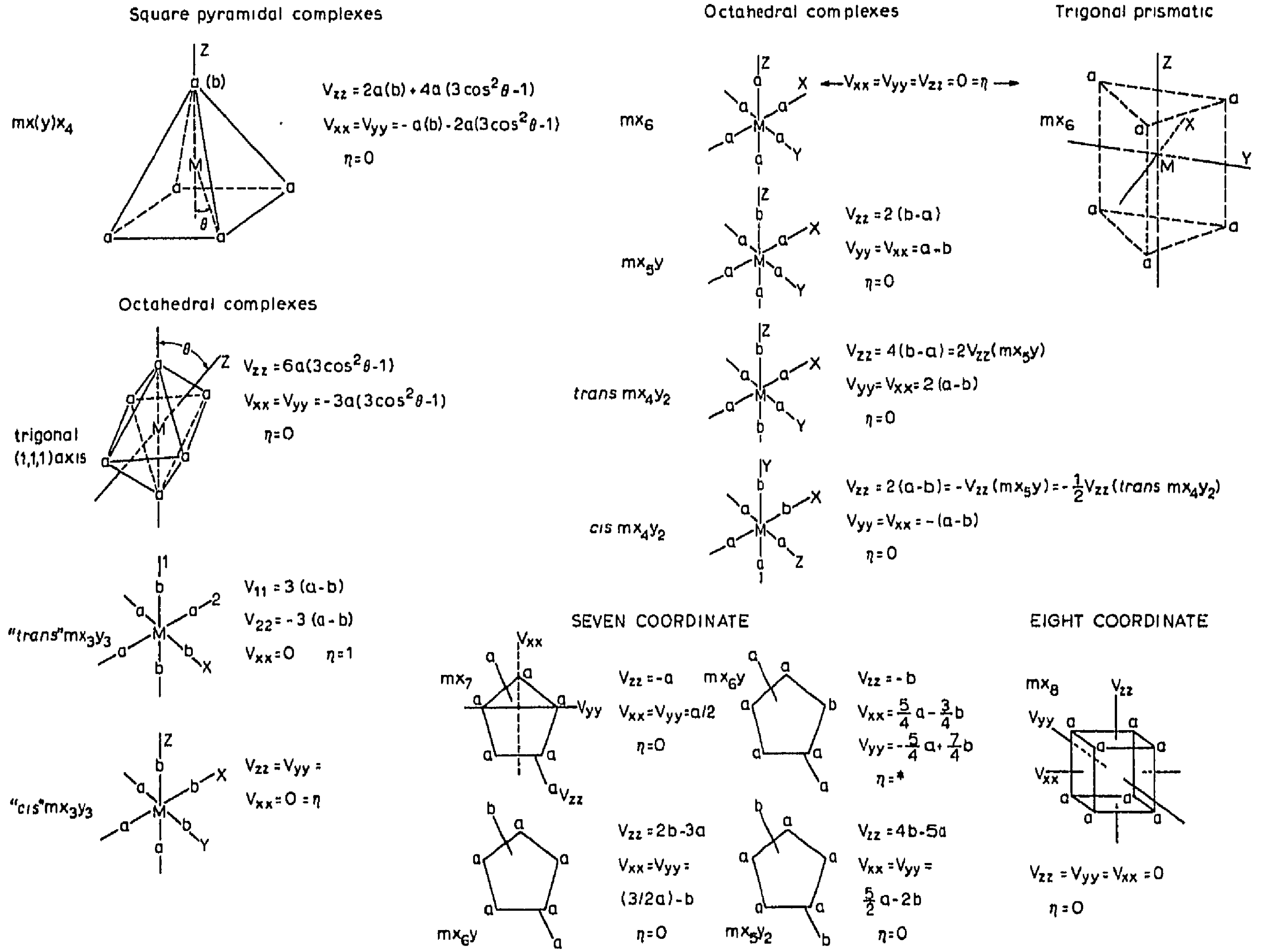


Fig. 3. Point charge calculations of diagonal elements of the electric field gradient tensor for various coordination polyhedra (reproduced by permission from refs. 14 and 15).

TABLE 1

Cartesian and spherical polar expressions for the elements of the electric field gradient tensor

$V_{xx} = q(3x^2 - r^2)r^{-5}$	$V_{xx} = q(3\sin^2\theta\cos^2\phi - 1)r^{-3}$
$V_{yy} = q(3y^2 - r^2)r^{-5}$	$V_{yy} = q(3\sin^2\theta\sin^2\phi - 1)r^{-3}$
$V_{zz} = q(3z^2 - r^2)r^{-5}$	$V_{zz} = q(3\cos^2\theta - 1)r^{-3}$
$V_{xy} = V_{yx} = 3qxyr^{-5}$	$V_{xy} = V_{yx} = 3qr^{-3}\sin^2\theta\sin\phi\cos\phi$
$V_{xz} = V_{zx} = 3qxzr^{-5}$	$V_{xz} = V_{zx} = 3qr^{-3}\sin\theta\cos\theta\cos\phi$
$V_{yz} = V_{zy} = 3qyzr^{-5}$	$V_{yz} = V_{zy} = 3qr^{-3}\sin\theta\cos\theta\sin\phi$

$V_{xx} = 0$ and $V_{yy} = -V_{zz}$. Thus there is no unique "Z" direction. The parameters a and b are charge-reciprocal cubic radii factors, i.e. $q_a < r_a^{-3} >$ etc., and are negative. In Fig. 3, $\eta =$ ✩ corresponds to the fact that the choice of axes is arbitrary until the relative magnitudes of a and b are established. Once this is done the V_{11}, V_{22}, V_{33} can be assigned V_{xx} etc. in accordance with eqn. (4).

With the aid of Fig. 3, we are now in a position to interpret the significance of sign designation for V_{zz}. For example, consider a regular *trans*-Ma_4b_2 octahedral system with the electric field gradient arising from the ligand charge distribution or metal valence shell covalence anisotropy induced by the distribution. The value of V_{zz} from Fig. 3 is $V_{zz} = 4b - 4a$. It is reasonable to assume that a more strongly bonding ligand (primarily sigma-donating in the present model) will have greater electron charge localization on the metal–ligand bond axis and correspond to a larger value of $q < r^{-3} >$. Thus assuming stronger sigma bonding and higher charge density along the unique b–M–b axis of the *trans* system, we have $b > a$. Since a and b are both negative, then the preceding expression for V_{zz} is *negative*. On the other hand a *trans* octahedral complex having stronger in-plane bonding ($a > b$) will show V_{zz} positive. The effects of π-bonding have not been specifically considered and are usually less important in the present context. However, strong in-plane π delocalization could, in principle, result in $V_{zz} < 0$. The foregoing analysis is applicable to the other coordination polyhedra of Fig. 3. However, ambiguities can result from the expressions for V_{zz} having different a and b coefficients when a and b are not significantly different. In any event, experimental results to be discussed subsequently generally verify the prediction $V_{zz} > 0$ for greater in-plane charge density while $V_{zz} < 0$ for greater axial density. To conclude, in all of the preceding, it is assumed that the coordination polyhedra are regular. Exceptions arise for significant deviation from regularity and these will be noted.

(d) Valence orbital contributions

The central atom valence orbitals correspond to continuous charge distributions whereas those of the ligands just discussed are relatively fixed along the bonding directions and at the equilibrium bond distances. Thus the calculation of the central atom electric field gradient tensor elements involves integration of the expressions of Table 1 over the appropriate orbitals. This is the same as finding the expectation values of the functions of Table 1 for the occupied valence orbitals. For this purpose, it is convenient to use the spherical polar forms of the tensor and hydrogenic wave functions. Thus in the case of

$d_z^2 = 4^{-1}5^{1/2}(3\cos^2\theta - 1)$

$$V_{zz} = \frac{5}{2\pi} q \langle r^{-3}\rangle_{nd} \int_0^{\pi}\int_0^{2\pi} (3\cos^2\theta - 1)^3 \sin\theta \, d\theta \, d\phi$$

$$V_{zz} = 4/7\, q \langle r^{-3}\rangle_{nd} \tag{14}$$

In the preceding, q is negative for an electron of charge $-e$ in the d_z^2 orbital and positive for a "hole" in this orbital. A complete array of such expectation values is given in Table 2 in units $q \langle r^{-3}\rangle$, where $\langle r^{-3}\rangle$ is the radial portion of the preceding integral for the orbital involved. The value of the V_{ii} for the real p orbitals will be useful in the discussion of tin systems while those for the d orbitals are of primary interest for iron complexes. The V_{ii} are, of course, zero for the spherically symmetric s orbital while the $\Sigma\, V_{ii}$ over all of the orbitals occupied in a half or completely filled manifold also vanishes.

TABLE 2

"Diagonal" elements of the electric field gradient tensor for hydrogenic orbitals

Orbital	$V_{xx}/q\langle r^{-3}\rangle$	$V_{yy}/q\langle r^{-3}\rangle$	$V_{zz}/q\langle r^{-3}\rangle$	η
p_x	+4/5	−2/5	−2/5	☆[a]
p_y	−2/5	+4/5	−2/5	☆
p_z	−2/5	−2/5	+4/5	0
d_{z^2}	−2/7	−2/7	+4/7	0
$d_{x^2-y^2}$	+2/7	+2/7	−4/7	0
d_{xy}	+2/7	+2/7	−4/7	0
d_{xz}	+2/7	−4/7	+2/7	☆
d_{yz}	−4/7	+2/7	+2/7	☆

[a] See text.

For later discussion it will be convenient to have the Z component of the electric field gradient for the t_{2g} orbitals with three-fold quantization. These are[16]

$$\begin{array}{lll} t_{2g}^0 = d_{z^2} & & V_{zz} = \frac{4}{7} q \langle r^{-3}\rangle \\ t_{2g}^+ = (2/3)^{1/2}\, d_{x^2-y^2} & -\,(1/3)^{1/2}\, d_{xz} & V_{zz} = \frac{-2}{7} q \langle r^{-3}\rangle \\ t_{2g}^- = (2/3)^{1/2}\, d_{xy} & +\,(1/3)^{1/2}\, d_{yz} & V_{zz} = \frac{-2}{7} q \langle r^{-3}\rangle \end{array} \tag{15}$$

In Table 2 the d_{xy}, $d_{x^2-y^2}$ and d_{z^2} orbitals have V_{ii} elements appropriately ordered with respect to eqn. (4) and $\eta = 0$ in each case. For the remaining orbitals, the "principal" axis would have to be redefined to satisfy the convention of eqn. (4). It is also important to point out that for the preceding discussion the molecular symmetry axis (if there is one) is assumed coincident with the principal axis of the electric field gradient. While often the case, this need not be so for a paramagnetic molecule in which a non-vanishing valence contribution is possible. For such paramagnetics, other information such as that determined from ESR or principal susceptibility measurements is necessary in order to deduce the orientation of these axes.

(e) Spin–orbit effects

To conclude this section, it is appropriate to discuss the effects of spin–orbit coupling on the valence contribution to the electric field gradient. In high-spin iron(II) salts exhibiting low-symmetry ligand field components (Δ), large relative to the spin–orbit coupling constant, ($\lambda_{\mathrm{FeII}} \approx -100$ cm^{-1}), spin–orbit effects are usually neglected. This neglect is, of course, less valid for iron(III) ($\lambda \approx -400$ cm^{-1}). To be specific, consider the case of an axially distorted octahedral low-spin iron(III) complex. Distortion along the threefold axis will lift the degeneracy of the $^2T_{2g}$ ground term giving ^2A and ^2E terms. A non-zero valence electric field gradient will then result from an uneven distribution of the hole in the t_{2g} manifold over the t_{2g}^{0}, $t_{2g}^{\pm}$ orbitals (eqn. (15)). In particular, if we consider a large[17] axial compression ($\Delta > 0$), then the hole will be located primarily in the degenerate $t_{2g}^{\pm}$ components of the excited ^2E and V_{zz} will be negative. (For $\Delta < 0$, the ground level is the $t_{2g}^{\pm}$ corresponding to an ^2A ground term, V_{zz} positive and approximately twice as large as for the case of $\Delta > 0$). The effect of spin–orbit coupling will be to mix the orbitals of the excited ^2E and ground ^2A to give three relatively well separated Kramers doublets with varying contribution of "hole".

Such mixing reduces the magnitude of V_{zz} and thus ΔE. Curves showing this reduction effect for various values of Δ/λ have been calculated by Gibb[17]. It should be emphasized, however, that the spin–orbit mixing does not change the sign of V_{zz}. Thus interpretations as to the nature of the orbital ground state based on signs of V_{zz} will be valid provided the distortion (Δ) is somewhat larger than λ. If the opposite is true, one is dealing with nearly pure spin–orbit states and correlation of the sign of V_{zz} with nature of distortion may be difficult if not ambiguous.

(ii) Magnetically perturbed Mössbauer spectra

(a) Iron-57

The angular dependence of the quadrupole transitions $|1/2 \pm 1/2\rangle \rightarrow |3/2, \pm 1/2\rangle$ (hereafter called the σ transition) and $|1/2, \pm 1/2\rangle \rightarrow |3/2, \pm 3/2\rangle$ (hereafter π) are $1 + 3/2 \sin^2\theta$ and $3/2\,(1 + \cos^2\theta)$ respectively[9] (where θ is the angle between the direction of γ-ray propagation and V_{zz}), with each transition having the same relative probability. In the absence of residual orientation effects or Karyagin asymmetry[18] (anisotropy of the recoil-free fraction), the foregoing expressions have equal values when averaged over the unit sphere. Thus symmetric quadrupole doublets are observed for polycrystalline tin-119*m* and iron-57 systems and the sign of quadrupole interaction is not determined. In single crystals this determination is possible since the π/σ intensity ratio changes considerably from a maximum of 3 for $\theta = 0°$ to 0.6 for $\theta = 90°$.

The magnetic perturbation technique of forcing a symmetric quadrupole doublet to yield an asymmetric pattern and thus allow determination of the sign of interaction was first proposed by Ruby and Flinn[19] and applied by Collins[6] to ferrocene. Ruby and

Flinn made theoretical calculations of the perturbed Mössbauer spectra of random powders in axial as well as transverse fields up to 84 kgauss. They found that for $\eta = 0$ and an initial quadrupole of the order of 2.0 mm/sec, the quadrupole lines became distinguishable at less than 50 kgauss applied. Examination of the center of Fig. 1 shows that the σ transition is four-fold degenerate while the π is two-fold. Hence for positive quadrupole interaction, application of a sufficiently large magnetic field will lift the nuclear degeneracy such that a "quartet" of transitions is observed at lower energy than the doublet corresponding to the magnetically split π. This is strictly true for an axially symmetric ($\eta = 0$) electric field gradient and roughly the case for values of $\eta \leqslant 0.6$. Such a result is seen in Fig. 2(b), where an apparent "triplet" is at negative velocity and doublet at positive[6]. The fact that a triplet instead of quartet is observed is due to the presence of all orientations (θ) of V_{zz} with respect to applied field. This would occur in a randomly oriented isotropic powder sample. Thus the central components of the quartet are severely overlapped in the "band" spectrum for a powder. This leads to the usual observation of a triplet. Negative quadrupole interaction will correspond to the observation of the triplet at positive velocity.

The contribution of a particular orientation of V_{zz} and applied field H to the observed powder spectrum is proportional to sin θ. Since sin θ is at a maximum for $\theta = 90°$, one would expect best resolution for the outer components of the σ transition and poorest for those of the π in view of their respective angular splitting factors (right side of Fig. 1). Hence relatively well resolved, narrow-width triplets and somewhat more broadened doublets are often observed for iron-57.

