The Orientation of the Electric-field-gradient Tensor from Single-crystal Mössbauer Measurements

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The problem of determining the orientation of the electric-field-gradient tensor from Mössbauer single-crystal data is discussed generally in terms of the point symmetries of the resonant site and the space group. The effects of finite thickness, polarization, and anisotropy in the recoilless fraction are all taken into account. In many important cases it is possible to determine the relevant parameters from only one crystal by using a combination of polarized and unpolarized radiation, and several examples are discussed in detail.

THE electric-field-gradient (e.f.g.) tensor at a nucleus can be studied by Mössbauer spectroscopy, and provides useful information concerning the asymmetry of the chemical environment.[1] The magnitude and orientation of the tensor relative to the crystal axes can be fully specified by five parameters, but at least three of these can not be obtained from the Mössbauer spectrum of an isotropic powder. A classic paper by Zory [2] presented a method

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[1] T. C. Gibb, ' Principles of Mössbauer Spectroscopy,' Chapman and Hall, London, 1976.

[2] P. Zory, *Phys. Rev.*, 1965, **140**, A1401.

for determining all the tensor parameters from the angular dependence of the Mössbauer spectrum in a single crystal, and illustrated the approach with data for $FeCl_2 \cdot 4H_2O$. This work has been used as the basis for several subsequent papers on other compounds (*e.g.* $Fe[NH_4]_2[SO_4]_2 \cdot 6H_2O$ and $Fe[SO_4] \cdot 7H_2O$ by Chandra and Puri [3]). However, to simplify the analysis of the data it is usually assumed that the mean-square displacement tensor and hence the recoilless fraction are isotropic, and that the crystals are ' thin ' so that there is no saturation of the absorption intensity. The first assumption can introduce major errors when there are two or more non-equivalent orientations of the resonant site. The neglect of saturation is perhaps more serious, but it was not realized until much later [4] that the necessary correction involved the polarization of the absorption cross-section. I have also pointed out [5] that the work by Zory implicitly assumed that one of the minor axes of the e.f.g. tensor lies along the crystallographic *c* axis. There is no such restriction under the $P2_1/c$ space group, and the orientation of the tensor was redetermined [5] using a combination of polarized, and unpolarized, source experiments with full thickness corrections of the data.

A recent re-examination of the Zory method by Zimmermann [6] has shown that for the $P2_1/c$ space group the angular dependence of the single-crystal spectrum cannot provide a unique solution, but with additional data from applied-field experiments he was able to derive a solution in agreement with the polarized-source work. Zory did not consider the question of uniqueness, and Zimmermann has only analysed the specific case of monoclinic symmetry. Polarized-source measurements in this laboratory on several compounds have been analysed numerically by a tedious trial and error approach.[5,7-9]

In this paper I seek to establish guidelines for the determination of the e.f.g. tensor in a crystal of arbitrary space group where all the sites are crystallographically equivalent and the nuclear transition involves the spin states $I = \frac{1}{2}$ and $\frac{3}{2}$. Major emphasis is placed on the low-symmetry space groups, and some examples are discussed in detail.

RESULTS AND DISCUSSION

The Electric-field gradient and Intensity Tensors.—The electric-field gradient at the Mössbauer nucleus is a traceless symmetric tensor of the second rank with nine values V_{ij} $(i,j = p, q, r)$ in a Cartesian-axis system p, q, r. A principal-axis system x, y, z can be defined such that the tensor is diagonal with $|V_{zz}| \geqslant |V_{yy}| \geqslant |V_{xx}|$, and can then be completely specified by five parameters, V_{zz}, the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, and three angles α, β, and γ to define the orientation of x, y, z with respect to p, q, r. The tensor is invariant with respect to rotation by π about a major axis so that the solution for α,β,γ can be restricted to the range 0—π.

The observed quadrupole splitting Δ for a $\frac{1}{2} \rightarrow \frac{3}{2}$ Mössbauer transition is given by (1) where eQ is the

$$\Delta = \tfrac{1}{2}\, eQV_{zz}\, (1 + \tfrac{1}{3}\eta^2)^{\frac{1}{2}} \tag{1}$$

nuclear quadrupole moment. The spectrum comprises a symmetrical doublet *provided* that the absorber is an isotropic powder. If the absorber is a single crystal (*i.e.* is polarized) the two lines have different intensities which are dependent on the orientation of the tensor with respect to the direction of observation.

The most convenient parameters to record are the absorption areas of the lines at high and low Doppler velocity, I^{h} and I^{l} respectively. Zimmermann [6] has recently shown that the intensity for an infinitely thin absorber with one absorbing nucleus per unit cell can be represented by (2) where $I = I^{\mathrm{h}} + I^{\mathrm{l}}$, $I^{\mathrm{h}}{}_{ij}$ are the

$$I^{\mathrm{h}}/I = \sum_{i,j} I^{\mathrm{h}}{}_{ij}\, e_i e_j \;(i,j = p, q, r) \tag{2}$$

components of an intensity tensor in the p, q, r co-ordinate system, and $e_p = \sin\Theta\cos\Phi$, $e_q = \sin\Theta\sin\Phi$, and $e_r = \cos\Theta$ are the direction cosines of the direction of observation relative to p, q, r. The trace is given by (3),

$$I^{\mathrm{h}}{}_{pp} + I^{\mathrm{h}}{}_{qq} + I^{\mathrm{h}}{}_{rr} = \tfrac{3}{2} \tag{3}$$

and it is convenient to define a traceless intensity tensor by (4) which is now diagonal in the same principal-axis

$$I_{ij} = I^{\mathrm{h}}{}_{ij} - \tfrac{1}{2}\,\delta_{ij} \tag{4}$$

system as the e.f.g. tensor. Furthermore, the asymmetry parameter is given by (5) and there is a useful

$$\eta = (I_{xx} - I_{yy})/I_{zz} \tag{5}$$

$$\mathrm{sign}\,(V_{zz}) = \mathrm{sign}\,(I_{zz}) \tag{6}$$

$$16[I_{rr}{}^2 + \tfrac{1}{3}\,(I_{pp} - I_{qq})^2 + \tfrac{4}{3}\,(I_{pq}{}^2 + I_{pr}{}^2 + I_{qr}{}^2)] = I_{\Delta} = 1 \tag{7}$$

relation (7). If the traceless intensity tensor I_{ij} can be determined, numerical diagonalization can be used to obtain η and hence V_{zz} from the eigenvalues, and α,β,γ from the direction cosines, D_{ij}. (α is an anticlockwise rotation about r, followed by an anticlockwise rotation β about the new q axis, and finally an anticlockwise rotation γ about the new r axis.) The signs for D_{ij} are chosen so that the determinant is positive, and relations (8)—(10) are applicable.

$$\beta = \arccos\,(D_{rr}) \tag{8}$$

$$\alpha = \arccos\,(D_{rp}/\sin\beta) \tag{9}$$

$$\gamma = \arccos\,(-D_{pr}/\sin\beta) \tag{10}$$

If there are N sites in the unit cell which are crystallographically equivalent but differ in orientation then an

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[3] K. Chandra and S. P. Puri, *Phys. Rev.*, 1968, **169**, 272.

[4] R. M. Housley, U. Gonser, and R. W. Grant, *Phys. Rev. Letters*, 1968, **20**, 1279.

[5] T. C. Gibb, *Chem. Phys.*, 1975, **7**, 449.

[6] R. Zimmermann, *Nuclear Instr. Methods*, 1975, **128**, 537.

[7] T. C. Gibb, *J. Phys.* (*C*), 1975, **8**, 229.

[8] T. C. Gibb, *Chem. Phys. Letters*, 1975, **30**, 137.

[9] T. C. Gibb, *J.C.S. Dalton*, 1976, 1237.

averaged macroscopic intensity tensor can be defined by (11) where I^{n}_{ij} is the value at the nth site. The tensors

$$I^{\mathrm{M}}_{ij} = \frac{1}{N}\sum_{n=1}^{N} I^{n}_{ij} \qquad (11)$$

at the different sites are related by the crystal symmetry. However, the macroscopic intensity tensor I^{M}_{ij}, which has the symmetry of the space group rather than that of the resonant site, does not necessarily contain sufficient information to fully determine the individual site tensor I^{n}_{ij}. The quantity I^{M}_{Δ} can be defined, equivalent to I_{Δ} of equation (7) except that $I^{\mathrm{M}}_{\Delta} \neq 1$. Furthermore, equation (11) implicitly assumes that all the sites have the same recoilless fraction in the direction of observation, and this is also not necessarily true. One major problem is that no single-crystal absorber is truly thin, and in practice I^{M}_{ij} cannot be determined accurately without considering corrections for absorber thickness and polarization. Nevertheless the symmetry properties of the intensity tensor are very useful.

Mean-square Displacement Tensor.—The recoilless fraction in a direction w is related to the mean-square displacement of the nucleus $\langle w^2\rangle$ by (12) where $k =$

$$f = \exp(-k^2\langle w^2\rangle) \qquad (12)$$

$2\pi/\lambda$ is the wavevector of the γ-ray. $\langle w^2\rangle$ can also be represented in terms of a symmetric mean-square displacement tensor by (13). This is similar to equation (2)

$$\langle w^2\rangle = \sum_{i,j} \langle ij\rangle\, e_i e_j \; (i,j = p, q, r) \qquad (13)$$

except that there is no restriction on the trace of the tensor which is therefore fully specified by six parameters. The principal-axis system is *not necessarily* identical with that of the e.f.g. and intensity tensors. When there is more than one orientation of an equivalent site then $\langle w^2\rangle$ will in general differ at each site except in particular directions determined by the crystal symmetry. Examples of this are considered in due course.

Polarized Absorption in a Thick Absorber.—The intensity tensor refers specifically to an infinitely thin absorber with unpolarized incident radiation. A more exact approach is to consider absorption in a thick absorber, and additional information can be obtained by using polarized incident radiation. The necessary equations will now be developed.

The expression of the absorption intensity as a function of source polarization and absorber thickness can be derived from a more general result by Blume and Kistner.[10] The incident radiation can be represented by a 2×2 density matrix, ρ, which is a linear combination of the unit matrix and the Pauli matrices, σ. $\boldsymbol{P}$ is a vector

$$\rho = \tfrac{1}{2}(\boldsymbol{I} + \boldsymbol{P} \,.\, \boldsymbol{\sigma}) \qquad (14)$$

in Poincaré space representing the polarization with the three parameters $P_1 = P\cos2\chi\cos2\psi$, $P_2 = P\cos 2\chi\sin2\psi$, and $P_3 = P\sin2\chi$. If $P = 0$ the radiation is unpolarized, and $P = 1$ corresponds to complete polarization. When $\chi = 0$ the radiation is linearly polarized $\left(e.g.\text{ along the } s \text{ axis if } \psi = 0, t \text{ axis if } \psi = \frac{\pi}{2}, \text{ and at } 45° \text{ to the } s \text{ axis if } \psi = \frac{\pi}{4}\right)$, and when $\chi = \frac{\pi}{4}$ the radiation is circularly polarized.

The refractive index of the absorber at a distance w along the direction of propagation can also be written as a 2×2 matrix with elements n_{st}, *etc.*, and thus equation (15) is obtained together with (16)—(19) and $k = 2\pi/\lambda$ is

$$nkw = a + \boldsymbol{b} \,.\, \boldsymbol{\sigma} = a + b_1\sigma_1 + b_2\sigma_2 + b_3\sigma_3 \qquad (15)$$

where

$$a = \tfrac{1}{2}\, kw\, (n_{ss} + n_{tt}) \qquad (16)$$

$$b_1 = \tfrac{1}{2}\, kw\, (n_{ss} - n_{tt}) \qquad (17)$$

$$b_2 = \tfrac{1}{2}\, kw\, (n_{st} + n_{ts}) \qquad (18)$$

$$b_3 = \tfrac{1}{2}\, kw\, (n_{st} - n_{ts}) \qquad (19)$$

the wavevector of the γ-ray. The intensity of the radiation at w is given by (20) where $b = (b_1^2 + b_2^2 + b_3^2)^{\frac{1}{2}}$ and $\hat{b} = \boldsymbol{b}/b$. This is the general result derived by Blume and Kistner.

$$\begin{aligned} I(w) = \exp[\mathrm{i}(a - a^*)][&\cos b^* \cos b + (\hat{b}^* \,.\, \hat{b}) \sin b^* \sin b \\ &- \mathrm{i}(\hat{b}^* \,.\, \boldsymbol{P}) \sin b^* \cos b + \mathrm{i}(\hat{b} \,.\, \boldsymbol{P}) \sin b \cos b^* \\ &+ \mathrm{i}\boldsymbol{P} \,.\, (\hat{b}^* \Lambda \hat{b}) \sin b^* \sin b] \end{aligned} \qquad (20)$$

This unwieldy expression can be simplified under two specific conditions. First, if time-reversal invariance holds then n is a symmetric matrix and $n_{st} = n_{ts}$ so that $b_3 = 0$. Secondly, if the matrix is diagonal, *i.e.* $n_{st} = n_{ts} = 0$, then $b_2 = 0$. It is shown later that in the present context this condition can always be realized by a similarity transformation corresponding to a rotation of the s and t axes by an angle ε. The incident polarization is now effectively $P_1 = P\cos2\chi\cos2(\psi + \varepsilon)$, *etc.* The refractive index n has imaginary (absorption) and real (dispersion) components; designating the imaginary diagonal values in the rotated st co-ordinate system as $n_{ss}{}^{\mathrm{i}}$ and $n_{tt}{}^{\mathrm{i}}$, equation (20) can now be evaluated as in (21).

$$\begin{aligned} I(w) = {} & \tfrac{1}{2}[1 + P\cos2\chi\cos2(\psi + \varepsilon)] \exp(-2\, kw\, n_{ss}{}^{\mathrm{i}}) \\ & + \tfrac{1}{2}[1 - P\cos2\chi\cos2(\psi + \varepsilon)] \exp(-2\, kwn_{tt}{}^{\mathrm{i}}) \end{aligned} \qquad (21)$$

For a quadrupole splitting produced by an arbitrary number j of crystallographically equivalent sites it has been shown[11] that dispersion has no effect on absorption, *i.e.* we need only consider the imaginary components of the refractive index. These are given by (22)

$$2kwn^{\mathrm{i}} = \sum_{jk} \frac{a\, n\, f_j\, \sigma_0}{(x - x_{jk})^2 + 1} \begin{pmatrix} \rho_{ss}{}^{jk} & \rho_{st}{}^{jk} \\ \rho_{ts}{}^{jk} & \rho_{tt}{}^{jk} \end{pmatrix} \qquad (22)$$

where there are n sites of type j per unit area in equivalent orientation with a recoilless fraction of f_j, σ_0 is the resonant cross-section, a is the isotopic abundance for the

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[10] M. Blume and O. C. Kistner, *Phys. Rev.*, 1968, **171**, 417.

[11] R. W. Grant, H. Wiedersich, R. M. Housley, G. P. Espinosa, and J. O. Artman, *Phys. Rev.*, 1971, **B3**, 678.