Inspection of the eigenfunction labels on the right of Fig. 1 shows that the components

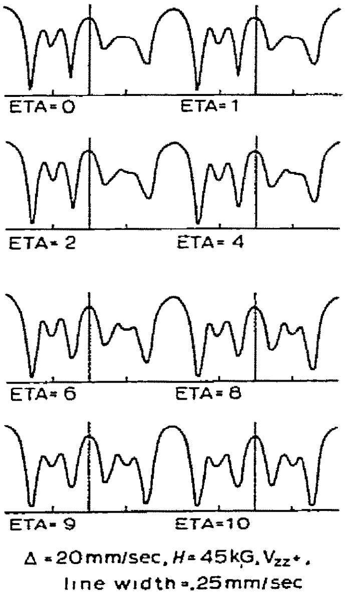


Fig. 4. Magnetically perturbed Mössbauer spectra as a function of increasing asymmetry parameter (reproduced by permission from ref. 20).

of the $|1/2, \pm 1/2>$ and $|3/2, \pm 1/2>$ states are not pure but are mixed to varying degrees. This is especially the case with the latter for departure from axial symmetry. The effect of a non-zero asymmetry parameter is shown rather clearly in the series of theoretical spectra[20] (longitudinal applied field) of Fig. 4. In the limiting case of $\eta = 1$, a symmetric spectrum of two triplets is observed. Corresponding to this there is no principal component of the electric field gradient tensor and the "sign" of such ceases to have meaning. It is also noteworthy that a non-zero asymmetry parameter does not have a significant effect on the perturbed spectrum until $\eta \approx 0.6$. Hence for iron-57 complexes, simple inspection is usually adequate for discernment of the velocity ordering of the triplet and doublet patterns and determination of the sign of ΔE. However, comparison with theoretical spectra is sometimes necessary in cases of poor resolution. To aid in such comparison, a Fourier transform "spectral sharpening" technique has been devised[21].

(b) Tin-119

Magnetically perturbed spectra of tin-119 systems are often more complicated than those of iron-57 in that typical triplet—doublet patterns are not always observed, for reasons which follow. The magnetic moments[22] of the ground ($I = 1/2$) and excited ($I = 3/2$) states of tin-119 are −1.041 and 0.67 nuclear magnetons respectively and are somewhat larger than the corresponding moments for iron-57 (0.0903 (ref. 23) and −0.1549 (ref. 24)). Further, the excited state quadrupole moment of tin-119 (−0.08 barn)[5] is smaller than that of iron-57 (varying values ranging from 0.18 to 0.30 barn). Thus with iron-57, the quadrupole splitting can still be the primary perturbation for relatively large applied fields while with tin the reverse may be true. For the latter an even more complicated situation arising from comparable magnetic (Zeeman) and quadrupole interactions is feasible. Hence observed spectra are not always interpretable by simple inspection. As an aid for interpretation Gibb[22] has calculated theoretical magnetically perturbed spectra for tin-119 as a function of ΔE, η and several values of applied field in both the longitudinal and transverse orientations. They allow for simple comparison for the purpose of determining the sign of ΔE and approximate magnitude of η. It is interesting to note that as for iron-57, a non-zero asymmetry parameter does not have significant effect on spectral shape until η is at least of the order 0.6. In conclusion, it is useful to point out two extreme cases arising in the perturbed spectra of tin-119 compounds. If the quadrupole interaction is zero or small, a symmetric Zeeman split spectrum consisting of two sets of triplets is observed for fields of the order 50 kgauss. When the quadrupole interaction is large ($\Delta E \simeq 3.5$–4 mm/sec) relative to applied field the σ transition often splits to a characteristic quartet while the π transition yields a broader doublet (assuming $\eta = 0$). A quartet at lower energy then implies $\Delta E > 0$, $V_{zz} < 0$.

(c) Effective magnetic fields

In addition to the sign of ΔE and magnitude of η, it is also possible to determine the effective magnetic field (H_{eff})from perturbed Mössbauer spectra. This is of considerable use in iron coordination chemistry in that H may be related to features of electronic structure such as oxidation and spin state as well as degree of covalency and nature of magnetic anisotropy. Measurement of effective magnetic fields also allows determination of the presence or absence of *intramolecular* antiferromagnetism in coordination systems that are otherwise magnetically dilute. This latter aspect will be considered in more detail when some specific exchange-coupled iron complexes are discussed.

The effective magnetic field H at a Mössbauer nucleus is related to the applied field (H_0) and internal hyperfine field (H_n) by

$$H_{eff} = H_0 + H_n \tag{16}$$

We are interested primarily in powder spectra of quadrupole split diamagnetic or rapidly relaxing paramagnetic systems. However, the cases of slow relaxation and pure Zeeman interaction are considered first. The following situations arise.

(1) $\Delta E = 0$, $H_n \neq 0$ (randomly oriented), $H_0 = 0$

In this instance the characteristic six-line Zeeman pattern (Fig. 5(a), (b))[25] of a magnetically ordered system is observed. This corresponds to the allowed transitions among the magnetically split $I = 1/2$ ground and $I = 3/2$ excited states with magnetic field relaxation time long relative to the nuclear Larmor precession frequency.

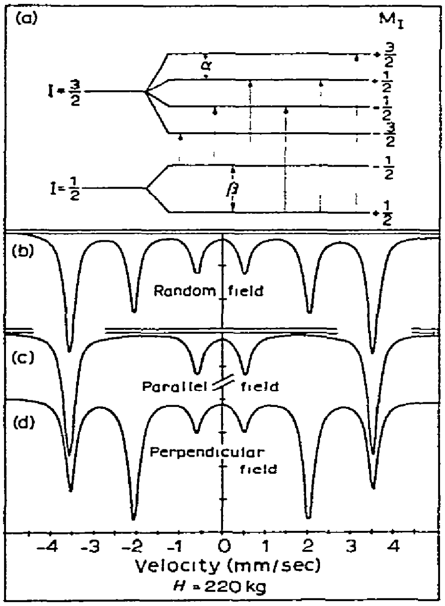


Fig. 5. Zeeman split spectra for zero quadrupole interaction (reproduced by permission from ref. 25).

(2) $\Delta E = 0$, $H_n = 0$, $H_0 \neq 0$ and parallel to the γ-ray

This situation corresponds to an effective magnetic field equal to the applied, and the result is the spectrum of Fig. 5(c). One sees that transitions 2 and 5 vanish owing to their $\sin^2\theta$ dependence ($\theta = 0$ between γ-ray propagation direction and H_0). The total Zeeman splitting of transitions 1–6 is $3\alpha + \beta$ and is, of course, proportional to the applied field. The quantities $\alpha = g_{3/2}\beta_N H$ and $\beta = g_{1/2}\beta_N H$ where $g_{3/2}$ and $g_{1/2}$ are the excited and ground state gyromagnetic ratios and β_N is the nuclear magneton. For iron-57, the ratio $\beta/\alpha = g_{1/2}/g_{3/2}$ has been determined using Mössbauer spectroscopy and has the value[24] −1.715. The ground state gyromagnetic ratio has been measured independently using NMR[23] and is 0.1828. Thus with the preceding values of α, β etc. and a known applied field, the total splitting $3\alpha + \beta$ is determined. In the case of the Mössbauer calibrant α-iron, the splitting is 10.66 mm/sec, corresponding[24] to H_n = 330 kgauss. Single-line ($\Delta E = 0$) absorbers such as $K_4Fe(CN)_6$ and TiFe alloy[26] exhibit spectra such as that illustrated in Fig. 5(c). Hence the perturbed Mössbauer spectra of such a system in conjunction with the internal field of α-iron can be used for calibration of superconductive magnet systems as well as velocity calibration.

(3) $\Delta E = 0$, $H_n = 0$, $H_0 \neq 0$ and perpendicular to the γ-ray

The comments for this case are similar to those for case (2), except that transitions 2 and 5 are intensified relative to 1, 3, 4 and 6 which are all expected to be weaker from their $1 + \cos^2\theta$ dependence (Fig. 5(d)).

Although the case $\Delta E \neq 0, H_n \neq 0, H_0 = 0$ with $H_n \gg \Delta E$ is important, it will be discussed in detail subsequently when some iron coordination systems exhibiting this behavior are considered. Two other situations of particular relevance to this paper are now included. Both of these involve application of an external magnetic field to a quadrupole split tin or iron system. However, the quadrupole perturbation is assumed to be larger than the magnetic interaction. Thus spectra like that of Fig. 2(b) are expected and for convenience examples with axial symmetry are discussed.

(4) $\Delta E \neq 0$, $H_n = 0$, $H_0 \neq 0$, $\Delta E \gg H_0$ and $H_{eff} = H_0$

This corresponds to the perturbed spectrum of a quadrupole split diamagnet or rapidly relaxing paramagnet at room temperature. Under these circumstances the Curie susceptibility is either zero or small while spin–lattice relaxation times are also small. Hence an externally applied magnetic field causes negligible magnetization and $H_{\text{eff}} \approx H_0$. The approximate value of H_{eff} is determined from the observed triplet splitting (Δ_t) for a spectrum such as Fig. 2(b), using the relation

$$H_{\text{eff}} = (\Delta_t/10.66)\,((3\alpha + \beta)/(2\alpha + \beta))\,330 \qquad (17)$$

where $3\alpha + \beta$ and $2\alpha + \beta$ are the theoretical doublet and triplet splittings respectively. Since[24] $\beta = 1.715\alpha$, eqn. (17) simplifies to

$$H_{\text{eff}} = (\Delta_t/10.66)\,(4.715/3.715)\,330 = 1.269\,\Delta_t \qquad (18)$$

Some brief comment about the relative magnitudes of the doublet and triplet splittings is in order. The theoretical values for these quantities differ. However, for the perturbed spectrum of an isotropic powder, the doublet to triplet splitting ratio is in practice nearly unity. This is due to the "band" nature of a powder spectrum with the greatest broadening usually occurring for the π transition. Thus the apparent doublet and triplet splittings are nearly equal.

(5) $\Delta E \neq 0, H_0 \neq 0, \Delta E > H_0, H_{eff} > H_0$

Paramagnetic systems at low temperature may exhibit the foregoing behaviour. Spin–lattice relaxation times are now longer and Curie susceptibility high. Thus a relatively small external field results in large magnetization. The effective field as measured by the triplet splitting is larger than the applied and can often be expressed as a Brillouin function of H_0, magnetic moment and temperature. A spectrum like that of Fig. 2(b) may still be observed or the triplet replaced by a resolved quartet. Finally, significant magnetic anisotropy will be evident from a triplet to doublet splitting ratio deviating from unity.

C. SOME EXPERIMENTAL ASPECTS

(i) Magnetic apparatus

Magnetic fields of the order 25 to 30 kgauss are usually required in order to obtain resolved perturbed spectra of iron-57 compounds. This is especially the case for diamagnetic compounds or for room temperature perturbed spectra where Curie-law susceptibilities are normally smaller. At very low temperatures for which Curie-law susceptibility and accompanying internal field may be large, relatively small (10–15 kgauss) applied fields often lead to resolved spectra. In view of the smaller ratio of excited to ground state magnetic moments, even larger ($\approx$ 50 to 60 kgauss) fields are necessary for tin investigations. These fields can be conveniently generated using superconducting solenoids and thus the need for liquid helium is apparent. Superconducting magnet–cryostat systems for these purposes have been discussed by Craig[27]. The calibration of superconductive magnetic systems can be achieved through the usual rotating coil Gaussmeter or Hall probe methods. An indirect and less expensive technique of calibration consists of determining the perturbed Mössbauer spectrum of a single line ($\Delta E = 0$) absorber such as $K_4Fe(CN)_6$ or TiFe alloy[26]. The total splitting of such spectra is directly proportional to the applied field.

(ii) Computer simulation of spectra

Most magnetically perturbed Mössbauer spectra are determined in axial (also called longitudinal) geometry for which the applied field H and direction of γ-ray propagation E_γ are parallel. Computations of theoretical powder spectra for transverse fields ($H \perp E_\gamma$) have been thought mathematically more difficult for some time although such calculations have been performed for tin-119 systems[22]. The only series of published theoretical spectra for iron-57 is that of Collins and Travis[20] for longitudinal fields using modified versions of the programs of Gabriel and Ruby[28]. However, a number of investigations to be discussed show that the typical triplet–doublet pattern observed in axial geometry is also the case for transverse powder spectra when $\eta = 0$.

(iii) Resolution of spectra

Among the factors influencing resolution of magnetically perturbed Mössbauer spectra the magnitude of line width and quadrupole splitting of the unperturbed spectra are of considerable importance. Fig. 6 shows a series[25] of perturbed spectra for relatively small quadrupole splitting as a function of increasing η. In these examples it is still possible to determine the sign of ΔE and approximate magnitude of η by inspection. With the large magnetic fields necessary to completely remove the degeneracy of the σ and π transitions, smaller quadrupole splittings result in extensive overlap of the split σ and π components making interpretation difficult. As a "rule of thumb", quadrupole splittings of the order 0.4 to 0.6 mm/sec ($\approx$ 3 Γ) are a necessity for observation of "useful" resolved spectra in the sense of determination of the sign of ΔE. Even then the magnitude of η may no longer be determined.

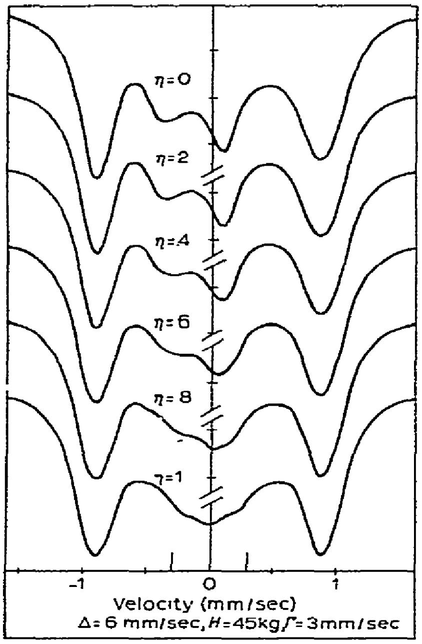


Fig. 6. Magnetically perturbed Mössbauer spectra as a function of increasing asymmetry parameter η (reproduced by permission from ref. 25).

The shape and resolution of perturbed spectra are also a function of distortions of the unperturbed spectrum. Distortions related to sample preparation and, in particular, residual micro-crystal orientation can be avoided by making the sample as isotropic as possible. The usual method of achieving this with solid samples is pulverization. Problems of orientation associated with liquid samples are more difficult to overcome as the freezing necessary prior to determination of the Mössbauer spectrum may result in non-random orientation. This is dramatically illustrated in the case of cyclobutadiene iron tricarbonyl[29] (liquid at room temperature), a compound whose molecular symmetry suggests $\eta = 0$. When filter paper was used as a matrix for the liquid complex apparent orientation was noted, in that the quadrupolar peaks were of unequal intensity. This had a significant effect on the perturbed spectrum. Instead of the triplet–doublet expected for $\eta = 0$, two doublets were observed at 26 kgauss. It should be mentioned that Karyagin asymmetry was not ruled out as a cause of the preceding asymmetry although it is not expected in a tetrahedral tricarbonyl. When the compound was adsorbed on dry silica gel and this powder pulverized, a symmetric unperturbed spectrum was observed while $\eta \approx 0$ for the perturbed spectrum. This technique is dangerous, however, in that interactions with the active sites of silica gel can cause changes in the chemical nature of the adsorbate.