Mössbauer nuclide, x is related to the energy E and the width of the Mössbauer line Γ by $x = 2E/\Gamma$, and the kth absorption line occurs at energy x_{jk}. The absorber density matrix ρ is normalized such that $\sum_k \rho_{ss}{}^{jk} = \sum_k \rho_{tt}{}^{jk} = 1$ and $\sum_k \rho_{st}{}^{jk} = \sum_k \rho_{ts}{}^{jk} = 0$. If all the sites have the same recoilless fraction f, and ρ is diagonal then we obtain (23) and (24) where $C_{\mathrm{A}} = anf\sigma_0$ is the effective absorption cross-section and is dimensionless.

$$2kwn_{ss}{}^{\mathrm{i}} = \sum_k \rho_{ss}{}^{k}C_{\mathrm{A}}/[(x - x_k)^2 + 1] \qquad (23)$$

$$2kwn_{tt}{}^{\mathrm{i}} = \sum_k \rho_{tt}{}^{k}C_{\mathrm{A}}/[(x - x_k)^2 + 1] \qquad (24)$$

The absorption at a Doppler shift $y = 2E_0\mathrm{v}/c\Gamma$ relative to a Lorentzian-source emission line is given by (25)

$$\varepsilon(y) = (\kappa f_{\mathrm{s}}/\pi)\int_{-\infty}^{\infty} [1 - I(w)]\mathrm{d}x/[1 + (x + y)^2] \qquad (25)$$

where f_{s} is the source recoilless fraction and $1 - \kappa$ is the fraction of ' background ' radiation present. The area of the spectrum, S, is given by (27).

$$\varepsilon(y) = \tfrac{1}{2}(\kappa f_{\mathrm{s}}/\pi)\int_{-\infty}^{\infty} \{[1 + P\cos2\chi\cos2(\psi + \varepsilon)]\text{-}$$
$$[1 - \exp(-2kwn_{ss}{}^{\mathrm{i}})] + [1 - P\cos2\chi\cos2(\psi + \varepsilon)]\text{-}$$
$$[1 - \exp(-2kwn_{tt}{}^{\mathrm{i}})]\}\frac{\mathrm{d}x}{1 + (x + y)^2} \qquad (26)$$

$$S = \int_{-\infty}^{\infty} \varepsilon(y)dy \qquad (27)$$

In the event that the k lines in the spectrum do not overlap the individual terms in the exponential can be separated so that the absorption maxima are given by (28)

$$\varepsilon(0)_k = \tfrac{1}{2}\kappa f_{\mathrm{s}}\{[1 + P\cos2\chi\cos2(\psi + \varepsilon)]R(\rho_{ss}{}^{k}C_{\mathrm{A}}) \qquad (28)$$
$$+[1 - P\cos2\chi\cos2(\psi + \varepsilon)]R(\rho_{tt}{}^{k}C_{\mathrm{A}})\}$$

$$\text{where } R(x) = 1 - \exp(-x/2)J_0(\mathrm{i}x/2) \qquad (29)$$

and $J_0(x)$ is a zero-order Bessel function of imaginary argument. Similarly, the area of the absorption line is given by (30) and $J_1(x)$ is a first-order Bessel function with imaginary argument.

$$S_k = \tfrac{1}{2}\kappa f_{\mathrm{s}}\pi\{[1 + P\cos2\chi\cos2(\psi + \varepsilon)]K(\rho_{ss}{}^{k}C_{\mathrm{A}})$$
$$+[1 - P\cos2\chi\cos 2(\psi + \varepsilon)]K(\rho_{tt}{}^{k}C_{\mathrm{A}})\} \qquad (30)$$

$$\text{where } K(x) = x\exp(-x/2)[J_0(\mathrm{i}x/2) + J_1(\mathrm{i}x/2)] \qquad (31)$$

If the source radiation is unpolarized ($P = 0$) then we obtain (32) which is the result used previously.[4,7,12]

$$S_k = \kappa f_{\mathrm{s}}\pi[\tfrac{1}{2}K(\rho_{ss}{}^{k}C_{\mathrm{A}}) + \tfrac{1}{2}K(\rho_{tt}{}^{k}C_{\mathrm{A}})] \qquad (32)$$
$$S_k{}^{s} = \kappa f_{\mathrm{s}}\pi K(\rho_{ss}{}^{k}C_{\mathrm{A}}) \qquad (33)$$

If the source is linearly polarized along s ($P = 1, \psi + \varepsilon = 0$) then equation (33) is applicable, and if linearly polarized along t $\left(P = 1,\ \psi + \varepsilon = \frac{\pi}{2}\right)$ then (34) is obtained, which are the results applied intuitively in the earlier work.[7] The more general equation (26) derived here is useful in that it expresses the absorption as a

$$S_k{}^{t} = \kappa f_{\mathrm{s}}\pi K(\rho_{tt}{}^{k}C_{\mathrm{A}}) \qquad (34)$$

function of an arbitrary source polarization. Furthermore, in instances where the resonant lines are not completely resolved it can be incorporated into a ' transmission-integral ' calculation to fully correct for both saturation *and* polarization.

The Absorber Density Matrix.—The absorber density matrix for a $\frac{1}{2},\frac{3}{2}$ transition with a quadrupole interaction has been derived elsewhere.[13] It can be re-expressed in a more general form in terms of the asymmetry parameter η and the Euler transformation D (ϕ, θ, δ) relating the observation Cartesian-co-ordinate system s, t, w to that for the e.f.g. x, y, z as (35)—(37) (*N.B.* in

$$\rho_{ss} = \tfrac{1}{2} \pm \tfrac{1}{4}\omega(a\cos^2\delta + b\sin^2\delta + \eta c\sin 2\delta) \qquad (35)$$

$$\rho_{tt} = \tfrac{1}{2} \pm \tfrac{1}{4}\omega(a\sin^2\delta + b\cos^2\delta - \eta c\sin 2\delta) \qquad (36)$$

$$\rho_{st} = \rho_{ts} = \pm\tfrac{1}{4}\omega[\tfrac{1}{2}(a - b)\sin 2\delta - \eta c\cos 2\delta] \qquad (37)$$

where

$$a = 1 + \eta\cos2\phi \qquad (38)$$

$$b = 1 - 3\sin^2\theta - \eta\cos^2\theta\cos 2\phi \qquad (39)$$

$$c = \cos\theta\sin 2\phi \qquad (40)$$

$$\omega = (1 + \tfrac{1}{3}\eta^2)^{-\frac{1}{2}} \qquad (41)$$

ref. 13 the value $\delta = 0$ was implicit). The upper sign refers to the $\pm\frac{1}{2}\rightarrow\pm\frac{3}{2}$ (π) transition and the lower sign to the $\pm\frac{1}{2}\rightarrow\pm\frac{1}{2}$ (σ) transition (which are of course only pure states for $\eta = 0$).

It is to be noted that the density matrix is always real, so that the resonance lines can only be linearly polarized, there being no elliptical component in any direction. If ρ is calculated in an arbitrary co-ordinate system s, t, w, then a similarity transformation exists corresponding to a rotation by (42) to a new co-ordinate system s', t', w in

$$\varepsilon = \tfrac{1}{2}\arctan[-2\rho_{st}/(\rho_{ss} - \rho_{tt})] \qquad (42)$$

which ρ is diagonal. This result was used earlier in the evaluation of equation (21) which is thus general for the quadrupole interaction. If there are j sites which are crystallographically equivalent, but differ in orientation with respect to the observation axes, then the sums $\rho_{ss}{}^{k} = \sum_k \rho_{ss}{}^{jk}$, *etc.* can be evaluated provided that all the elements are transformed to a common basis system by the appropriate similarity transformations. However, if the recoilless fraction is not isotropic, then the summation has to be written in the more general form $\rho_{ss}{}^{k}C_{\mathrm{A}} = an\sigma_0\sum_j f_j\rho_{ss}{}^{jk}$, *etc.* It has been shown[13] that the symmetry properties of the crystal can be used to define directions in which ρ will be diagonal, and I now extend this to a discussion of the crystallographic space groups.

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[12] T. C. Gibb, *J. Phys.* (*C*), 1974, **7**, 1001.

[13] R. M. Housley, R. W. Grant, and U. Gonser, *Phys. Rev.*, 1969, **178**, 514.

Influence of Site Symmetry and Space Group.—The e.f.g., intensity, and mean-square displacement tensors depend on both the point group of the resonant site and the space group of the crystal. However, the number of combinations of these which are distinguishable is conveniently small. In considering all the resonant sites in the crystal it can be seen that any two sites related by a simple translation, or by an inversion operation followed by a translation, have the identical symmetric second-rank tensor properties (V_{ij}, I_{ij}, and $\langle ij \rangle$ are invariant) and are therefore entirely equivalent. It is therefore only the point symmetry of the space group which concerns us. Furthermore, two site orientations related by a mirror plane for example can also be considered as being related by an inversion followed by a two-fold rotation. Thus the point groups $2(C_2)$, $m(C_s)$, and $2/m(C_{2h})$ can be treated collectively as the Laue group $2/m(C_{2h})$. In this way the 32 point groups can be reduced to the 11 Laue-symmetry groups. The point symmetry of the resonant site may be lower than that of the space group, resulting in there being more than one distinct orientation of that site in the unit cell. In some instances the tensor properties remain invariant. The Table shows the 11 Laue-symmetry groups together with the number of resonant sites which have to be considered in each case. Both the International and Schönflies symbols are given.

The minimum number of resonant sites to be considered for each point symmetry [a]

Space-group symmetry / Site symmetry	Cubic		Hexagonal		Trigonal		Tetragonal		Orthorhombic	Monoclinic	Triclinic
	$m3m$ (O_h)	$m3$ (T_h)	$6/mmm$ (D_{6h})	$6/m$ (C_{6h})	$\bar{3}/m$ (D_{3d})	$\bar{3}$ (C_{3i})	$4/mmm$ (D_{4h})	$4/m$ (C_{4h})	mmm (D_{2h})	$2/m$ (C_{2h})	1 (C_{2i})
$\bar{1}$	24	12	12	6	6	3	3	4	4	2	1
$2/m$	12	6	6 [b]	3	3		4 [b]	2	2	1	
mmm	6	3	3				2		1		
$4/m$	3						1	1			
$4/mmm$	3						1				
$\bar{3}$	4	4	1	1	1	1					
$\bar{3}/m$	4		1		1						
$6/m$			1	1							
$6/mmm$			1								
$m3$	1	1									
$m3m$	1										

[a] The sites indicated do not necessarily exist in all the space groups of that symmetry. [b] The two-fold axis may be parallel or perpendicular to the n fold axis.

Those cases where only one site has to be considered will be examined first, followed by the more complicated examples with multiple sites.

One effective site orientation. When the orientation of the resonant site is effectively unique, then only five distinct cases can arise

(1) *Cubic symmetry*. If the Laue-symmetry group is $m3m$ or $m3$, *i.e.* for all the cubic space groups, the e.f.g. and intensity tensors vanish ($V_{ij} = I_{ij} = 0$) and there is no quadrupole splitting.

(2) *Axial symmetry*. If the point group has hexagonal, trigonal, or tetragonal symmetry the direction of z is along the six, three, or four-fold symmetry axis, $V_{xx} = V_{yy} = -\frac{1}{2}V_{zz}$, and the asymmetry parameter $\eta = 0$. Only the sign of V_{zz} remains to be determined. The intensity as a function of the angle θ between the direction of observation and the principal axis z is given by (43)

$$I^{\mathrm{h}}/I = \tfrac{1}{2} \pm \tfrac{1}{8}(3\cos^2\theta - 1) \qquad (43)$$

where the upper (lower) sign refers to a positive (negative) sign of eQV_{zz}. The observed intensity ratio in only one orientation of a single crystal (with $\theta \leqslant 54.7$ or $\theta \geqslant 54.7°$) provides a unique solution for the sign of V_{zz}. An accurate measurement of the intensity ratio is not essential, and thickness correction of the data is not required. Examples of compounds where this procedure has been applied [14,15] include $[Fe_2(CO)_9]$ and $[Co(NH_3)_6][Fe(CN)_6]$.

(3) *Orthorhombic symmetry*. The three orthorhombic symmetry groups 222 (D_2), $mm2$ (C_{2v}), and mmm (D_{2h}) have the three principal axes defined as the crystallographic axes but in an unknown order, and the problem is to determine the sign of V_{zz}, the magnitude of η, and the correct choice of axes. If the principal axes are chosen arbitrarily to be the Cartesian set p,q,r then the intensity tensor is already in diagonal form and the observed intensity can be expressed in terms of polar angles Θ and Φ as (44). Because of the trace condition

$$I^{\mathrm{h}}/I = I^{\mathrm{h}}_{pp}\sin^2\Theta\cos^2\Phi + I^{\mathrm{h}}_{qq}\sin^2\Theta\sin^2\Phi + I^{\mathrm{h}}_{rr}\cos^2\Theta \qquad (44)$$

[equation (3)], it is only necessary to determine I^{h}/I accurately in *two* different directions (conveniently by rotating the same crystal) to obtain values for I^{h}_{pp}, I^{h}_{qq}, and I^{h}_{rr}. The traceless values (I_{pp}, *etc.*) now indicate the correct choice of principal axes to obtain $0 \leqslant \eta \leqslant 1$. However, to obtain an accurate value for η it is essential to refine the data by carrying out a proper thickness correction using the density-matrix equations. Of particular note is that the mean-square displacement $\langle w^2 \rangle$ will be dependent on direction.

An alternative procedure is to determine the area ratio in only one arbitrary direction of observation w using both unpolarized and linearly polarized radiation (from for example a source of ^{57}Co in iron metal magnetized normal to w so that $P = 1$ and $\chi = 0$). The appropriate

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[14] T. C. Gibb, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc.* (*A*), 1968, 890.

[15] T. C. Gibb, *J.C.S. Dalton*, 1977, 1910.

density matrix for an s, t, w axis system defined by Φ, Θ, $\lambda = 0$ so that s and t correspond to the directions of linear polarization in the source $\left(\psi = 0, \frac{\pi}{2}\right)$ can be calculated from equations (35)—(37) as a function of η. The co-ordinate system can then be rotated by an angle ε [equation (42)] to give the diagonal values $(\rho_{ss})'$ and $(\rho_{tt})'$. The area ratio with the unpolarized source follows directly from equation (32) and is given by (45).

$$I_1 = I^{\mathrm{h}}/I^{\mathrm{l}} = \frac{K[(\rho_{ss}{}^{\mathrm{h}})'C_{\mathrm{A}}] + K[(\rho_{tt}{}^{\mathrm{h}})'C_{\mathrm{A}}]}{K[(\rho_{ss}{}^{\mathrm{l}})'C_{\mathrm{A}}] + K[(\rho_{tt}{}^{\mathrm{l}})'C_{\mathrm{A}}]} \qquad (45)$$

The area ratio for linear polarization along s is obtained from equation (30) and is given by (46), and for linear polarization along t by (47).