The other distortion of importance in the resolution of perturbed Mössbauer spectra was alluded to in the preceding paragraph and cannot be eliminated by variation of sample preparation. This is anisotropy of the recoil-free fraction of Karyagin–Goldanskii asymmetry[18]. If the Mössbauer fraction is truly isotropic, the ratio of π to σ intensities will be unity in the absence of residual orientation effects. In the case of Karyagin asymmetry, the π to σ intensity ratio deviates from unity and is temperature-dependent, approaching one only at low temperatures. The effect of this asymmetry on perturbed iron-57 Mössbauer spectra has been considered in a theoretical study by Travis and Collins[30]. For small to intermediate η (0 to 0.5) the magnetically split σ and π transitions are still distinguishable as the triplet–doublet respectively even if Karyagin asymmetry is operative. However, for $\eta \approx 1$, calculated spectra show a triplet–doublet-type pattern while a symmetric triplet–triplet is expected. It should be emphasized that the foregoing theoretical observations have not been verified experimentally. In addition most perturbed spectra are determined with the absorber at 4.2°K. Thus the Karyagin effect is not expected to cause serious distortion at such temperatures since for the demonstrated examples[31, 32] of Karyagin asymmetry the π to σ intensity ratio is essentially unity at 4.2°K. Verification of Travis and Collin's theoretical results must await determination of the appropriate room-temperature perturbed spectra.

D. RESULTS OF MAGNETICALLY PERTURBED MÖSSBAUER STUDIES

(i) Iron compounds

(a) Iron salts

The most extensive series of magnetically perturbed Mössbauer spectra of simple iron(II) salts are those of Grant et al.[33]. Many of the salts order at 4.2°K and thus most of the perturbed spectra were determined at room temperature in fields from 30 to 55 kgauss. The compounds studied are given in Table 3 along with the signs of V_{zz} and the approximate magnitude of η. Compounds (1)–(4) show low-temperature quadrupole splittings varying from nearly one and a half to twice those of (6) and (7) and correspond to orbitally non-degenerate ground states.

In a theoretical analysis of the temperature dependence of ΔE of compounds (1) through (5) and (7), Ingalls[34] has assigned orbital ground state wave functions for which the predicted signs of V_{zz} agree with those of Table 3 except for compound (7). Thus, for example, the orbital ground state of $\mathrm{Fe\,SiF_6 \cdot 6H_2O}$ is ^2A corresponding to a trigonal compression and V_{zz} negative. In Ingalls' analysis, the predicted ground state for compound (7) is d_{xy}. However, the smaller ΔE and $V_{zz} < 0$ for this are more consistent with an orbital

TABLE 3
Perturbed Mössbauer results for some simple ferrous salts

Compound	V_{zz}	η
(1) $FeSO_4$	+	0
(2) $FeSO_4 \cdot 7H_2O$	+	0
(3) $FeCl_2 \cdot 4H_2O$	+	0
(4) $FeSiF_6 \cdot 6H_2O$	−	0
(5) $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	+	0.7
(6) $FeCO_3$	+	0
(7) $FeC_2O_4 \cdot 2H_2O$	−	0.7

doublet ground level composed of linear combinations of d_{xz} and d_{yz} as might result from a tetragonal elongation.

The carbonate, (6), is best interpreted in terms of elongation along the three-fold axis of the octahedron. The ground state is thus an orbital doublet ($t_{2g}^{\pm}$) corresponding to a smaller ΔE and V_{zz} positive as observed. Ono and Ito[35] have analyzed the Zeeman spectrum of ordered $FeCO_3$ at 4.2°K with results in agreement with the perturbation study of Grant et al.[33]. These studies are clear-cut indications of the applicability of a simple crystal field approach to the interpretation of perturbed Mössbauer spectra of ferrous salts.

The compound $FeSiF_6 \cdot 6H_2O$ does not order at 4.2°K and Johnson[36] has made a more detailed analysis of its magnetically perturbed spectra at 4.2°K and lower. For single crystals oriented such that the applied field is parallel to the trigonal axis, the π transition was observed as a well defined doublet while the σ collapsed to a broad peak. This accords with the angular splitting functions given in Fig. 1. When the external field is applied normal to the trigonal axis, spectra similar to those of the powder are observed. Such a result is expected in view of the greatest weight to the $\theta = 90°$ orientation of microcrystals. The effective fields determined from the powder spectra are of the order of three to four times the applied field while the room temperature spectrum of $FeSiF_6 \cdot 6H_2O$ shows nearly equal effective and applied fields. The importance of larger susceptibility and longer spin–lattice relaxation time at low temperatures are apparent.

The compound $Fe(NH_4)_2(SO_4)_2 : 6H_2O$ (compound (5) of Table 3) contains the hexa-aquo ferrous ion in a rhombic crystal field and is rather atypical in that both η and ΔE are highly temperature-dependent. Analysis of the temperature dependence of ΔE in powders has led Ingalls[34] to assign the orbital ground state as d_{xy}. In another investigation of single crystals, Ingalls et al.[37] have determined the ratio of π to σ intensity at 300 and 4.2°K. They conclude that V_{zz} is positive while η varies from ≈ 0.7 at 300°K to 0.3 at 4.2°K. The room-temperature perturbed spectrum of Grant[38] agrees with the preceding intensity study. Collins and Travis[20] have determined the perturbed spectrum of compound (5) at 4.2°K and observe a resolved quartet at negative velocity and doublet at positive. Their results also agree with the foregoing intensity results.

It is worthwhile to point out that the large variation of ΔE for compound (5) (1.7 mm/sec at 300°K to 2.7 at 4.2°K) is not explained by the variation of η. A value $\eta = 1$

will increase ΔE by only about 11% and in the present case the variation of η is in the wrong direction. Ingalls et al.[37] have found that a model involving temperature-dependent rhombic crystal field splittings reasonably explains the observed variation of ΔE.

Magnetically perturbed Mössbauer spectroscopy can be applied to the problem of the type of distortion in a given coordination polyhedron. A good example of this is part of a study of some tetrahedral iron(II) salts by Edwards et al.[39]. In particular, the perturbed spectra of $[N(CH_3)_4]_2FeCl_4$ and [N,N'-di-CH_3-4,4'-bipyridine] $FeCl_4$ were determined in fields of the order of 30 kgauss at 80 and 4.2°K respectively. Two simple distortions for the $FeCl_4{}^{2-}$ tetrahedron are compression or elongation with respect to the two- or three-fold axes. For the latter, the degeneracy of the ground e_g levels is not removed[16] and hence no quadrupole splitting results. A two-fold elongation will lift this degeneracy to destabilize the d_{z^2} orbital resulting in the $d_{x^2-y^2}$ orbital as ground state and V_{zz} positive. In the preceding salts V_{zz} is negative and consistent with a compression and ground state d_{z^2} orbital. Similarly (two-fold axial) compressed tetrahedra are observed in nearly all of the reported single-crystal X-ray studies[40] of $FeCl_4{}^{2-}$ salts.

For the higher-temperature perturbed spectrum of $[N(CH_3)_4]_2FeCl_4$, the internal field is only $\approx$ 20 kgauss, in accord with small magnetization at 80°K. At 4.2°K both of the preceding salts show small effective fields. This is attributed to components of the internal field normal to the distortion axis and of sign opposite to that of the applied field.

An interesting study of the substitution of iron(II) impurities for the metal ion at the tetrahedral sites of cubic ZnS (zinc blende) and hexagonal ZnS (Wurtzite) has been made by Gerard et al.[41]. The perturbed spectra (30 kgauss, 4.2°K) for the ferrous impurity in both zinc blende and Wurtzite showed V_{zz} positive, indicating a $d_{x^2-y^2}$ ground state and elongation along the two-fold axis at tetrahedral sites. In this study large internal fields were not induced by the 30 kgauss applied; however, no reason for this was suggested.

Simple iron(III) salts are typically high-spin and the ground term is ^6A. Thus zero or small and nearly temperature-independent quadrupole effects are usually observed[42]. Obenshain et al.[43] have studied the perturbed spectra of polycrystalline samples of the octahedral hydrate $FeNH_4(SO_4)_2 \cdot 12H_2O$. This material shows a single broad Mössbauer absorption to as low as 1.8°K (i.e. $\Delta E \approx 0$) and only orders[44] at 0.04°K. Thus perturbed spectra similar to those discussed in case (2) (p. 49) and shown in Fig. 5(c) are observed. Axial fields varying from 2 to 24 kgauss were applied with the temperature varying from 4.2 to 1.8°K. One purpose of this investigation was to study the effect of variation of H/T on line widths and intensities for the components of a pure Zeeman spectrum. At large H/T, a four-line hyperfine split spectrum (lines 2 and 5 vanish in the axial field) was observed. At smaller H lines 1 and 6 broaden and all but vanish while the centermost peaks 3 and 4 are only slightly affected.

A useful study[45] and extension of the point-charge approach to a point-multipole model of the electric field gradient has been achieved in a magnetically perturbed Mössbauer investigation of the normal cubic spinels $ZnFe_2O_4$ and $CdFe_2O_4$. In these compounds, the ferric ions occupy octahedral "B" sites while the zinc and cadmium fill tetrahedral "A" sites. Although the quadrupole splittings of these systems are small, the room-temperature perturbed spectra are sufficiently resolved to allow unequivocal determination of V_{zz} as negative. In both spinels, using accurate crystallographic data and a rapidly converging lattice summation technique, the electric field gradient at the octahedral sites is calculated. The primary results are that the point-charge contribution to V_{zz} is positive in $ZnFe_2O_4$ and near zero in $CdFe_2O_4$. The dominant contribution to the electric field gradient originates in the dipole moments of the oxygen ions and is negative.

Some interesting investigations of spin–spin relaxation in octahedral iron(III) were carried out as part of magnetically perturbed Mössbauer studies of $FeCl_3 \cdot 6H_2O$. The exact coordination of this system is not certain. In one perturbation study[46], $Fe(H_2O)_4Cl_2^+$ is assumed, while in another the $Fe(H_2O)_6^{3+}$ ion[47]. In any event, the environment is sufficiently distorted as to result in significant zero-field splitting of the iron(III) sextet. The zero-field splitting parameter D is apparently positive[48] as line-width asymmetry (Γ_-/Γ_+) of the small quadrupole increases with increasing temperature. This is believed to correspond to occupation of the more slowly relaxing $m_s = \pm 3/2$ and $\pm 5/2$ Kramers doublets relative to sole population of the rapidly relaxing $m_s = \pm 1/2$ at 4.2°K. Since it is the lower-energy transition that broadens with increasing temperature, the foregoing investigators' *assumption*, that H_n is relaxing parallel to V_{zz}, implies V_{zz} negative, i.e. it is the π transition that is undergoing the temperature-dependent broadening.

While it has not been demonstrated directly, the overall behavior of $FeCl_3 \cdot 6H_2O$ does appear most consistent with V_{zz} being negative. In particular, application of an external field at higher temperatures where the $m_s \pm 3/2$ and $m_s \pm 5/2$ Kramers doublets are significantly populated results in components of internal field fluctuating normal to V_{zz}. Under these circumstances the σ transition (at higher energy if V_{zz} is negative) is expected to broaden[49]. This is observed to be the case as the spectrum initially becomes symmetric for smaller fields. Eventually the sense of line-width asymmetry is reversed for larger applied fields. In conclusion, it is important to the preceding studies that the sign of V_{zz} in $FeCl_3 \cdot 6H_2O$ be determined directly, perhaps using the single-crystal orientation technique. Only then can one be certain of the orientation of the fluctuating internal field relative to the principal axis of V_{zz}.

As part of a general investigation of the hyperfine interactions in tetrahedral iron(III) salts, Edwards and Johnson[50] have determined the magnetically perturbed spectra of $[N(CH_3)_4]FeCl_4$ (1), $[ArPh_4]FeCl_4$ (2), $[N(C_2H_5)_4]Fe(NCO)_4$ (3), $[N(C_2H_5)_4]FeCl_4$ (4) and $[N(C_2H_5)_4]FeBr_4$ (5). Compounds (1) – (3) remain paramagnetic to temperatures of the order of 2°K while (4) and (5) order near 4°K. For (1) and (2) the quadrupole splittings are nearly zero and six-line spectra such as that of Fig. 5(d) are observed in transverse fields. It is interesting to note that relatively small applied fields (e.g. only 7.5 kgauss for $[N(CH_3)_4]FeCl_4$ were necessary in order to obtain fully resolved hyperfine spectra. It was found possible to correlate the magnitude of internal field H_n with degree of covalency of coordinated ligand, as shown by the following series of increasing covalency: $FeCl_4^-$ (470 kgauss), $FeBr_4^-$ (420 kgauss), $Fe(NCO)_4^-$ (390 kgauss).

The compound $[N(C_2H_5)_4]Fe(NCO)_4$ is quadrupole split ($\Delta E = 0.86$). Its perturbed spectrum is like that of Fig. 5(d) except that the center of the inner four transitions is shifted toward lower energy relative to the center of transitions 1 and 6 because of the non-zero quadrupole. For axial symmetry this shift may be related to the angle θ between H_n and the principal axis of V_{zz} by the relation

$$S_1 - S_2 = -\Delta E(3\cos^2\theta - 1) \tag{19}$$

where S_1 is the separation of transitions 1 and 2 and S_2 that of transitions 5 and 6. Thus for pure Zeeman splitting, as in Figs. 5(a)–(d), $S_1 - S_2 = 0$. A graph of $S_1 - S_2$ versus θ along with an exemplary Mössbauer spectrum is given in Fig. 7. In this figure, it is assumed that the Zeeman splitting is a significantly greater perturbation than the quadrupole interaction. It is seen that for the $S_1 - S_2 \leqslant \Delta E$, two values of θ corresponding to opposite signs for V_{zz} are possible and the angle θ cannot be determined from the six-line combined interaction spectrum alone. An independent measure of the sign of V_{zz}, e.g. from the magnetically perturbed spectrum at a temperature where the material is paramagnetic or a study of the π/σ intensity in a single crystal, enables unique determination of the angle θ from the Zeeman–quadrupole spectrum. For $[N(C_2H_5)_4]Fe(NCO)_4$, $S_1 - S_2 \approx -1.2$ mm/sec and is of absolute value greater than ΔE. Inspection of Fig. 6 shows that V_{zz} is therefore positive and closer to being parallel to H_n. In a point-charge approach a positive V_{zz} corresponds to elongation of the $Fe(NCO)_4^-$ tetrahedron along the two-fold axis.

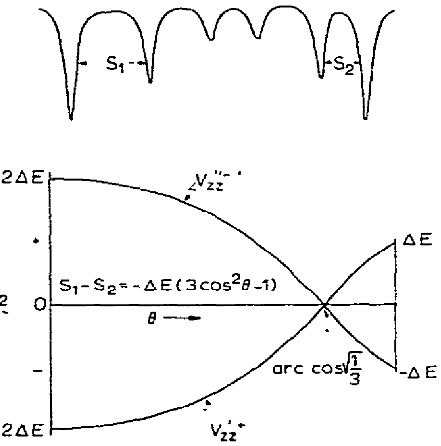


Fig. 7. The parameters of a combined Zeeman–quadrupole split spectrum.

(b) Iron(II) and iron(III) organo-metallic complexes–low-spin d^6

Consistent interpretation of magnetically perturbed Mössbauer spectra of low-spin iron(II) complexes has been possible using the point-charge approach. In consideration of covalency, the usual assumption is that sigma-donation is more important than π-donation or delocalization. However a series of compounds[51–53] in which all of these effects should be considered to some extent is given in Table 4. All of the compounds are pseudo-octahedral and approximately axially symmetric *trans* D_{4h} or *cis* C_{2v}. They show typical triplet–doublet spectra of varying degrees of resolution and H(applied) $\approx$ H(effective), as expected for diamagnets. For compound (1) it is reasonable to assume that the in-plane isocyanide sigma bonding is stronger than that of the axial chlorine leading to the prediction of V_{zz} and therefore ΔE positive in a point or donated charge approach. The corresponding *cis* complex (2) should have ΔE negative (Fig. 3) and about half as large as that

TABLE 4
Perturbed Mössbauer results for some low-spin ferrous complexes

Complex	ΔE (300°K)	Ref.
(1) *trans*-$FeCl_2(p\text{-}CH_3O \cdot C_6H_4 \cdot NC)_4$	1.55	51
(2) *cis*-$FeCl_2(p\text{-}CH_3O \cdot C_6H_4 \cdot NC)_4$	−0.83	51
(3) *trans*-$FeCl_2$ (1,2-bis-diethylphosphino)$_2$	1.29	52
(4) *trans*-$Fe(CN)_2(C_2H_5 \cdot NC)_4$	−0.60	52
(5) *trans*-$FeH(p\text{-}CH_3 \cdot O \cdot C_6H_4 \cdot NC)$ (1,2 bis-diethylphosphino)$_2$	−1.14	53
(6) $Na_3[Fe(CN)_5NH_3] \cdot H_2O$	0.67	52
(7) $K_3[Fe(CN)_5H_2O] \cdot 7H_2O$	0.80	52

observed for (1). Compound (3) has the same sign for ΔE as (1) but of slightly smaller magnitude. This suggests a smaller difference in sigma bonding strength between the axial chlorine and in-plane phosphorus chelates compared with that in the preceding *trans* isocyanide. However, back-donation via π delocalization to empty d orbitals on the phosphorus atoms of the phosphino chelate might also be invoked to explain the decreased ΔE of (3) relative to that of (1) and such π effects cannot be ignored. In compounds (4) and (5) the axial sigma bonding is now stronger than in-plane (i.e. V_{zz} negative) although less so in the case of (4), for which ΔE is small. Compounds (6) and (7) are of the Ma_5b type, for which it is seen from Fig. 3 that $\Delta E(Ma_5b) = -\Delta E(cis\text{-}Ma_4b_2)$. Thus the fact that ΔE of compounds (6) and (7) is $\approx -\Delta E(2)$ indicates that cyanide ion and aryl isocyanides are roughly comparable as ligands. The positive splittings of (6) and (7) indicate stronger in-plane bonding, as might be expected if these are viewed as being formed by replacing one CN^- of the hexacyano by a weaker (sigma-wise) NH_3 or H_2O. In conclusion, Clark et al.[124] have recently proposed a general but relatively simple molecular orbital approach to the correlation of the quadrupole splitting and stereochemistry of tin(IV) compounds. The extension of this treatment to low-spin iron(II) complexes has been outlined[124] and should serve as a useful addition to previous semiquantitative molecular-orbital approaches.

Sodium nitroprusside, $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ is a low d^6 system for which π-delocalization is important in explaining the Mössbauer behavior. Its quadrupole splitting ($\approx$ 1.73 mm/sec) is positive and $\eta \approx 0$ as determined magnetically by Grant[38] for the undiluted solid at 11°K. Oosterhuis and Lang[54] obtain the same results for the perturbed spectrum of a frozen aqueous solution in a transverse field of 29 kgauss. Single-crystal studies[4] of the angular variation of π/σ transition intensity also show V_{zz} positive. The foregoing results are in part explicable in terms of strong (π) axial delocalization from the metal d_{xz} and d_{yz} orbitals to the nitrosyl group. However, the quadrupole splitting of $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ is of the same sign but greater than twice those for the pentacyanides (6) and (7) of Table 4. This indicates that the strong in-plane sigma donation by the cyanide and axial delocalization by the nitrosyl are synergistic in producing a large positive ΔE.

The perturbed Mössbauer spectrum of the pseudo-octahedral $[Fe(terpyridine)_2](ClO_4)_2$ have been determined[55] in order to interpret the unusually large ΔE ($\approx$ 3.3 mm/sec) of the corresponding low-spin iron(III) complex. In $[Fe(terpyridine)_2](ClO_4)_2$, the tridentate terpyridine coordinates in such a manner that the central pyridine nitrogens are most strongly bound. The resulting overall symmetry is approximately D_{2d} with a unique central nitrogen–iron–central nitrogen axis of strong sigma bonding. The perturbed spectra at 300 and 4.2°K in transverse and axial fields respectively correspond to V_{zz} negative and $\eta = 0$, as expected for an axially symmetric compression. As will be discussed subsequently, the sign of V_{zz} is also negative for $[Fe(terpyridine)_2](ClO_4)_3$ and, in fact, the valence contribution to V_{zz} is negative, as calculated from the EPR data for this complex. The large ΔE of this system is thus attributed to an additive covalence anisotropy contribution to the total electric field gradient of sign and magnitude the same as those found for $[Fe(terpyridine)_2](ClO_4)_2$. The possibility of using the Mössbauer data for the low-spin ferrous complex to estimate the magnitude and sign of covalence anisotropy contribution to ΔE in the corresponding low-spin ferric complex also seems reasonable from other perturbed Mössbauer studies. Pairs such as $[Fe(bipyridine)_3](ClO_4)_2$ (V_{zz} negative and $\eta \approx 0$ from H(transverse) $\approx$ 20 kgauss at 300°K) and $[Fe(bipyridine)_3](ClO_4)_3$ (V_{zz} positive and $\eta = 0$) have ΔE values such that when splitting of the ferrous system is subtracted from that of the ferric the result obtained is in good agreement with that calculated as the valence contribution for the ferric using EPR data[56].

The magnetically perturbed Mössbauer spectrum of the biologically important ferrous cytochrome c has been determined by Lang et al.[57] at 4.2°K. This is a pseudo-octahedral low-spin d^6 system with both axial and in-plane nitrogen coordination. The observed perturbed spectrum at H(applied) = 25.7 kgauss (transverse) corresponds to V_{zz} positive ($\Delta E = 1.17$ mm/sec) in accord with stronger in-plane bonding by the heme moiety. The spectrum appeared as a relatively sharp triplet at negative velocity and a broader triplet at positive, indicating a large non-zero asymmetry parameter. Thus the in-plane Fe–N bonds may not all be equivalent.

An interesting group of low-spin iron(II) compounds in which η varies has been studied by Dale et al.[58]. The compounds investigated are phthalocyanine $Fe(pyridine)_2$ ($\Delta E = +1.96$ mm/sec, $\eta \approx 0$); $Fe(1,2\text{-cyclohexanedioxime})_2(imidazole)_2$ ($\Delta E = 1.30$ mm/sec, η large) and $Fe(1,2\text{-cyclohexanedioxime})_2(NH_2)_2$ ($\Delta E = +1.72$ mm/sec, η large). The bis-pyridine complex has been used in connection with model studies of the prosthetic groups of low-spin heme systems such as the previously discussed cytochrome c. Similarly, V_{zz} is positive, corresponding to stronger in-plane bonding by the phthalocyanine relative to axial pyridine and η is clearly close to zero. The *trans*-imidazole–oxime system also appears to have V_{zz} positive although a well resolved triplet–doublet spectrum is not observed owing to the large η and smaller ΔE in this compound. Finally, the ammonia-substituted complex exhibits a spectrum quite similar to that of ferrous cytochrome c, i.e. V_{zz} positive and η large (~ 0.5–0.6).

Low-spin d^7. There are relatively few stable low-spin d^7 or formally iron(I) compounds. However, for those that exist, their magnetically perturbed Mossbauer spectra have been quite useful in interpretation of electronic structure. One such complex contains the $[Fe(CN)_5NO]^{3-}$ ion ($\Delta E = 1.25$ mm/sec) obtained by reduction of sodium nitroprusside in aqueous solution. Its Mössbauer spectrum has been determined for frozen aqueous solutions and compared to similar spectra of $[Fe(CN)_5NO]^{2-}$. As previously,discussed, the latter ion shows V_{zz} positive, $\eta \approx 0$, with quadrupole splitting resulting from covalence anisotropy between (d_{xz}, d_{yz}) and d_{xy}. In a transverse field of 29 kgauss, Oosterhuis and

Lang[54] observed V_{zz} negative and $\eta \leqslant 0.5$ for $[Fe(CN)_5NO]^{3-}$. From the molecular orbital calculation of Manoharan and Gray[59] for the nitroprusside ion and the measured g values of $Fe(CN)_5NO^{3-}$, the additional electron of the latter ion is believed to reside in an antibonding π molecular orbital of primarily nitrosyl character. In addition, the EPR spectrum reflects axial symmetry. Thus, using the coefficients of the preceding molecular orbital and assuming the molecular symmetry and principal axes to coincide, Oosterhuis and Lang calculated ΔE and obtained good agreement with the observed value.

The other low-spin d^7 complex for which there are detailed Mössbauer data is the five-coordinate nitrosyl-iron-bis-(N,N-diethyldithiocarbamate) system investigated by Johnson et al.[60]. The quadrupole splitting, 0.89 mm/sec at 4.2°K, is positive ($\eta = 0$) as determined from perturbed spectra in transverse fields ranging from 15 to 30 kgauss and at temperatures as low as 1.5°K. This complex is more complicated than the preceding pentacyano system in that bonding electrons are thought to make a sizeable contribution to ΔE. In this circumstance the nature of the orbital ground state cannot be unambiguously inferred from simple correlation with the observed sign of V_{zz}. In fact, computer analysis of the perturbed Mössbauer spectra using hyperfine interaction parameters obtained by EPR showed best agreement between calculated and observed spectra for a d_{z^2} ground state corresponding to V_{zz} negative. The authors assumed that this was the correct orbital ground state with the observed positive V_{zz} due to lattice and bonding electron contributions. However, no analysis of these effects was given.

The temperature dependence of the effective magnetic field as determined from the perturbed spectrum of the foregoing dithiocarbamate was helpful in demonstrating the low-spin d^7 nature of this system. In particular, it was found possible to fit the variation of effective field (H_{eff}) as a function of temperature and applied field (H_0) using the relation

$$H_{\text{eff}} = H_n B_S(uH_0/kT) - H_0 \tag{20}$$

where H_n is the saturation value of internal field and $B_S(uH_0/kT)$ is a Brillouin function of the magnetic moment corresponding to spin S. A unique fit was found[60] for $S = \frac{1}{2}$ such that

$$B_{\frac{1}{2}}(uH_0/kT) = \tanh\,(uH_0/kT) \tag{21}$$

and the value of H_n obtained is -110 ± 5 kgauss. The calculated[61] free ion values of H_n for $S = 5/2$ (iron(III)) and $S = 2$ (iron(II)) are -630 and -550 kgauss respectively, corresponding to fields per unpaired electron of 126 and 137.5 kgauss. Thus the foregoing value of -110 kgauss appears quite reasonable for an $S = \frac{1}{2}$ low-spin d^7 system.

Triplet d^6. Most of the known triplet iron(II) complexes exhibit small quadrupole effects and are not readily investigated using the magnetic perturbation technique. For example, Konig and Kanellakopulos[62] have studied the perturbed spectrum of the ^3A system Fe(phenanthroline)$_2$(oxalate)$\cdot 5H_2O$ at 4.2°K using longitudinal fields of 20 and 40 kgauss. The quadrupole splitting of this system (0.24 mm/sec at 4.2°K) is sufficiently small that the perturbed spectrum is essentially a symmetric pattern from which the sign of V_{zz} is not unambiguously determined.

Ferrous phthalocyanine is a square-planar triplet iron(II) system which shows large splitting ($\Delta E = 2.70$ mm/sec) at 4.2°K and has been studied magnetically by Dale et al.[63]. Perturbed spectra in transverse fields of 30 kgauss were determined at 4.2 and 100°K in an effort to deduce the orientation of the molecular symmetry axis with respect to the magnetic symmetry axis and principal axis of the electric field gradient tensor. The primary results are that the principal and molecular symmetry axes coincide and are normal to the symmetry axis of magnetic properties which lies essentially in the xy plane of the molecule. Although V_{zz} is positive and $\eta = 0$, it was concluded that these observations cannot be simply correlated with any of four possible triplet configurations. This results from the fact that covalency effects are important in the molecule and, in fact, the valence electric field gradient arising from any one of the four non-bonding triplet ground states is thought to be outweighed by that due to covalence anisotropy and bonding electrons.

High-spin d^6. A relatively small number of high-spin iron(II) complexes have been investigated using magnetically perturbed Mössbauer spectroscopy. In some of these, there still remain problems of interpretation. For example, the pseudo-octahedral bis(phenanthroline) systems $\mathrm{Fe(phen)_2Cl_2}$ and $\mathrm{Fe(phen)_2(N_3)_2}$ have been studied[64] at 4.2°K and room temperature[65]. In the liquid helium studies axial fields of about 10 kgauss were all that was necessary to result in well resolved triplet—doublet patterns while for room temperature investigation, fields of about 40 kgauss were required to obtain comparable resolution. In all of these studies V_{zz} is negative and has axial symmetry. Two simple possibilities arise for the symmetry of the iron in the phenanthroline systems, *trans*-D_{4h} and *cis*-C_{2v}. Although no single-crystal studies have been performed, many other data apparently exclude the case of *trans*-monodentates in these complexes[66, 67]. Thus with chloride or azide *cis*, one has a unique N—Fe—N axis corresponding to a tetragonal compression. The orbital ground state would then be a singlet composed primarily of the non-bonding metal d_{xy}. There is a wealth of evidence, e.g. from the temperature dependence of powder susceptibility[68] and especially the large quadrupole splittings[69] of these systems to support an orbitally non-degenerate (^5B) ground state separated from ^5E by an axial splitting of about 700 to 800 cm^{-1}. However, a d_{xy} ground state corresponds to V_{zz} positive, opposite to what is observed. The fact that V_{zz} is negative may indicate that bonding electrons, e.g. those sigma-donated to the metal d_{z^2} orbital, play the dominant role in determining the sign of V_{zz} and one cannot determine the orbital ground state by correlation with the observed sign of V_{zz}. If such is the case, it is then reasonable to assume that the molecular symmetry and principal axes coincide.

An alternative interpretation of the results for the preceding bis-phenanthroline compounds involves a mixed ground singlet of the form $\psi = \alpha \mid xy > + \beta \mid yz > + \gamma \mid xz >$ where the coefficients α, β and γ are real[70]. For a well isolated singlet of this form, the magnitude of ΔE will be appropriate to an orbital singlet and constant[64] for all values of α, β and γ such that $\alpha^2 + \beta^2 + \gamma^2 = 1$. However, the asymmetry parameter η and sign of V_{zz} will vary from 0 to 1 and V_{zz} negative to positive depending on the relative values of

α, β and γ. Such mixing might possibly occur from covalency effects and an additional rhombic component to the ligand field. However, there is some argument as to whether this approach is valid, since spin–orbit coupling is neglected[71, 72].