$$I_2 = \frac{(1 + \cos 2\varepsilon)K[(\rho_{ss}{}^{\mathrm{h}})'C_{\mathrm{A}}] + (1 - \cos 2\varepsilon)K[(\rho_{tt}{}^{\mathrm{h}})'C_{\mathrm{A}}]}{(1 + \cos 2\varepsilon)K[(\rho_{ss}{}^{\mathrm{l}})'C_{\mathrm{A}}] + (1 - \cos 2\varepsilon)K[(\rho_{tt}{}^{\mathrm{l}})'C_{\mathrm{A}}]} \qquad (46)$$

$$I_3 = \frac{(1 - \cos 2\varepsilon)K[(\rho_{ss}{}^{\mathrm{h}})'C_{\mathrm{A}}] + (1 + \cos 2\varepsilon)K[(\rho_{tt}{}^{\mathrm{h}})'C_{\mathrm{A}}]}{(1 - \cos 2\varepsilon)K[(\rho_{ss}{}^{\mathrm{l}})'C_{\mathrm{A}}] + (1 + \cos 2\varepsilon)K[(\rho_{tt}{}^{\mathrm{l}})'C_{\mathrm{A}}]} \qquad (47)$$

For maximum sensitivity one requires that ε be small, and the initial experiment may show a better choice of polarization axes. The method requires that the recoilless fraction be known in only one direction, but the numerical refinement of the data to obtain η is more complex so that this advantage is largely negated in the orthorhombic case. However, the principles involved become more useful for lower symmetries where more directions of observation are otherwise required.

(4) *Monoclinic symmetry.* In the point groups 2 (C_2), m (C_s), and $2/m$ (C_{2h}) only one principal axis of the e.f.g. is constrained to lie along a two-fold axis (or normal to a mirror plane which is equivalent in effect). There are therefore three parameters to determine, the sign of V_{zz}, the magnitude of η, and the angle of rotation α of the principal axis system in the plane normal to the two-fold axis. If the latter is defined as being the r axis of a p, q, r axis system based on the crystal axes then $I^{\mathrm{h}}{}_{pq} = I^{\mathrm{h}}{}_{qp}$ are now finite and we obtain (48).

$$I^{\mathrm{h}}/I = I^{\mathrm{h}}{}_{pp} \sin^2\Theta \cos^2\Phi + 2I^{\mathrm{h}}{}_{pq} \sin^2\Theta \cos\Phi \sin\Phi + I^{\mathrm{h}}{}_{qq} \sin^2\Theta \sin^2\Phi + I^{\mathrm{h}}{}_{rr} \cos^2\Theta \qquad (48)$$

Using the trace condition, measurements of I^{h}/I for *three* orientations can determine all the values of the intensity tensor, diagonalization of which then gives α, η, and the sign of V_{zz}. Once again a proper thickness correction is essential.

Alternatively, the polarized measurements described for orthorhombic symmetry can be used except that Φ is replaced by $\Phi - \alpha$.

(5) *Triclinic symmetry.* The triclinic point groups 1 (C_1) and $\bar{1}$ (C_i) place no restrictions on the orientation of the e.f.g. tensor and the five parameters include the three Euler angles α, β, and γ. This represents the least favourable situation. All the nine values of the intensity tensor are finite and *five* measurements of I^{h}/I with thickness corrections is the minimum number required to specify the e.f.g. tensor. The directions of observation can be chosen once the crystal habit is known. If only one crystal plane is obtainable, the combination of polarized and unpolarized measurements in say two directions will probably provide a unique solution, but each case will require individual treatment following the principles already outlined.

Multiple site orientations. When the point symmetry of the resonant site is lower than that of the space group then the macroscopic intensity tensor has the symmetry of the latter (assuming that the recoilless fraction is isotropic). In a few instances where both symmetries are axial, *e.g.* $4/m$ and $4/mmm$ (see Table), there is no effect on the e.f.g. and intensity tensors; only one site has to be considered, and the previous arguments can still be applied. For symmetries lower than axial, the inclusion of more than one site orientation results in the macroscopic intensity tensor containing insufficient information to specify the orientation of the e.f.g. tensor, and I shall now show how these limitations affect specific cases.

(1) *Triclinic sites in monoclinic space group.* The simplest case to consider is a monoclinic space group, the two distinct triclinic sites therein being effectively related in orientation by a two-fold axis (as already shown, a mirror plane is equivalent in effect to a two-fold axis). A p, q, r axis system can be defined such that r is the effective two-fold axis. The observation-axis system s, t, w is given by the Euler transform $D(\Phi,\Theta,\lambda)$. The terms $\langle pr \rangle$ and $\langle qr \rangle$ in the mean-square displacement tensor change sign under a two-fold rotation, and therefore $\langle w^2 \rangle$ can only remain invariant if $\Theta = 0$ or 90°, *i.e.* for observation parallel or normal to r. The appropriate density matrices have been evaluated previously.[7,12] In the orientation with $\Theta = 90°$ (observation normal to r axis) the diagonal matrix elements ($\rho_{st} = 0$) are obtained from equations (35)—(37) using the relations (49)—(55).

$$\sin^2\theta = 1 - (\hat{w} \cdot \hat{z})^2 = \kappa \qquad (49)$$

$$\cos 2\phi = [(\hat{w} \cdot \hat{x})^2 - (\hat{w} \cdot \hat{y})^2]/\kappa \qquad (50)$$

$$\cos^2\theta \cos 2\phi = [(\hat{w} \cdot \hat{x})^2 - (\hat{w} \cdot \hat{y})^2](\hat{w} \cdot \hat{z})^2/\kappa \qquad (51)$$

$$\cos\theta \sin 2\phi = 2(\hat{w} \cdot \hat{x})(\hat{w} \cdot \hat{y})(\hat{w} \cdot \hat{z})/\kappa \qquad (52)$$

$$\sin^2\delta = (\hat{t} \cdot \hat{z})^2/\kappa \qquad (53)$$

$$\cos^2\delta = (\hat{s} \cdot \hat{z})^2/\kappa \qquad (54)$$

$$\sin\delta \cos\delta = -(\hat{s} \cdot \hat{z})(\hat{t} \cdot \hat{z})/\kappa \qquad (55)$$

where
$$\hat{w} \cdot \hat{x} = \cos\gamma \cos\beta \cos(\alpha - \Phi) - \sin\gamma \sin(\alpha - \Phi) \qquad (56)$$

$$\hat{w} \cdot \hat{y} = -\sin\gamma \cos\beta \cos(\alpha - \Phi) - \cos\gamma \sin(\alpha - \Phi) \qquad (57)$$

$$\hat{w} \cdot \hat{z} = \sin\beta \cos(\alpha - \Phi) \qquad (58)$$

$$\hat{s} \cdot \hat{z} = \sin\beta \sin(\alpha - \Phi) \qquad (59)$$

$$\hat{t} \cdot \hat{z} = \cos\beta \qquad (60)$$

The t axis is parallel to the two-fold axis.

The density-matrix elements are dependent on the e.f.g. parameters, η, α, β, and γ, and on the direction of observation Φ which is known. These equations may be evaluated numerically in the search for solutions to experimental data,[5,7,9] but this approach is not entirely satisfactory.

Zimmermann[6] pointed out that the intensity tensor elements I_{pr} and I_{qr} also change sign under the action of a two-fold rotation so that $I^{M}_{pr} = I^{M}_{qr} = 0$. The observable tensor thus has monoclinic symmetry, and two components of the local site tensor are not recorded. However, from equation (7) the condition (61) imposes a

$$I_{pr}^2 + I_{qr}^2 = \frac{3}{64}(1 - I^{M}{}_{\Delta}) \equiv L^2 \qquad (61)$$

constraint on the system such that defining $I_{pr} = L\cos\psi$ and $I_{qr} = L\sin\psi$ expresses the intensity tensor in terms of a single unknown parameter ψ $(0 < \psi < \pi)$. If the values of I^{M}_{ij} can be determined, then the parameters η, α, β, and γ can be expressed as a function of ψ, and it only requires an independent determination of η to solve the system uniquely. This procedure was demonstrated[6] in principle for $FeCl_2{\cdot}4H_2O$, but is also subject to criticism.