A final explanation of the negative V_{zz} in the bis(phenanthroline) systems is that the primary symmetry is closer to D_3 than C_{2v}-tetragonal. The precursor tris(phenanthroline) systems have approximately D_3 symmetry and are trigonally distorted. Compression along the three-fold axis would result in an orbital ground singlet t_{2g}^0 corresponding to V_{zz} negative as illustrated in Fig. 8. The effect of an additional C_2 ligand field component from *cis*-monodentates would be to act as a perturbation on the primary trigonal field. This would further lift the degeneracy of $e_g^{\pm}$ and $t_{2g}^{\pm}$ (right of Fig. 8) and mix them to some extent. Thus one has V_{zz} negative and an orbital singlet ground term in accord with most of the existing data for Fe(phenanthroline)$_2$Cl$_2$ and Fe(phenanthroline)$_2$(N$_3$)$_2$. It is apparent from the three preceding analyses that there may not be a unique interpretation of the perturbed Mössbauer spectrum of a given system, especially when it is paramagnetic and has a high degree of metal–ligand covalency.

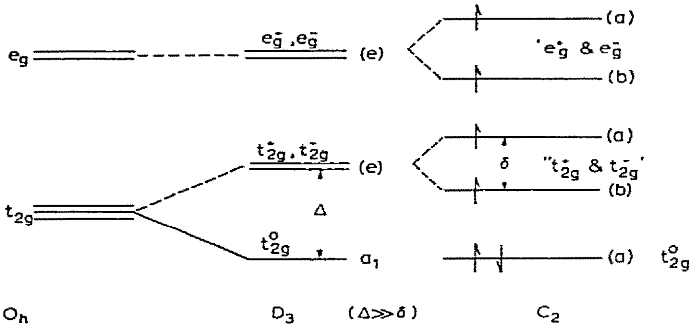


Fig. 8. Energy level diagram for a trigonally distorted Fe^{II} complex having an additional low-symmetry component of C_2 symmetry.

Essentially all of the tris(phenanthroline) and bipyridine ferrous complexes as well as their substituted derivatives are low-spin except for two. These are [Fe(2-CH$_3$-phenanthroline)$_3$](ClO$_4$)$_2$, which exhibits a quintet to singlet equilibrium[73] and [Fe(2-Cl-phen)$_3$]-(ClO$_4$)$_2$ which has a spin quintet ground state to at least 4.2°K. The paramagnetism of the latter two systems is probably related to steric factors involving the "2" substitution such that the ligand field is no longer strong enough to force spin pairing at room temperature. The 2-Cl system[74] has $\Delta E = 1.00$ mm/sec at 300°K and 2 mm/sec at 4.2°K with the latter value being about two thirds those for the previously discussed bis(phenanthroline) compounds. The quadrupole splitting for the high-spin form of the 2-CH$_3$ system has been found[75] to vary over nearly the same values as the 2-Cl. It is reasonable to assume that the distortion of these systems is either a tetragonal or trigonal compression resulting in an orbital ground singlet (^5A, ^5B) and $\Delta E \approx 3$ to 3.5 mm/sec, or an elongation such that ΔE is ≈ 1.5 to 2.0 mm/sec corresponding to a ground ^5E. The observed small

ΔE values lead one to choose the latter ground state. The magnetically perturbed spectra of Fe(2-Cl-phenanthroline)$_3$(ClO$_4$)$_2$ at 4.2°K in axial fields of 35 and 70 kgauss show V_{zz} *negative* and η small. The sign is consistent with a tetragonal distortion yielding a ^5E ground state composed primarily of d_{xz}, d_{yz} orbitals or trigonal such that the ground level corresponds to ^5A (d_{z^2}), where the ^5E state is preferred on the basis of the magnitude of ΔE. It is interesting to note that Konig et al.[75] indicate V_{zz} positive for the high-spin form of the 2-CH$_3$ complex from a study of the temperature dependence of its quadrupole splitting. It is difficult to see how the electronic structures of the 2-Cl and 2-CH$_3$ are so different as to result in different signs for their quadrupole interactions.

As part of a general study of pseudo-tetrahedral iron(II) complexes of polyimine ligands, the perturbed Mössbauer spectra of Fe(2,9-di-CH$_3$-phenanthroline)Cl$_2$ have been determined[76] at 4.2°K. The quadrupole interaction is positive and axially symmetric. This suggests stabilization of the $d_{x^2-y^2}$ orbital (or a linear combination of d_{z^2} and $d_{x^2-y^2}$ orbitals which is weighted heavily with the latter) by elongation along the two-fold axis. The single-crystal X-ray study[77] of Zn(2,9-di-CH$_3$-phen)Cl$_2$ (the corresponding iron complex is isomorphous) indicates such an elongation with its greatly decreased N–Zn–N angle ($\approx 81°$). Other mono-polyimine ferrous systems for which there are perturbed Mössbauer data are Fe(phenanthroline)Cl$_2$ and Fe(bipyridine)Cl$_2$, with V_{zz} positive in both cases[78]. However, there is evidence to indicate that these are associated to five- or six-coordinate polymeric species in the solid state and are not directly comparable to the foregoing 2,9-di-CH$_3$-phenanthroline system.

There are relatively few perturbed Mössbauer investigations of high-spin iron(II) in distinctly non-cubic environments. The system Fe(terpyridine) (NCS)$_2$ is believed to contain five-coordinate iron(II) of stereochemistry intermediate between square pyramidal and trigonal bipyramidal[79]. The room temperature and liquid helium perturbed spectra of this complex show V_{zz} positive[80]. For the extremes of regular trigonal bipyramidal or square pyramidal coordination, V_{zz} negative is predicted from simple crystal field assumptions. It is probable that π covalence and bonding electrons are important. A possible explanation of the positive quadrupole is π stabilization to give a d_{xy} ground state with the overall structure closer to square pyramidal.

Another non-cubic iron(II) complex for which the perturbed Mössbauer spectra have been determined is the eight-coordinate tetrakis-(1,8-naphthyridine) iron(II) perchlorate[81]. A single-crystal X-ray study[82] showed this compound to have a distorted dodecahedral environment. The quadrupole interaction is unusually large (4.54 mm/sec at 4.2°K). The perturbed Mössbauer spectrum (4.2°K) for a longitudinal field of 40 kgauss showed V_{zz} positive and $\eta = 0$. An interpretation of these results in relation to the observed effective field and possible ground state configurations is advanced. No detailed explanation of the large value of ΔE is given although its magnitude suggests the effects of bonding electrons are important.

High-spin d^5. Many high-spin iron(III) complexes show zero or very small quadrupole effects owing to the nominal spherical symmetry of the half filled d shell and corresponding zero valence contribution to the electric field gradient. Thus, for example, the high-spin tris(pyrolidyl-dithiocarbamate) iron(III) has a quadrupole splitting of only 0.2 mm/sec.

Its perturbed spectrum in a transverse field of 30 kgauss is like that of Fig. 5(d) reflecting the small quadrupole.

For high-spin iron(III), observable quadrupole splittings are related to asymmetry in the ligand charge distribution or covalence anisotropy. Those few high-spin iron(III) complexes exhibiting relatively large splitting are useful for testing the point charge model and relating perturbed spectra data to the bonding properties of ligands as well as stereochemistry. A series of FeCl(β-diketonate)$_2$ complexes have recently been studied for such purposes. The complexes studied[83, 84], viz. $FeCl(CH_3 \cdot CO \cdot CH \cdot CO \cdot CH_3)_2$, $FeCl(ph \cdot CO \cdot CH \cdot CO \cdot CH_3)_2$ and $FeCl(ph \cdot CO \cdot CH \cdot CO \cdot ph)_2$, are square-pyramidal five-coordinate with the chloride in the axial position. The difference between the axial and in-plane sigma-bonding in these systems is reflected in quadrupole splittings of approximately 1.0 mm/sec for all three compounds. While all three complexes contain high-spin iron(III), there is evidence that the first two systems show weak intramolecular antiferromagnetic exchange. The diphenyl compound is apparently a dilute paramagnet. These result in distinctly different perturbed Mössbauer spectral behavior. For the dilute paramagnet a combined Zeeman split-quadrupole spectrum is observed. This system is distinguished from the others in that its hyperfine field is temperature-dependent over the temperature range 1.8 to 4.2°K for applied fields as large as 30 kgauss. This accords with the temperature-dependent Curie susceptibility of a simple paramagnet whose magnetization varies as H/T. In the dimethyl and phenyl-methyl complexes, the weak antiferromagnetic exchange results in a series of energy levels described by the total spin S_T ($S_T = 0, 1, 2, 3, 4, 5$) for which the energy $E_{S_T} = -J[S_T(S_T + 1) - 35/2]$, where J is the exchange interaction parameter. When J is negative, as in the present systems, the ground state is the non-magnetic singlet. In the absence of nearby (magnetic) excited states ($S_T \neq 0$) the perturbed spectrum at 4.2°K is expected to be something like the usual triplet–doublet with the internal field equal to the applied field and essentially temperature-independent.

Instead of this behavior, combined Zeeman–quadrupole spectra having temperature-independent internal fields linear in the applied field are observed. Zero field splitting is expected to mix components of excited states with the ground singlet giving a temperature-independent susceptibility and the observed spectral behavior.

The zero field splitting of these systems is such that a broadened, asymmetrical quadrupole is observed at 300°K, gradually becoming symmetrical as the temperature is decreased. This behavior is consistent[48] with a temperature-dependent spin–spin relaxation and a positive zero field splitting parameter D. At high temperatures the more slowly relaxing $m_s = \pm\frac{3}{2}, \pm\frac{5}{2}$ Kramers doublets are occupied, while at liquid helium temperature the rapidly relaxing $m_s = \pm\frac{1}{2}$ doublet is almost exclusively populated. The component (σ or π) of the quadrupole that broadens first with increasing temperature depends on the angle[49] between the fluctuating magnetic field and the principal axis of V_{zz}. For axial symmetry a field fluctuating parallel to V_{zz} broadens the π transition while fluctuation perpendicular broadens the σ. As will be discussed, V_{zz} is positive in these systems. Thus the fact that the transition at higher energy (the π) undergoes broadening indicates that the changing internal field is closer to being parallel to V_{zz}.

For the preceding di-methyl and phenyl-methyl complexes it is difficult to determine the sign of V_{zz} by inspection of their complex combined interaction spectra. Analysis of the more resolved spectrum of the di-phenyl system indicates V_{zz} positive although the details of the authors' analysis are not clear. From a simple point charge model and considering sigma-bonding most important, V_{zz} positive is expected for all three complexes, i.e. one has a plane of strong sigma bonding relative to a single axial ligand. Perturbed Mössbauer spectra in large fields at room temperature may be helpful in unambiguously determining the sign of V_{zz} in the foregoing complexes.

Johnson[85] has studied the perturbed Mossbauer spectra of the biologically important ferric hemin (ferric porphyrin chloride), another $S = \frac{5}{2}$ square-pyramidal system. This material shows relaxation broadening of the type just considered for positive zero field splitting, i.e. a broadened spectrum at room temperature and a symmetric quadrupole at 4.2°K. There is no evidence of intramolecular exchange as the perturbed spectra at 30 kgauss over the range 1.6 to 4.2°K are temperature-independent combined interaction spectra that can be treated using a Brillouin function of H/T. Analysis of these six-line spectra indicate V_{zz} positive in accordance with strong in-plane bonding by the porphyrin moiety.

A number of magnetically dilute rhombic, high-spin iron(III) EDTA complexes have recently[86] been studied using small applied fields in an attempt to correlate Mossbauer and detailed electron spin resonance data. Small spin decoupling fields of the order 100 gauss allow for sharpening of hyperfine spectra. The crystal field parameters derived from these spectra compare with electron spin resonance results. The advantage of the Mössbauer study lies in the fact that the crystal field parameters are obtained from more easily interpreted fixed field experiments.

Binuclear iron(III) compounds. Magnetically perturbed Mössbauer studies of polynuclear iron(III) complexes have been very useful in the elucidation of their electronic structure. Essentially all of the systems studied so far are binuclear and contain the $\mathrm{Fe^{III}{-}O{-}Fe^{III}}$ grouping as a path for antiferromagnetic exchange. For complexes containing an approximately linear ($\mathrm{Fe^{III}{-}O{-}Fe^{III}}$ angle $> 150°$) bridge, the exchange interaction, J, is strong ($\approx -100\ \mathrm{cm^{-1}}$). Under these circumstances, it is not possible to distinguish between individual iron atoms having $S = \frac{3}{2}$ or $S = \frac{5}{2}$ spin by usual susceptibility techniques or isomer shifts of unperturbed Mössbauer spectra. The perturbed Mössbauer spectra of a series of such strongly coupled complexes have been determined at 4.2°K in axial fields up to 26 kgauss. The systems studied[87,88]: $[\mathrm{Fe(salen)}]_2\mathrm{O}$ (V_{zz} positive); $[\mathrm{Fe(phen)_2Cl}]_2\mathrm{OCl_2}\cdot 5\mathrm{H_2O}$ (V_{zz} negative), and $[\mathrm{FeBH_2O}]_2\mathrm{O(ClO_4)_4}$ (V_{zz} negative) (B = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo)[12,3,1]octadeca-1(18), 2, 12, 14, 16-pentaene) contain five-, six- and seven-coordinate iron(III) respectively and are axially symmetric. The salen complex has also been studied by Okamura et al.[89] using transverse fields of the order 30 kgauss and Buckley et al.[90] in even larger longitudinal fields ($\approx$ 90 kgauss) with the same result, V_{zz} positive. It was found possible to predict the observed sign of V_{zz} in the preceding compounds using simple point charge and sigma bonding considerations alone. This furnishes strong support for the $S = \frac{5}{2}$ spin state for the individual ferric ions.

As mentioned previously, intramolecular antiferromagnetism results in a spin singlet ground level for which the internal field must vanish. In the systems under consideration $J \gg kT$ at 4.2°K and thus the ground singlet would be exclusively populated. In addition, zero field splitting is expected to be considerably less than the exchange interaction and hence any temperature-independent susceptibility effect should also be negligible. The perturbed spectra are in accord with the preceding observation in that the usual triplet–doublet pattern is observed with effective field approximately equal to applied.

The ligand salen also forms the binuclear complex, [Fe(salen)Cl]$_2$, a dimer of the five-coordinate Fe(salen)Cl. The Fe^{III}–O–Fe^{III} angle is quite close to 90° with the resulting antiferromagnetic exchange much weaker ($J \approx -10$ cm^{-1}). In spite of the small J value, its perturbed spectral behavior at 4.2°K is much like that of the preceding strongly exchange-coupled systems[90, 91]. The spectra are characterized by V_{zz} negative and $\eta \approx 0$ and as with [Fe(salen)$_2$O] a large internal field is not expected. Buckley et al.[90] did find the applied and effective fields to be of the same order but with the observed effective field always slightly less than that applied. The origin of this behavior is not well understood.

Lechan et al.[92] have determined the perturbed spectra of [Fe(salen)Cl]$_2$ from $4.2 < T < 22$°K in axial fields as large as 80 kgauss. These workers have analyzed the temperature dependence of the effective field and obtained an hyperfine field of −192 kgauss per unit spin compared with −220 kgauss for ionic iron(III) compounds. The value of the exchange interaction ($J = -6.7$ cm^{-1}) as determined in this study is in reasonable agreement with that found (−7.5 cm^{-1}) from the temperature dependence of the magnetic susceptibility[93].

The perturbed spectra of the products obtained by recrystallization of [Fe(salen)Cl]$_2$ from various solvents have also been determined[94]. As this dimer is relatively easily cleaved, the possibility of five- or six-coordinate monomers arises. *Slow* recrystallization from nitromethane apparently results in a dimeric nitromethane adduct as the perturbed spectral behavior is almost identical to that of the starting dimer. *Rapid* crystallization from nitromethane as well as pyridine results in completely different perturbed spectra[95]. They are highly broadened, exhibit large hyperfine fields and V_{zz} is now positive. These observations are consistent with monomeric five-coordinate products showing considerable magnetic anisotropy. The fact that six-line Zeeman spectra are not observed even in applied fields as large as 25 kgauss indicates fast relaxation in these products.

Quartet iron(III). Quartet iron(III) is rather rare. One of the more extensively studied series of such complexes consists of the mono-halo-bis-(dialkyl-dithiocarbamate)-iron(III) systems. The compounds are five-coordinate square-pyramidal and have ^4A ground terms, neglecting zero field splitting[96]. The large positive quadrupole splitting (≈ 2.7 mm/sec) may be explained in terms of bonding electrons alone (i.e. strong in-plane bonding) since electron spin resonance and electronic spectral data indicate a vanishing valence contribution to the electric field gradient. The sign of the zero field splitting in these systems depends on the nature of the axial halogen and for Fe(diethyldithiocarbamate)$_2$Cl D is negative[97]. Thus relaxation broadening of its Mössbauer spectrum is expected and observed to occur as the temperature is decreased. This system is especially interesting in that it shows a ferromagnetic transition[98, 99] at 2.43°K giving rise to a well resolved combined quadrupole–Zeeman spectrum. Such spectra are, however, also possible for antiferromagnets as well as slowly relaxing paramagnets. In order to clearly demonstrate that the preceding transition is ferromagnetic, Rickards et al.[100] have looked at the perturbed Mössbauer spectra of Fe(diethyldithiocarbamate)$_2$Cl in transverse fields at temperatures below the presumed Curie temperature. The field variation of the peak intensities and the field and temperature dependences of the effective internal field were found most consistent with true ferromagnetic behavior.

Low-spin iron(III). Magnetically perturbed Mössbauer studies of low-spin iron(III) complexes are of particular interest in that they can often be correlated with electron spin resonance results. Thus one can determine the detailed nature of the orbital ground state wave function. A good example of such correlation is found in the perturbed spectra–ESR behavior of the $[\mathrm{Fe(bipy)_3}]^{3+}$ cation. The quadrupole splitting of $[\mathrm{Fe(bipy)_3}](\mathrm{ClO_4})_3$ is relatively large (≈ 2 mm/sec) and reflects a considerable low symmetry ligand field component. As the distortion of the system is probably axial and trigonal in nature, the quadrupole splitting is simply viewed as localization of a "hole" in the t_{2g}^{0} or $t_{2g}^{\pm}$ orbitals. There is the added complication that these orbitals (and thus the location of the hole) are mixed among each other by spin–orbit coupling to give three Kramers doublets of the form[101]

$$\psi \pm = a_i \,|\pm|^{\pm}> + b_i\,|\zeta^{\pm}> + c_i|\mp|^{\pm}>$$

or[102]

$$\begin{aligned} |+> &= \sin\alpha\,|0^{+}> + \cos\alpha\,[(\tfrac{2}{3})^{\frac{1}{2}}|-2^{-}> + (\tfrac{1}{3})^{\frac{1}{2}}|\,1^{-}>] \\ |-> &= \sin\alpha\,|0^{-}> + \cos\alpha\,[(\tfrac{2}{3})^{\frac{1}{2}}|\,2^{+}> - (\tfrac{1}{3})^{\frac{1}{2}}|-1^{+}>] \end{aligned} \tag{22}$$

Provided the axial field is large relative to λ, the primary nature of the ground Kramers doublet can be ascertained from the perturbed Mössbauer spectrum. The magnetically perturbed spectrum of $[\mathrm{Fe(bipy)_3}](\mathrm{ClO_4})_3$ shows $\eta \approx 0$ and V_{zz} positive[103], implying axial elongation (negative trigonal field). A positive principal component of the electric field gradient tensor also correlates with a hole primarily in t_{2g}^{0} corresponding to a ^{2}A ground term in the absence of spin–orbit mixing. The effects of such mixing are assessed from the ESR data[104] of $[\mathrm{Fe(bipy)_3}](\mathrm{PF_6})_3$. The ESR spectra of frozen H_2SO_4 solutions of $[\mathrm{Fe(bipy)_3}](\mathrm{PF_6})_3$ reflect axial symmetry ($g_1 = 2.60, g_2 = 2.60, g_3 = 1.61$). The computer fit to these g values for a $^{2}T_{2g}$ ground term perturbed by the combined action of a low-symmetry ligand field and spin–orbit coupling results in $g_{x,\,y} = 2.60, g_z = 1.61$; $\Delta(\text{trigonal}) = -1200\ \mathrm{cm^{-1}}$; and a ground Kramers doublet whose coefficients are $a_1 = 0.25$, $b_1 = 0.97$, $c_1 = 0.00$. It is seen that the ground Kramers doublet is composed of almost entirely t_{2g}^{0}, in agreement with the perturbed spectra results. The quadrupole splitting calculated using the foregoing coefficients agrees quite well with that observed after correction for a small lattice contribution. The latter may be estimated from the quadrupole splitting of the corresponding low-spin ferrous system.

It has also been possible to correlate the perturbed Mössbauer and ESR data[55] of $[\mathrm{Fe(terpyridine)_2}](\mathrm{ClO_4})_3$. The quadrupole splitting of this system is unusually large (≈ 3.3 mm/sec) and part of this is believed due to an additive contribution from bonding electrons. This is supported by the fact that V_{zz} has the same sign (negative) for the analogous low-spin iron(II) complex[55], i.e. ΔE of $[\mathrm{Fe(terpyridine)_2}](\mathrm{ClO_4})_2 \approx -1.1$ mm/sec. The symmetry of these systems is close to D_{2d}, and thus Kramers doublets composed of linear combinations of d_{xz}, d_{yz} and d_{xy} are appropriate for the discussion of the orbital ground state and ESR data. Analysis[105] of the ESR data shows a large negative axial field for $[Fe(terpyridine)_2](ClO_4)_3$ ($\Delta \approx -1700\ cm^{-1}$) and a ground Kramers doublet composed essentially of a hole in the d_{xy}. This corresponds to V_{zz} negative as observed through perturbed Mössbauer spectra at 300 and 4.2°K. The valence contribution to the quadrupole splitting can be calculated from ESR data using the equations

$$
\begin{aligned}
V_{xx} &= \tfrac{2}{7} \langle r^{-3} \rangle [-\tfrac{1}{2}(1-3b^2) - 3ac] \\
V_{yy} &= \tfrac{2}{7} \langle r^{-3} \rangle [-\tfrac{1}{2}(1-3b^2) + 3ac] \\
V_{zz} &= \tfrac{2}{7} \langle r^{-3} \rangle [1-3b^2] \\
\Delta E &= \tfrac{1}{2} eQ\, [V_{zz}^2 + \tfrac{1}{3}(V_{xx}-V_{yy})^2]^{1/2}
\end{aligned}
\tag{23}
$$

where only the ground Kramers doublet need be considered at 4.2°K. The coefficients a, b and c of this doublet are obtained from the ESR g values using the relations of Griffith[101]

$$
\begin{aligned}
g_x &= 2[2ac - b^2 + kb\,(c-a)\sqrt{2}] \\
g_y &= 2[2ac + b^2 + kb\,(c+a)\sqrt{2}] \\
g_z &= 2[a^2 - b^2 + c^2 + k\,(a^2 - c^2)]
\end{aligned}
\tag{24}
$$

where k is the Stevens orbital angular momentum reduction factor[102]. The calculated valence contribution to ΔE in $[Fe(terpyridine)_2](ClO_4)_3$ is quite reasonable for an axial field of the order 1700 cm^{-1} and when subtracted from the observed ΔE leaves a contribution, presumably due to covalence anisotropy, of magnitude surprisingly close to the value of ΔE for $[Fe(terpyridine)_2](ClO_4)_2$. This is consistent with the fact that V_{zz} is negative in both the ferrous and ferric terpyridine complexes.

Magnetically perturbed Mössbauer studies of low-spin iron(III)–thio systems have also involved attempts at correlation with ESR data. For example, the system Fe(dithioacetylacetonate)$_3$ has been studied[105] at room temperature in axial and transverse fields of the order 40 and 20 kgauss respectively and also in an axial field of 35 kgauss at 4.2°K. These spectra show V_{zz} negative and η near zero, suggesting an orbital ground state such that there is a d_{xy} hole. Martin and Roos[106] have determined the temperature dependence of the quadrupole splitting with the result that the low symmetry ligand field splitting is of the order -800 to $-1000\ cm^{-1}$. Such a negative low-symmetry component corresponds to a ^2A ground term and a hole primarily in the d_{xy} orbital. Analysis of the ESR data of Fe(dithioacetylacetonate)$_3$ as well as the other low-spin thio systems is complicated by the effects of covalency and configuration interaction with higher energy ^2T terms. In the present system one would expect a ground Kramers doublet having coefficient b (eqn. (22)) largest.

Rickards et al.[107, 108] have studied the perturbed Mössbauer and ESR behavior of the following sulfur systems: $[(\text{phenyl})_4\text{P}]_3[\text{Fe}\{\text{S}_2\text{C}_2(\text{CN})_2\}_3]$, a tris-dithiolene and the persulfides $\text{Fe(ttd)}_2\text{(dtt)}$, Fe(ttd)(dtt)_2, where ttd is tri-thioperoxy-*p*-toluate, dtt is dithio-*p*-toluate, both strong field ligands. These workers have found it possible to correlate the observed signs for V_{zz} with ESR results; however, the same problems of configuration interaction as previously noted are encountered.

The magnetically perturbed Mössbauer spectra of a number of low-spin iron(III) complexes exhibiting small quadrupole effects have also been studied. In particular, Oosterhuis and Lang[109] have determined perturbed spectra for single crystals of $K_3Fe(CN)_6$ in transverse fields up to 29 kgauss at 4.2°K. The spectra are combined Zeeman split—quadrupole spectra from which V_{zz} is deduced negative, in agreement with the coefficients of the ground Kramers doublet ($a = 0.524$, $b = 0.702$, $c = 0.482$). These authors have also studied the angular dependence of the π/σ transition intensity ratio of a single crystal, with the result V_{zz} negative.

The Mössbauer behavior of an important series of tris(*N*, *N*-dialkyl-dithiocarbamate)-iron(III) complexes exhibiting ^6A to ^2T spin equilibria has been investigated by Rickards et al.[110–112]. Most of these systems are low-spin at liquid helium temperature and the detailed perturbed spectra of the di-methyl and di-*n*-butyl have been studied to as low as 1.2°K. Both of these systems show slightly quadrupole-shifted Zeeman patterns for which the authors' analysis indicates V_{zz} positive. Both the magnitude and sign of ΔE for these compounds are consistent with the coefficients of the ground Kramers doublet, provided near cubic symmetry is assumed.

(c) Complexes of π-donor and acceptor ligands

This group of iron compounds is important in that their perturbed spectra allow simple correlations with point charge models and give considerable information on the bonding properties of ligands. An interesting study of this type has been conducted for some pseudo-tetrahedral iron(—II) complexes by Mazak and Collins[113]. Among these compounds some representative systems are: $\text{Fe(CO)}_2\text{(NO)}_2$, $V_{zz} < 0$, $\eta \approx 0.85$; $\text{KFe(CO)}_3\text{NO}$, $V_{zz} > 0$, $\eta \approx 0$; $\text{Fe(phenyl}_3\text{P)}_2\text{(NO)}_2$, $V_{zz} < 0$, $\eta \approx 0.76$. These systems are formally viewed as $3d^{10}$ and are diamagnetic. The electric field gradient has its origin in the ligand positions and bonding properties as the valence contribution vanishes. It is interesting to note that η is near unity for the preceding FeA_2B_2 systems, as predicted by the point charge model and confirms the fact that these systems are only slightly distorted from tetrahedral symmetry. The investigation of Mazak and Collins also contains useful mathematical expressions for V_{zz} and η for various distortions of an FeA_2B_2 compound. The point charge model discussed previously in conjunction with the observed signs of V_{zz} leads to the following order of $q\langle r^{-3}\rangle$ in the preceding compounds: $\text{(phenyl)}_3\text{P} > \text{CO} > \text{NO}$, an order consistent with the overall σ donor and π delocalization abilities.

Some diene systems whose perturbed Mössbauer spectra have been determined are: butadiene·Fe(CO)_3, $V_{zz} < 0$, $\eta = 0$ (ref. 20); cyclobutadiene·Fe(CO)_3, $V_{zz} > 0$, $\eta = 0$ (ref. 29), and tetramethyl cyclobutadiene·Fe(CO)_3, $V_{zz} > 0$, $\eta = 0$ (ref. 20). Using a point charge model as outlined by Mazak and Collins for tetrahedral FeA_3B systems, and making the considerable assumption that the diene groups can be treated as somewhat localized monodentate ligands, results in the following order of $q\langle r^{-3}\rangle$ butadiene > CO > cyclobutadiene or tetramethyl-cyclobutadiene. Whether or not the foregoing order is reasonable must await further details of the electronic structure of these systems. However, greater π-back-bonding to the cyclic systems is a factor consistent with such an order.

Another important diene compound is ferrocene, the complex for which the first[6] perturbed powder spectrum was published. The principal component of the electric field gradient is positive ($\eta \approx 0$), in accord with molecular orbital calculations of Shustorovich and Dyatkina[114] and Dahl and Ballhausen[115]. The primary bonding between the cyclopentadienide (π-C_5H_5—) rings and iron is believed[116] to be donation from filled π MO's of the rings to empty d_{xz} and d_{yz} orbitals of the metal. Hence, if the bonding electrons are the origin of the electric field gradient, ΔE is expected to be rather large and negative. The positive sign of V_{zz} is explicable in terms of an additional non-bonding contribution through occupation of the metal orbitals of δ symmetry, namely d_{xy} and $d_{x^2-y^2}$ for which V_{zz} is positive.

Other cyclopentadiene systems for which there are perturbed (iron-57) Mössbauer data include (π-C_5H_5)$Fe(CO)_2SnCl_3$ (ref. 117) and [π-$C_5H_5Fe(CO)_2]_2Sn(NCS)_2$ (ref. 118). Each of these systems shows $V_{zz} > 0$ and η small. There have been no detailed interpretations of these results. X-ray data[119] indicate distorted tetrahedral coordination about the iron of the foregoing chloride. The large ΔE (≈ 2 mm/sec) and small η accord with such an asymmetric environment. It should be recalled that for near-regular tetrahedral FeA_2B_2 or FeA_2BB', where $B \approx B'$, a large value of η is expected.

(ii) Tin compounds

The body of literature concerned with the magnetically perturbed Mössbauer spectra of tin coordination compounds is considerably smaller than that for iron-57. To some extent this is because considerably larger applied fields are often needed in order to observe well resolved tin-119 spectra. These experiments must nearly always be performed at liquid helium temperature, owing to the smaller recoilless fraction of tin sources and absorbers and lower signal-to-noise ratios of the perturbed spectra. However, most important is the previously mentioned fact that the resulting spectra are not always readily interpreted by simple inspection. Recently[22], comparative theoretical spectra for such interpretation have been published.