It is not always possible to measure η at the same temperature as in the single-crystal measurement. Thus Zimmerman quotes an η value at 200 K and an intensity tensor at 300 K. The intensity tensor cannot be corrected for thickness effects directly since it does not contain any expression of the polarization correction. Consequent errors can only be reduced by making observations in several very different directions which immediately restricts the method to large crystals. The six directions recommended by Zimmermann include two where the recoilless fractions are not identical at both sites, and his final equations are only valid for $I_{pq} = 0$ which is not a general condition.

A more satisfactory procedure is to use a combination of data obtained with both polarized and unpolarized sources. For example, with the direction of observation normal to the two-fold axis one can measure the experimental parameter I_1 with an unpolarized source and I_2 and I_3 with a polarized source. The values of I_2 and I_3

$$I_1 = I^{h}/I^{l} = \frac{K(\rho_{ss}{}^{h}C_A) + K(\rho_{tt}{}^{h}C_A)}{K(\rho_{ss}{}^{l}C_A) + K(\rho_{tt}{}^{l}C_A)} \qquad (62)$$

$$I_2 = K(\rho_{tt}{}^{h}C_A)/K(\rho_{tt}{}^{l}C_A) \qquad (63)$$

$$I_3 = K(\rho_{ss}{}^{h}C_A)/K(\rho_{ss}{}^{l}C_A) \qquad (64)$$

also depend on ψ and can be used to resolve the ambiguity. Unfortunately, a close inspection of the available data for the intensity tensor in $FeCl_2{\cdot}4H_2O$ shows that they are not fully self-consistent. However, they are in reasonable accord with the solution proposed from accurate polarization data by a trial-and-error approach.[5]

In order to demonstrate the new method more clearly I have measured the intensity ratio of the spectrum of $Fe[NH_4]_2[SO_4]_2{\cdot}6H_2O$ for a single crystal at three different orientations normal to the two-fold axis (these measurements extend the earlier work[7,12]). The dependence of the intensity on Φ may be expressed as in (65). The experimental values obtained from a crystal

$$I^{h}(\Phi) = \cos^2\Phi\, I^{h}{}_{pp} + \sin^2\Phi\, I^{h}{}_{qq} + 2\cos\Phi\sin\Phi\, I^{h}{}_{pq} \qquad (65)$$

containing 37.2 mg cm^{-2} of iron were $I^{h}(108°) = 0.466$, $I^{h}(138°) = 0.355$, and $I^{h}(168°) = 0.390$. These values were initially corrected to give approximate zero-thickness values using a recoilless fraction of $f = 0.27$. (Although the value of f will not necessarily be the same in all the three orientations, the crystal is quite thick and saturating strongly enough to reduce the sensitivity to any errors in f. This point may be appreciated more easily by referring to Figure 4 of ref. 5.) Solution of three simultaneous equations gives values of $I^{h}{}_{pp}$, $I^{h}{}_{qq}$, and $I^{h}{}_{pq}$, with $I^{h}{}_{rr}$ then being given by the trace condition in equation (3). Values for α, β, γ and η can then be calculated as a function of ψ, and the thickness correction improved by successive approximations (only 2—3 steps are necessary) to give a self-consistent result.

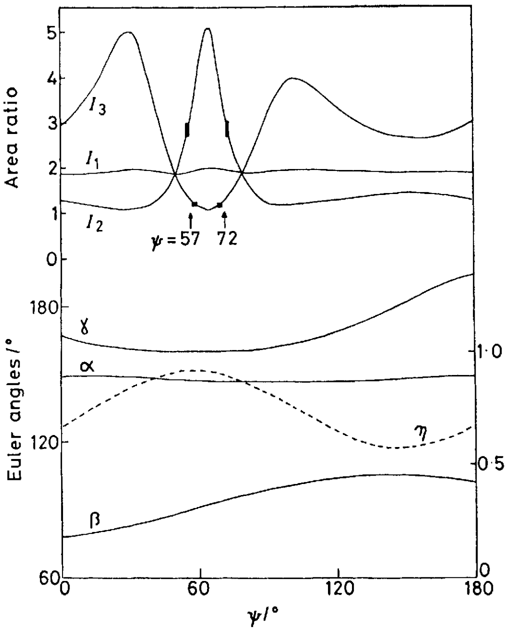

FIGURE 1 Dependence of α, β, γ, and η on the value of ψ from experimental data for $Fe[NH_4]_2[SO_4]_2{\cdot}6H_2O$. The calculated values for I_1, I_2, and I_3 are also shown, together with the experimental values for I_2 and I_3 which indicate two solutions at ψ = 57 and 72°

The final values for the traceless macroscopic intensity tensor were $I^{M}{}_{pp} = -0.105$, $I^{M}{}_{qq} = 0.071$, $I^{M}{}_{rr} = 0.034$, and $I^{M}{}_{pq} = 0.184$. The values of α, β, γ and η as a function of ψ are shown in Figure 1, together with values for I_1, I_2, and I_3 for $\Phi = 138°$ and a crystal of thickness 29.5 mg cm^{-2}. The experimental values[7] for I_2 and I_3 are indicated and result in two solutions, both with eQV_{zz} negative in sign: (A) $\alpha = 147$, $\beta = 93$, $\gamma = 160°$, and $\eta = 0.90$, for $\psi = 57°$; (B) $\alpha = 148$, $\beta = 89$, $\gamma = 160°$, and $\eta = 0.91$, for $\psi = 72°$. These are almost identical.

However, it can be shown that an additional polarized-source experiment for $\Phi = 168°$ would give a unique solution and thus specify the intensity tensor at each site. However, the same experiment for $\Phi = 108°$ does not give such a clear distinction. It is thus possible to ' design ' additional experiments once the general experimental situation has been defined. The above results can be compared to the previous trial-and-error estimates[7] (converted to have a negative sign for eQV_{zz}) of $\alpha = 140$, $\beta = 90$, $\gamma = 155°$, and $\eta = 1.0$. The agreement is satisfactory. The calculated values I^h (108, 138, 168) = 0.467, 0.352, and 0.386 for $\psi = 57°$ and I^h (108, 138, 168) = 0.467, 0.354, and 0.390 for $\psi = 72°$ are in excellent agreement with experiment, and differ considerably from the zero-thickness values of I^h (108, 138, 168) = 0.446, 0.291, and 0.328.

However, there remains a fundamental ambiguity in that this solution only applies to one of the two sites; the rotation of π about the r axis results in the alternative solution $\pi + \alpha,\beta,\gamma$ but the correct assignment to a given site can only be inferred.

(2) *Monoclinic sites in orthorhombic symmetry.* If the space group is orthorhombic, but the local site symmetry is only monoclinic, then two sites have to be considered. A typical example is $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$ with space group $P_{nnm}(D_{2h}^{12})$. The p,q,r axis system is related to the crystallographic axes such that one of the major axes of the e.f.g. must lie along r and the two sites are effectively related in orientation by two-fold rotations about p and q. The intensity tensor has four values, I_{pp}, I_{qq}, I_{rr}, and I_{pq} of which only I_{pq} changes sign under two-fold rotation. Thus $I^{M}{}_{pq} = 0$ and the macroscopic intensity tensor only defines three of the four values, but from equation (7) one finds (66). If all the four tensor

$$I_{pq}{}^2 = \tfrac{3}{64}\,(1 - I^{M}{}_{\Delta}) \qquad (66)$$

components are known, then the value of the angle ζ, which specifies the rotation about r into the principal-axis system, is given by $\zeta = \tfrac{1}{2}\arctan\,[\pm 2I_{pq}/(I_{pp} - I_{qq})]$, but the ambiguity in the sign of I_{pq} in equation (66) results in a choice of sign for α and thus in the assignment of axes to the two sites.