(a) Tin(II)

Gibb et al.[120] have determined the sign of the quadrupole coupling constants ($e^2V_{zz}Q$) in a number of stannous salts (SnF_2, SnO, SnS, $Sn_3(PO_4)_2$, Sn C_2O_4) with the result that they are all positive and hence V_{zz} is negative. These, like most tin(II) systems, have distorted trigonal pyramidal stereochemistries[121]. Further, as these compounds are diamagnetic, it is reasonable to assume that the molecular symmetry axis (if any) and the principal axis of the electric field gradient tensor coincide. Thus the preceding negative V_{zz} suggests greater electron density in the nonbonding $5p_z$ orbital relative to $5p_x$ and $5p_y$ of tin in three-coordination. Here the $5d$ orbitals are neglected and have been shown[122] to have only a small effect on the magnitude of V_{zz} in tin compounds. The opposite case of higher electron density in the p_x and p_y orbitals results in V_{zz} positive, although this has not as yet been reported for pyramidal stannous compounds. Thus, for example, the following trigonal tin(II) complexes have also been studied[123] and all show V_{zz} negative: $NaSnF_3$, $NaSn_2F_5$, $SnSO_4$, $Sn(HCO_2)_2$, $Sn(AcO)_2$ and $K_2Sn(C_2O_4)\cdot H_2O$. The preceding observation of a negative sign for V_{zz} in distorted stannous systems is also explicable in terms of the point charge model for a pseudo-tetrahedral MA_3B system, where B is a lone pair and $q < r^{-3} >$ of B is greater than that of A. However, neither the point charge nor simple imbalance of p-orbital occupation approach appears to explain adequately the magnitude of ΔE in tin(II) compounds.

(b) Tin(IV)

Stannic complexes comprise a rich area for Mössbauer study. This is the case in view of the variety of coordination numbers and polyhedra exhibited by tin(IV). Further, there are often X-ray and infrared dipole moment as well as a variety of other kinds of data with which to correlate Mössbauer results. Finally as will be seen, molecular orbital[124] and point charge[13] approaches usually work quite well for stannic systems. Thus perturbed Mössbauer investigations can be valuable in yielding useful additional information about the bonding properties of ligands, as well as the possibility of higher coordination by solid state association.

Before considering perturbed Mössbauer spectra of various stannic systems, it is important to state some results extremely useful in the interpretation of these spectra. The first is that the electric field gradient at the stannic ion is primarily due to covalence anisotropy, i.e. the difference in electron densities in tin–ligand bonds. Another way of stating this is that the magnitude of the valence electric field gradient is greater than that of the lattice where the latter is due to the charge on the coordinated ligand atoms or more distant atoms in the lattice. The second important point is that the sign of the principal component of the electric field gradient is often determined by the disposition of the tin–carbon (alkyl or aryl) sigma bonds in that the higher covalence of these bonds puts greater electron charge on the tin atom than polar bonds to more electronegative groups such as halides, pseudohalides, anionic oxygen, etc. Thus with axial organic groups V_{zz} will be negative and ΔE positive. For in-plane organo ligands, as in a trigonal bipyramidal complex having equatorial alkyl or aryl and perhaps axial halogen, V_{zz} will be positive, and similarly for *trans*-halo octahedral systems. The preceding statements about signs assume relatively regular coordination environments. In the absence of this, detailed crystallographic data (e.g. C–Sn–C angles) are necessary in conjunction with point charge calculations. This will be seen to be the case for *cis*-organo octahedral systems. For regular stereochemistries the following are the results of point charge calculations, with the relative magnitudes and sign of V_{zz} given in parentheses: tetrahedral R_3SnX (+2), trigonal bipyramidal R_5SnX_2 (+3 to +4), *cis* octahedral R_2SnX_4 (+2), *trans*-R_2SnX_4 (–4). $RSnX_5$ (–2). Notice that for single weak axial ligand such as X = Cl in R_5SnX, V_{zz} is expected positive while for a single axial ligand as in $RSnX_5$, V_{zz} is negative.

Among the first magnetically perturbed Mössbauer investigations of tin(IV) complexes are those of Goodman and Greenwood[125] and Erickson[126]. Goodman and Greenwood investigated the perturbed spectra of SnO_2, $(CH_3)_2SnMoO_4$ and $(CH_3)_2SnCl_2$. The stannic oxide exhibits a very small quadrupole effect and thus the perturbed spectrum is an approximately symmetric pattern of two sets of triplets reflecting the quadrupole interaction as a small perturbation on the Zeeman splitting. The latter two complexes are associated in the solid state to give octahedral tin(IV) in which the methyl groups are *trans*. Thus in view of preceding discussions we would expect V_{zz} negative (corresponding to strong bonding along the C–Sn–C axis) and positive quadrupole interaction. Goodman and Greenwood assumed V_{zz} positive, which is effectively the same as assuming Q of tin-119 to be positive. This error of interpretation was later resolved by Erickson[126].

Erickson and co-workers[127] have also determined the perturbed Mössbauer spectra of $(CH_3)_2SnF_2$ and $(CH_3)_2Sn(C_5H_7O_2)_2$, complexes of known *trans*-methyl octahedral structure. As expected, both show V_{zz} negative. The perturbed Mössbauer results clearly confirm the polymeric nature of systems such as $(CH_3)_2SnF_2$ and $(CH_3)_2SnO_2$ in the solid state.

The single-crystal X-ray investigation[128] of dichloro-diphenyl tin, $(C_6H_5)_2SnCl_2$, has recently been reported. Contrary to the foregoing dimethyl complexes, this material is not associated in the solid state to give octahedral coordination about the tin. It contains relatively distorted tetrahedra that are well isolated from each other. Its perturbed spectrum has not yet been determined, but the complex may exhibit an intermediate value of η in view of its distortion. For near-"regular" R_2SnX_2 tetrahedra $\eta \approx 1$ is expected and should decrease with increasing angular distortion from T_d.

A number of perturbed Mössbauer studies[129–133] of stannic tin in a variety of stoichiometries and coordination environments have been conducted and show that the point charge or more properly the "donated" charge approach to bonding in these systems is a relatively good model. The complexes studied are listed in Table 5. On the whole it is seen that the results are consistent with the previous discussions of the foregoing models except for some of the *cis* octahedral compounds. In the latter (e.g. compounds 7, 8, 9, 10 of Table 5), if regular symmetry is assumed, V_{zz} positive and a corresponding ΔE negative are expected. Further, the ratio $\Delta E(trans)/\Delta E(cis)$ should be ≈ 2, as is observed. The fact that the signs of ΔE for some of the *cis* complexes are opposite to those predicted has been adequately explained in terms of distortion from regular sterochemistry. In particular, enlargement of the C–Sn–C angle to greater than 90° will change the sign of V_{zz}. The entries 6 and 11 in Table 5 are recently studied[133] examples of *cis–trans* tin(IV) compounds where $\Delta E(trans)/\Delta E(cis) \approx -2$ as would normally be predicted. This was determined from perturbed Mössbauer spectra at 60 kgauss applied.

The dominance of the tin–carbon bonds in determining the sign of V_{zz} in stannic systems is further exemplified by the octahedral pyridine *N*-oxide adduct of dimethyl tin dichloride. There is considerable variation among the ligands of $(CH_3)_2SnCl_2(C_5H_5NO)_2$ as regards their sigma-bonding strength. The sign of V_{zz} is negative[134] and $\eta \approx 0$. This accords with the single-crystal X-ray study of the material as it shows *trans*-methyls, *trans*-chlorides and *trans*-oxygens such that the strongest bonding is along the C–Sn–C axis normal to the plane determined by chlorines and oxygens.

The perturbed Mössbauer spectra for adducts of organo-tin(IV) chlorides of the form (*n*-propyl)$SnCl_3$, (*n*-propyl)$_2SnCl_2$ and (phenyl)$_nSnCl_{4-n}$ ($n = 1, 2, 3$) with various nitrogen bases have recently been studied[135]. Correlations of the magnitudes and signs of ΔE were found a considerable aid in formulation of the stereochemistries of the adduct products. In particular the adducts of (phenyl)$_3SnCl$ with ligands such as piperidine, morpholine, etc. give negative quadrupole splittings of the order −2.5 to −3.0 mm/sec and are consistent with trigonal bipyramidal geometry with equatorial methyl groups. Compounds such as (phenyl)$_2SnCl_2$ and (*n*-propyl)$_2SnCl_2$ give adducts with piperidine, γ- and β-picoline and isoquinoline whose quadrupole splittings are positive and vary from +3.5 to +4.0

TABLE 5
Perturbed Mössbauer results for some organo-tin(IV) complexes

Complex and stereochemistry	V_{zz}	Ref.
(1) $(Me_2N)_2(EtSnCl_5)$ octahedral	–	129
(2) $Cs_2(Me_2SnCl_4)$ *trans* octahedral	–	129
(3) Me_2SnF_2	–	130
(4) $K_2Me_2SnF_4$	–	132
(5) $Bu_2Sn(O_2CCH.CHCO_2)_2$	–	132
(6) Sn(ethane-1,2-dithiolato)$_2$$(Et_2SO)_2$	+	133
(7) Me_2Sn(8-quinolinolato)$_2$ *cis* octahedral	–	131
(8) $(Ph)_2Sn$(8-quinolinolato)$_2$	–	131
(9) $(Ph)_2Sn(S_2CNEt)_2$	–	131
(10) $(Ph)_2Sn(NCS)_2$(phenanthroline)	–	131
(11) Sn(ethane-1,2-dithiolato) (bipyridine)	–	133
(12) $Me_4N(Me_3SnCl_2)$ trigonal-bipyramidal	+	129
(13) $Ph_3PCH_2Ph(Et_3SnCl_2)$	+	129
(14) $Me_4N(Ph_3SnCl_2)$	+	132
(15) $(Et_3SnCN)_n$	+	132
(16) $Et_4N(Me_2SnBr_3)$	–	132
(17) Me_3SnNCS	+	130
(18) Me_3SnOH	+	130
(19) Ph_3SnF	+	130
(20) Ph_3SnCl	+	130
(21) Bu_2SnO tetrahedral	–	130
(22) Me_2SnO	–	132
(23) $(Bu_3Sn)_2O$	+	132
(24) $Me_3SnC_6F_5$	+	132
(25) $Ph_3SnC_6F_5$	+	132

mm/sec, reflecting *trans*-CH_3 octahedral products. On the other hand, morpholine appears to form *cis*-methyl adducts, as evidenced by splittings of nearly half the preceding values and of positive sign, indicating highly increased C—Sn—C angles (> 110°). Finally, the (phenyl)$SnCl_3$ and (*n*-propyl)$SnCl_3$ also form adducts with the preceding bases such that splittings are observed to vary from +1.4 to +2.4 mm/sec, again suggesting distorted *cis* octahedral geometry.

The tin-119 perturbed Mössbauer spectra of a number of tetrahedral halides, pseudohalides, carboxylates and alkyls have been studied. These complexes are either of the form $[Fe\cdot\pi\text{-}C_5H_5(CO)_2]_2\cdot SnX_2$ (ref. 118) or $[Fe(\pi\text{-}C_5H_5)(CO)_2]SnX_3$ (refs. 117, 118). The sign of V_{zz} is negative for all of the $FeSnX_3$ systems save one[118], $[Fe\cdot(\pi\text{-}C_5H_5)(CO)_2]\cdot$ Sn(*n*-butyl)$_3$. The negative value of V_{zz} is explained in terms of either a point charge approach with considerable distortion of the bond angles from the regular tetrahedral, or qualitatively from the dominance of the tin bonding by a single very short Sn—Fe bond resulting in high electron density in a unique direction. A positive V_{zz} for the preceding butyl complex is attributed to a small degree of distortion from T_d in alkyl systems as well as the smaller electronegativity of alkyl groups relative to halides, etc. Finally, for the compound containing two Fe—Sn bonds, the sign (positive) and magnitude of ΔE are readily explained on a point charge basis using the detailed single-crystal X-ray data for these compounds. In particular Gibb et al.[136] have completed a detailed study of $[\mathrm{Fe}(\pi\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2]_2\mathrm{SnCl_2}$ in which the magnitude of η is accurately determined to be 0.65 ± 0.05. A large value of η is expected for a tetrahedral $\mathrm{SnA_2B_2}$ system and this, in conjunction with oriented single crystal results, indicates $q < r^{-3} >$ is larger for iron atoms as ligands about Sn than chlorine. That is, there is greater electron withdrawal to the more electronegative halogen.

E. CONCLUSIONS AND PROSPECTS FOR FUTURE WORK

It is apparent that magnetically perturbed Mössbauer spectroscopy is a powerful method in the study of the stereochemistry, bonding and electronic behavior of tin and iron complexes. The perturbation technique is certainly one of the simplest ways of obtaining the sign of quadrupole interaction, as orientation studies tend to be tedious and suffer the drawback of requirement of single crystals.

Other $I = \frac{1}{2}$, $I = \frac{3}{2}$ systems to which the method might be profitably applied in order to obtain more information from their Mössbauer spectra are tellurium-125 and gold-197.

The application of magnetically perturbed Mössbauer spectroscopy to natural biological systems is also a significant area. A good example of this kind of investigation is that of Johnson and Hall[137], who studied *Euglena* ferredoxin at 4.2°K in a transverse field of 30 kgauss. This system is an example of an iron—sulfur protein whose spin and electronic configuration have been problematical. In the preceding investigation, an internal field of the order of that applied was observed. This is a possible indication that either the sample contains diamagnetic low-spin iron(II), or that there is some type (perhaps antiferromagnetic) of magnetic interaction between paramagnetic centers. Other biologically important systems have been studied similarly but their review is outside the scope of the present paper.

The main stumbling blocks to the more general use of the magnetic perturbation method in chemistry laboratories are the expense of superconducting magnet systems and liquid helium. On the other hand, electromagnets capable of a transverse field of ≈ 20 kgauss (when used at a half-inch gap with one-inch cylindrical tapered pole faces) are already present in laboratories where susceptibility studies are conducted. The author has found such transverse electromagnet systems convenient for perturbation studies at room temperature. The degree of resolution is quite acceptable for iron-57. In relation to this, Lang[138] has recently shown that, contrary tc previous assumptions, the computer calculation and fitting of transverse spectra need not be more arduous and time-consuming than for the longitudinal case. If the appropriate coordinate system is chosen, the difference in computation time for the two geometries is nominal.

In summary, it is hoped that the review will lead more Mössbauer researchers to give serious consideration to the magnetic perturbation technique in attacking problems in coordination chemistry.

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REFERENCES

1 V.I. Goldanskii and R.H. Herber (Eds.), *Chemical Applications of Mössbauer Spectroscopy*, Academic Press, New York, 1968.
2 The Mössbauer effect and its application in chemistry, *Advan. Chem. Ser.*, 68 (1967).
3 R.V. Parish, *Progr. Inorg. Chem.*, 15 (1972) 101.
4 J. Danon and L. Iannarella, *J. Chem. Phys.*, 47 (1967) 382.
5 A.J.F. Boyle, D.St.P. Bunbury and E. Edwards, *Proc. Phys. Soc., London*, 79 (1962) 416.
6 R.L. Collins, *J. Chem. Phys.*, 42 (1965) 1072.
7 A. Abragam, *L'Effet Mössbauer et Ses Applications à l'Etude des Champs Internes*, Gordon and Breach, New York, 1964, p. 28.
8 H.M. Cohen and F. Reif, *Solid State Phys.*, 5 (1957) 321.
9 G.K. Wertheim, *Mössbauer Effect: Principles and Applications*, Academic Press, New York, 1964, p. 70.
10 C.E. Johnson, *Hyperfine Structure and Nuclear Radiations*, North-Holland, Amsterdam, 1968, p. 226.
11 G.A. Webb, *Coord. Chem. Rev.*, 4 (1969) 107.
12 R. Sternheimer and H.M. Foley, *Phys. Rev.*, 102 (1956) 731.
13 M.G. Clark, *Mol. Phys.*, 20 (1971) 257.
14 N.E. Erickson, *Pittsburgh Diffraction Conference*, 1966, and private communication.
15 E.O. Kazimir, *Ph.D. Dissertation*, Fordham Univ., New York, 1969.
16 C.J. Ballhausen, *Introduction to Ligand Field Theory*, McGraw-Hill, New York, 1962, p. 68.
17 T.C. Gibb, *J. Chem. Soc. A*, (1968) 1439.
18 S.V. Karyagin, *Dokl. Akad. Nauk SSSR*, 148 (1963) 1102; Engl. transl. *Dokl. Phys. Chem*, 148 (1964) 110.
19 S.L. Ruby and P.A. Flinn, *Rev. Mod. Phys.*, 36 (1964) 351.
20 R.L. Collins and J.C. Travis, *Mössbauer Eff. Methodol., Proc. Symp.*, 3 (1967) 123.
21 A.J. Stone, *Chem. Phys Lett.*, 6 (1970) 331.
22 T.C. Gibb, *J. Chem. Soc. A*, (1970) 2503.
23 G.W. Ludwig and H.H. Woodbury, *Phys. Rev.*, 117 (1960) 1286.
24 R.S. Preston, S.S. Hanna and J. Heberle, *Phys. Rev.*, 128 (1962) 2207.
25 J. Travis, *Ph.D. Disseration*, Univ. of Texas, Austin, Tex., U.S.A., 1968.
26 L.J. Swartzendruber and L H. Bennett, *J. Res. Nat. Bur Stand., Sect. A*, 74 (1970) 691.
27 P.P. Craig, *Mössbauer Eff. Methodol., Proc. Symp.*, 1 (1965) 135.
28 J.R. Gabriel and S.L. Ruby, *Nucl. Instrum. Methods*, 36 (1965) 23.
29 R.L. Collins, K. Maer, Jr. and J.C. Travis, *J. Inorg. Nucl. Chem.*, 30 (1967) 113.
30 J.C. Travis and R.L. Collins, *Proc. Symp. Low Energ. X Gamma Sources, 2nd, ORNL Rep. No. IIC-10, Austin, Tex., U.S.A.*, 1967.
31 R.H. Herber and S. Chandra, *J. Chem. Phys,*, 52 (1970) 6045.
32 R.H. Herber, S. Chandra and Y. Hazony, *J. Chem. Phys.*, 53 (1970) 3330.
33 R.W. Grant, H. Wiedersich, A.H. Muir, Jr., U. Gonser and W.N. Delgass, *J. Chem. Phys.*, 45 (1966) 1015.
34 R. Ingalls, *Phys. Rev. A*, 133 (1964) 787.
35 K. Ono and A. Ito, *Rev. Mod. Phys.*, 36 (1964) 351.
36 C.E. Johnson, *Proc. Phys. Soc., London*, 92 (1967) 748.
37 R. Ingalls, K. Ono and L. Chandler, *Phys. Rev.*, 172 (1968) 295.
38 R.W. Grant, *Mössbauer Eff. Methodol., Proc. Symp.*, 2 (1966) 23.
39 P.R. Edwards, C.E. Johnson and R.J.P. Williams, *J. Chem. Phys.*, 47 (1967) 2074.
40 T. Toan and L.F. Dahl, *J. Amer. Chem. Soc.*, 93 (1971) 2654.
41 A. Gerard, P. Imbert, H. Prange, F. Varret and M. Wintenberger, *J. Phys. Chem. Solids*, 32 (1971) 2091.
42 J.W.G. Wignall, *J. Chem. Phys,*, 44 (1966) 2462.
43 F.E. Obenshain, L.D. Roberts, C.F. Coleman, D.W. Forester and J.O. Thomson, *Phys. Rev. Lett.*, 14 (1965) 365.
44 A.H. Cooke, *Proc. Phys. Soc., London, Sect. A*, 62 (1949) 269.

45 B.J. Evans, S.S. Hafner and H.P. Weber, *J. Chem. Phys.*, 55 (1971) 5282.
46 M. Kaplan and T.X. Carroll, *Appl. Mössbauer Eff., Proc. Conf., Tihany, Hungary, June 1969*, Akademiai Kiado, Budapest, Hungary, p. 169.
47 N. Thrane, *Appl. Mössbauer Eff., Proc. Conf., Tihany, Hungary, June 1969*, Akademiai Kiado, Budapest, Hungary, p. 175.
48 M. Blume, *Phys. Rev. Lett.*, 18 (1967) 305.
49 M. Blume and J.A. Tjon, *Phys. Rev.*, 165 (1968) 446.
50 P.R. Edwards and C.E. Johnson, *J. Chem. Phys.*, 49 (1968) 211.
51 G.M. Bancroft, R.E.B. Garrod, A.G. Maddock, M.J. Mays and B.E. Prater, *Chem. Commun.*, (1970) 200.
52 G.M. Bancroft, R.E.B. Garrod and A.G. Maddock, *J. Chem. Soc. A*, (1971) 3165.
53 G.M. Bancroft, R.E.B. Garrod, A.G. Maddock, M.J. Mays and B.E. Prater, *J. Amer. Chem. Soc.*, 94 (1972) 647.
54 W.T. Oosterhuis and G. Lang, *J. Chem. Phys.*, 50 (1969) 4381.
55 W.M. Reiff, *162nd National A.C.S. Meeting, Inorg. Div., Washington, D.C., 1971*, paper 147.
56 W.M. Reiff, to be submitted for publication.
57 G. Lang, D. Herbert and T. Yonetani, *J. Chem. Phys.*, 49 (1968) 944.
58 B.W. Dale, R.J.P. Williams, P.R. Edwards and C.E. Johnson, *Trans. Faraday Soc.*, 64 (1968) 3011.
59 P.T. Manoharan and H.B. Gray, *J. Amer. Chem. Soc.*, 87 (1965) 3340.
60 C.E. Johnson, R. Rickards and H.A.O. Hill, *J. Chem. Phys.*, 50 (1969) 2594.
61 R.E. Watson and A.J. Freeman, *Phys. Rev.*, 123 (1961) 2027.
62 E. Konig and B. Kanellakopulos, *Chem. Phys. Lett.*, 12 (1972) 485.
63 B.W. Dale, R.J.P. Williams, P.R. Edwards and C.E. Johnson, *J. Chem. Phys.*, 49 (1968) 3445.
64 J.G. Cosgrove and R.L. Collins, *J. Chem. Phys.*, 55 (1971) 4238.
65 W.M. Reiff, unpublished results.
66 A.V. Ablov, A. Yu. Kon and T.L. Malinovskii, *Dokl. Chem.*, 167 (1966) 410.
67 J.G. Gibson and E.D. McKenzie, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 683.
68 G J. Long and W.A. Baker, *J. Chem. Soc. A*, (1971) 2956.
69 R.M. Golding, K.F. Mok and J.F. Duncan, *Inorg. Chem.*, 5 (1966) 774.
70 U. Ganiel, *Chem. Phys. Lett.*, 4 (1969) 87.
71 B.W. Dale, *J. Chem. Phys.*, 56 (1972) 4721.
72 J.G. Cosgrove and R.L. Collins, *J. Chem. Phys.*, 56 (1972) 4721.
73 H.A. Goodwin and R.N. Sylva, *Aust. J. Chem.*, 21 (1968) 83.
74 W.M. Reiff, to be submitted for publication.
75 E. Konig, G. Ritter, H. Spiering, S. Kremer, K. Madeja and A. Rosenkranz, *J. Chem. Phys.*, 56 (1972) 3139.
76 W.M. Reiff, *163rd National A.C.S. Meeting, Inorg. Div., Boston, Mass., 1972*, paper 160.
77 H.S. Preston and C.H.L. Kennard, *J. Chem. Soc. A*, (1969) 1956.
78 W.M. Reiff, to be submitted for publication.
79 W.M. Reiff, N.E. Erickson and W.A. Baker, *Inorg. Chem.*, 8 (1969) 2019.
80 W.M. Reiff, to be submitted for publication.
81 E. Konig, G. Ritter, E. Lindner and I.P. Lorenz, *Chem. Phys. Lett.*, 13 (1972) 70.
82 P. Singh, A. Clearfield and I. Bernal, *J. Coord. Chem.*, 1 (1971) 29.
83 B.W. Fitzsimmons and C.E. Johnson, *Chem. Phys. Lett.*, 6 (1970) 267.
84 M. Cox, B.W. Fitzsimmons, A.W. Smith, L.F. Larkworthy and K.A. Rogers, *J. Chem. Soc. A*, (1971) 2158.
85 C.E. Johnson, *Phys. Lett.*, 21 (1966) 491.
86 G. Lang, R. Aasa, K. Garbett and R.J.P. Williams, *J. Chem. Phys.*, 55 (1971) 4539.
87 W.M. Reiff, *J. Chem. Phys.*, 54 (1971) 4718.
88 W.M. Reiff, *159th National A.C.S. meeting, Phys. Div., Houston, Tex., U.S.A., 1970*, paper 127.
89 M.Y. Okamura, I.M. Klotz, C.E. Johnson, M.R.C. Winter and R.J.P. Williams, *Biochemistry*, 8 (1969) 1951.
90 A.N. Buckley, I.R. Herbert, B.D. Rumbold, G.V.H. Wilson and K.S. Murray, *J. Phys. Chem. Solids*, 31 (1970) 1423.

91 W.M. Reiff, *Mössbauer Eff. Methodol., Proc. Symp.*, 7 (1971) 213.
92 R. Lechan, C.R. Abeledo and R.B. Frankel, *Proc. Amer. Inst. Phys. Conf. Magn. Magn. Mater.*, 1971, 659.
93 W.M. Reiff, G.J. Long and W.A. Baker, *J. Amer. Chem. Soc.*, 90 (1968) 6347.
94 A.M. Buckley, B.D. Rumbold, G.V.H. Wilson and K.S. Murray, *J. Chem. Soc. A*, (1970) 2298.
95 W.M. Reiff, *Inorg. Chim. Acta*, 6 (1972) 267.
96 R.L. Martin and A.H. White, *Inorg. Chem.*, 6 (1967) 712.
97 G.C. Brackett, P.L. Richards and H.H. Wickman, *Chem. Phys. Lett.*, 6 (1970) 75.
98 H.H. Wickman, A.M. Trozzolo, H.G. Williams, G.W. Hull and F.R. Merritt, *Phys. Rev.*, 155 (1967) 563.
99 H.H. Wickman, *J. Chem. Phys.*, 56 (1972) 976.
100 R. Rickards, C.E. Johnson and H.A.O. Hill, *Trans. Faraday Soc.*, 65 (1969) 2847.
101 J.S. Griffith, *The Theory of Transition Metal Ions*, Cambridge University Press, London, 1961, p. 364.
102 K.W.H. Stevens, *Proc. Roy. Soc., Ser. A*, 219 (1953) 542.
103 W.M. Reiff, *Chem. Phys. Lett.*, 8 (1971) 297.
104 R.E. DeSimone and R.S. Drago, *J. Amer. Chem. Soc.*, 92 (1970) 2343.
105 W.M. Reiff, *Chem. Phys. Lett.*, in the press.
106 R.L. Martin and I.A.G. Roos, *Aust. J. Chem.*, 24 (1971) 2231.
107 R. Rickards, C.E. Johnson and H.A.O. Hill, *J. Chem. Soc. A*, (1971) 797.
108 R. Rickards, C.E. Johnson and H.A.O. Hill, *J. Chem. Soc. A*, (1971) 1755.
109 W.T. Oosterhuis and G. Lang, *Phys. Rev.*, 178 (1969) 439.
110 R. Rickards, C.E. Johnson and H.A.O. Hill, *J. Chem. Phys.*, 48 (1968) 5231.
111 R. Rickards, C.E. Johnson and H.A.O. Hill, *J. Chem. Phys.*, 51 (1969) 846.
112 R. Rickards, C.E. Johnson and H.A.O. Hill, *J. Chem. Phys.*, 53 (1970) 3118.
113 R.A. Mazak and R.L. Collins, *J. Chem. Phys.*, 51 (1969) 3220.
114 E.M. Shustorovich and M.E. Dyatkina, *Dokl. Akad. Nauk SSSR*, 128 (1959) 1234.
115 J.P. Dahl and C. Ballhausen, *Mat. Fys. Medd. Dan. Vid. Selsk.*, 33 (1961) No. 5.
116 F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 2nd edn., Interscience, New York, 1966, p. 764.
117 S.R. Bird, J.D. Donaldson, A.F. LeC. Holding, B.J. Senior and M.J. Tricker, *J. Chem. Soc. A*, (1971) 1616.
118 B.A. Goodman, R. Greatrex and N.N. Greenwood, *J. Chem. Soc., A*, (1971) 1868.
119 P.T. Greene and R.F. Bryan, *J. Chem. Soc. A*, (1970) 1696.
120 T.C. Gibb, B.A. Goodman and N.N. Greenwood, *Chem. Commun.*, (1970) 774.
121 J.D. Donaldson and B.J. Senior, *J. Inorg. Nucl. Chem.*, 48 (1968) 882.
122 N.N. Greenwood, P.G. Perkins and D.H. Wall, *Symp. Faraday Soc.*, 1 (1967) 51.
123 J.D. Donaldson, E.J. Filmore and M.J. Tricker, *J. Chem. Soc. A*, (1971) 1109.
124 M.G. Clark, A.G. Maddock and R.H. Platt, *J. Chem. Soc. Dalton*, (1972) 281.
125 B.A. Goodman and N.N. Greenwood, *Chem. Commun.*, (1969) 1105.
126 N.E. Erickson, *Chem. Commun.*, (1970) 1349.
127 E.O. Kazimir, M. Cefola and N.E. Erickson, *156th National A.C.S. Meeting, Inorg. Div., 1968*, paper 169.
128 P.T. Greene and R.F. Bryan, *J. Chem. Soc. A*, (1971) 2549.
129 R.V. Parish and C.E. Johnson, *Chem. Phys. Lett.*, 6 (1970) 239.
130 B.A. Goodman and N.N. Greenwood, *J. Chem. Soc. A*, (1971) 1862.
131 R.V. Parish, *Chem. Phys. Lett.*, 10 (1971) 224.
132 R.V. Parish and C.E. Johnson, *J. Chem. Soc. A*, (1971) 1906.
133 R.C. Poller and J.N.R. Ruddick, *J. Chem. Soc. Dalton*, (1972) 555.
134 B.W. Fitzsimmons, *J. Chem. Soc. A*, (1970) 3235.
135 B.A. Goodman, N.N. Greenwood, K.L. Jaura and K.K. Sharma, *J. Chem. Soc. A*, (1971) 1865.
136 T.C. Gibb, R. Greatrex and N.N. Greenwood, *J. Chem. Soc. Dalton*, (1972) 238.
137 C.E. Johnson and D.O. Hall, *Nature*, 217 (1968) 446.
138 G. Lang, *J. Chem. Soc. A*, (1971) 3245.