Once again the recoilless fraction is the same for both sites if the direction of observation is parallel or normal to one of the effective two-fold axes. The determination of the macroscopic intensity tensor requires measurements in at least two directions with a full thickness correction, and this procedure has already been described.[16] A more useful alternative is to use polarized radiation along only one direction of observation normal to a two-fold axis.[8] In general, the density matrices can be derived from the equations for monoclinic symmetry (49)—(55) with the appropriate restrictions on α, β, and γ. The area ratio for an unpolarized source is given by equation (62) and is a function of ζ and η only. The value of I_1 in $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$ is 0.927, which can be corrected by successive approximations to a thickness-corrected value of 0.906. Algebraic expression of ζ as a function of η is followed by calculating the polarized values I_2 and I_3 [equations (63) and (64)]. The result is a unique solution with eQV_{zz} positive in sign, $\eta = 0.10 \pm 0.05$, and $\zeta = \pm\,(40 \pm 2°)$ as shown in Figure 2. The boxes indicate the experimental results $I_1 = 0.927(11)$, $I_2 = 1.444(43)$, and $I_3 = 0.571(13)$.

(3) *Triclinic sites in orthorhombic symmetry.* The density matrices for four triclinic sites in orthorhombic symmetry may be obtained by combining the density matrices for monoclinic symmetry (49)—(55) with observation directions of $\pm\Phi$. However, the resulting equations depend on α, β, γ, and η. No less than three values of the intensity tensor are unspecified (I_{pq}, I_{qr}, and I_{pr}), and even if η is available by independent measurement it will be difficult to determine α, β, and γ.

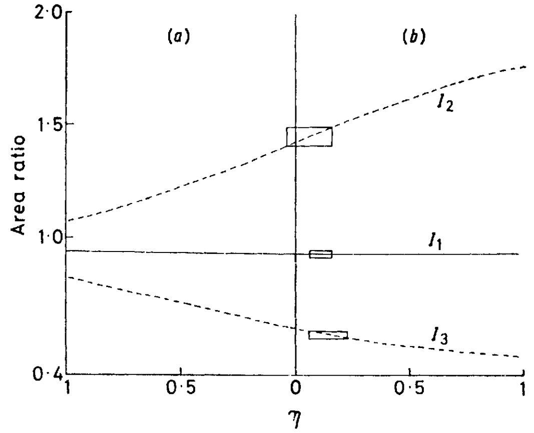

FIGURE 2 Results of polarized measurements on $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$ with the observation axis at 37.5° to the b axis in the bc plane: (a) y axis, (b) x axis in c. Using the observed value of I_1, the algebraic expression of ξ as a function of η leads to the value $\xi = \pm(40 \pm 2°)$. The values for I_2 and I_3 can then be used to obtain a unique solution with eQV_{zz} positive in sign and $\eta = 0.10 \pm 0.05$

(4) *Orthorhombic sites in axial symmetry.* When there are two orthorhombic sites in tetragonal symmetry the x,y,z axes are parallel to the crystallographic axes but in an unknown order. The recoilless fraction is invariant only along the four-fold (r) axis, or for $\Phi = 45°$, *i.e.* in the {110} planes. The traceless macroscopic intensity tensor with $I^{M}{}_{rr} = I_{rr}$ and $I^{M}{}_{qq} = I^{M}{}_{pp} = -\tfrac{1}{2}I_{rr}$ only specifies I_{rr} directly, but I_{pp} and I_{qq} are implied *via* equations (3) and (7) so that we obtain (67) and (68).

$$(I_{pp} - I_{qq})^2 = \tfrac{3}{16}\,[1 - 16(I^{M}{}_{rr})^2] \qquad (67)$$

$$I_{pp,qq} = -\tfrac{1}{2}\,I^{M}{}_{rr} \pm \frac{3^{\frac{1}{2}}}{8}\,[1 - 16(I^{M}{}_{rr})^2]^{\frac{1}{2}} \qquad (68)$$

The magnitude and sign of the principal value and the value of η can now be determined, but not the relative order of the axes p and q. There is therefore a fundamental ambiguity in the assignment of the p and q axes to the two equivalent sites.

The density matrices are independent of Φ but depend on which axis lies along the four-fold axis and on Θ.

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[16] R. W. Grant, R. M. Housley, and U. Gonser, *Phys. Rev.*, 1969, **178**, 523.

With the t axis normal to the four-fold axis the matrices are given by (69)—(71) where $x = \omega, -\frac{1}{2}\omega(1 + \eta)$,

$$\rho_{ss} = \tfrac{1}{2} \pm \tfrac{1}{4}x \qquad (69)$$

$$\rho_{tt} = \tfrac{1}{2} \pm \tfrac{1}{4}x\,(3\cos^2\Theta - 2) \qquad (70)$$

$$\rho = \tfrac{1}{2}(\rho_{ss} + \rho_{tt}) = \tfrac{1}{2} \pm \tfrac{1}{8}x(3\cos^2\Theta - 1) \qquad (71)$$

or $-\frac{1}{2}\omega(1 - \eta)$ for z, y, or x axis along the four-fold axis. The values of I_1, I_2, and I_3 [equations (62)—(64)] for zero thickness are plotted as a function of η in Figure 3 for $\Theta = 90°$ (which is the most suitable choice of direction) and eQV_{zz} defined as positive. Although the value of I_1 in isolation gives an unambiguous result, the polarized ratios I_2 and I_3 are much more sensitive, and in particular one component in the I_2 ratio is very small for z along the four-fold axis. A careful thickness correction for one set of data in an appropriate direction can specify the e.f.g. tensor.

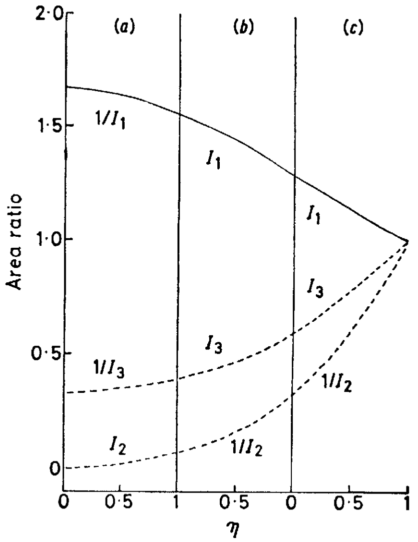

FIGURE 3 The area ratios I_1, I_2, and I_3 as a function of η for two orthorhombic sites in tetragonal symmetry calculated for zero thickness, $\Theta = 90°$, and eQV_{zz} defined as positive: (a) z, (b) y, and (c) x in four-fold axis. Note that the polarized ratios I_2 and I_3 are much more sensitive than the unpolarized value I_1 to the value of η.

The same density-matrix equations apply in principle for three orthorhombic sites in hexagonal symmetry, except that the recoilless fraction is only strictly invariant along the six-fold axis, which will probably not be favoured experimentally. However, by assuming f to be isotropic a reasonable determination can be made except that the error in the value of η may be larger.

(5) *Monoclinic sites in axial symmetry.* The case of two or four monoclinic sites in tetragonal ($4/m$ or $4/mmm$) symmetry with one axis of the e.f.g. tensor parallel to the four-fold axis is closely analogous to the orthorhombic case in that when f is isotropic the equations are identical and are independent of the rotation of axes in the plane normal to the four-fold axis. The equivalent plane to {110} in which f is invariant still exists, but its orientation is unknown, although the condition still holds along the four-fold axis. However, most of the information can be obtained with resonable accuracy except for the rotation angle. The same argument applies to three or six monoclinic sites in hexagonal ($6/m$ or $6/mmm$) symmetry with one axis of the e.f.g. tensor parallel to the six-fold axis.

If there are four monoclinic sites in tetragonal ($4/mmm$), three in trigonal ($3/m$), or six in hexagonal ($6/mmm$) symmetry with the unique axis normal to the major orientation axis then the density matrix is more complex. For example, for observation along the n-fold axis (with f isotropic) we have (72) for the z axis in the plane normal

$$\rho = \rho_{ss} = \rho_{tt} = \tfrac{1}{2} \mp \tfrac{1}{8}\omega\,(1 - \eta\cos 2\gamma) \qquad (72)$$

to the n-fold axis and an angle γ between the y axis and this plane, (73) for the x axis in the plane and an angle β

$$\rho = \rho_{ss} = \rho_{tt} = \tfrac{1}{2} \pm \tfrac{1}{8}\omega\,(2 - 3\sin^2\beta - \eta\sin^2\beta) \qquad (73)$$

$$\rho = \rho_{ss} = \rho_{tt} = \tfrac{1}{2} \pm \tfrac{1}{8}\omega\,(2 - 3\sin^2\beta + \eta\sin^2\beta) \qquad (74)$$

between the n-fold axis and z, and (74) for the y axis in the plane. The density matrix is thus a function of two parameters which cannot be separated.

(6) *Triclinic sites in axial symmetry.* When the point symmetry is triclinic but the space group is tetragonal, trigonal, or hexagonal the recoilless fraction is only invariant along the n-fold axis. The density matrix is then given by (75) which is independent of α, but a

$$\rho = \rho_{ss} = \rho_{tt} = \tfrac{1}{2} \pm \tfrac{1}{8}\omega\,(2 - 3\sin^2\beta + \eta\sin^2\beta\cos 2\gamma) \qquad (75)$$

complex function of β, γ, and η. Even under the assumption that f is isotropic, the equations for the angular dependence are too complex for practical application.

(7) *Sites in cubic symmetry.* When the site symmetry is lower than cubic but the space group is cubic the macroscopic intensity tensor is always diagonal ($I^{M}_{pp} = I^{M}_{qq} = I^{M}_{rr} = \frac{1}{2}$) and the spectrum is a symmetrical doublet in all orientations. Thus no information regardin the e.f.g. tensor can be obtained.

However, this result is only strictly true when the recoilless fraction is isotropic. This can be illustrated by considering three equivalent tetragonal-site orientations in cubic ($m3m$) symmetry, the four-fold axes being orthogonal. From equations (12) and (13) f will usually be angular dependent with a mean-square displacement given by (76). All the three sites contribute

$$\langle w^2\rangle = \sin^2\Theta\,\langle x^2\rangle + \cos^2\Theta\,\langle z^2\rangle \qquad (76)$$

equally only along the ⟨111⟩ directions for which $\cos^2\Theta = 1/3$. However, along the ⟨100⟩ directions, for example, the density matrix has the effective average value of (77)

$$\rho = \rho_{ss} = \rho_{tt} = \tfrac{1}{2} \pm \tfrac{1}{4}\,[(f_{\parallel} - f_{\perp})/(f_{\parallel} + 2f_{\perp})] \qquad (77)$$

where $f_{\parallel}$ and $f_{\perp}$ are the recoilless fractions parallel and normal to the four-fold axis and the average recoilless fraction is $f = \frac{1}{3}(f_{\parallel} + 2f_{\perp})$. The observed spectrum may therefore have a slight asymmetry. In principle, if the sign of eQV_{zz} is known this asymmetry will indicate whether $f_{\|} > f_{\perp}$; conversely, if the mean-square displacement tensor from X-ray data is clearly anisotropic it can be used to obtain the sign of eQV_{zz}.

When there are four equivalent trigonal sites a similar argument applies except that f is invariant and the spectrum is symmetrical along the $\langle 100 \rangle$ directions with (78) along the $\langle 111 \rangle$ directions.

$$\rho = \rho_{ss} = \rho_{tt} = \tfrac{1}{2} \pm \tfrac{1}{8}\,[(f_{\|} - f_{\perp})/(f_{\|} + 2f_{\perp}) \qquad (78)$$

For site symmetries lower than axial, similar relations can be derived, but in view of the large number of parameters they serve no useful purpose.

Overlapping Lines.—If the quadrupole splitting is small the two components of the resonance overlap and equations (30) and (32)—(34) are no longer strictly valid. We must revert to equation (26) because the k terms in the exponential cannot be separated. Evaluation of this expression involves a separate 'transmission integral' of the overlapping lines for *each* of the two basis polarizations, and is therefore more complicated than the equivalent powder calculation. However, the necessary numerical techniques are well established.[17,18]

In principle, this can be extended to the simultaneous curve fitting of several spectra in different orientations with the primary parameters as variables, and some work has been successfully carried out to this effect. However, it has been found that for quadrupole splittings of $\Delta \geqslant \tfrac{3}{2}\Gamma$ the area ratios obtained from curve-fitting simple overlapping Lorentzian profiles are sufficiently accurate for a study of the e.f.g. tensor. Therefore most materials of interest can be studied without this type of complication.

In compounds having more than one crystallographically distinct site the general principles described in this paper can be used without modification *provided* that the two or more components do not overlap significantly. Each component site can be treated independently. However, in $Fe[SO_4]\cdot 7H_2O$ for example there are two crystallographic sites of triclinic symmetry in the monoclinic unit cell which fortuitously give an almost identical Mössbauer spectrum, and therefore show only a simple doublet. The thickness correction of single-crystal spectra now requires a knowledge of two independent mean-square displacement tensors. The two e.f.g. tensors are specified by no less than 10 unknown parameters. The published single-crystal study using the Zory method is grossly inadequate,[3] but it may prove extremely difficult to accurately determine the orientations of the two tensors. In compounds with two sites and partial overlap of one of the components the transmission-integral method can probably be applied successfully.

Conclusions.—The original method of Zory as extended by Zimmermann refers specifically to sites of triclinic symmetry in crystals having a monoclinic space group. An unambiguous solution for the e.f.g. tensor can only be obtained if crystal plates can be grown in several orientations, and if η can be obtained by an independent measurement. Both conditions are severely restrictive since large crystals are not easily obtained, and it is not always feasible to determine η at the same temperature. Furthermore, the recoilless fraction is assumed to be isotropic, and thickness effects are ignored.

In this paper it has been shown that the problem of determining the orientation of the e.f.g. tensor can be expressed generally in terms of the point symmetries of the resonant site and space group. In nearly all instances where the space group has a symmetry lower than cubic it is possible to determine the relevant parameters from *one* crystal by using a combination of polarized and unpolarized radiation. In cases where there are n non-equivalent site orientations the primary ambiguity remaining is of assignment of the n different solutions.

This represents a major step forward in that many more substances can now be studied than hitherto. For example, the recent work on deoxygenated myglobin[19,20] using the Zory–Zimmermann methods resulted in a family of possible solutions, whereas the techniques presented here would have been able to give a full determination. It therefore seems likely that major progress can now be made in studying iron-bearing proteins and model compounds. Where an X-ray structure is known, the e.f.g. can be related to the chemical bonding at the iron site. Where only the space group is known, but the site symmetry is indicated by the stoicheiometry, the orientation of the e.f.g. may be of valuable assistance in elucidation of the structure near the active centre of the molecule.

[7/1491 *Received, 17th August, 1977*]

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