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Determination of Mossbauer Electric Field Gradient

V. K. GARG

Departamento de *Física* e *Química*, ***Universidade Federal*** do Espírito Santo,
29000 Vitória, ES, Brasil

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There are several reports of the electric quadrupole interactions available in the literature.[1-4] The present discussion is a short survey, introducing the electric quadrupole up to the experimental polarised studies.

Existem várias publicações sobre interações de quadrupolo elétrico na literatura - A presente discussão é um resumo, introduzindo o quadrupolo elétrico até o nivel de recentes estudos experimentais.

1. INTRODUCTION, STANDARD FORM OF EFG

The magnitude of the quadrupole splitting is pronortional to the Z componerit of the electric field gradient (EFG) tensor which interacts with the quadrupole moment of the nucleus. For $I = 3/2$, the quadrupole splitting can be expressed as

$$Q.S. = \frac{1}{2} e^2 q Q(1 + \eta^2/3)^{1/2} \qquad (1)$$

Where Q is the quadrupole moment of the nucleus

$$eq = V_{zz} = \text{- the Z component of the EFG} \qquad (2)$$
$$e = \text{proton charge}$$

and o is the asymmetry parameter

$$\frac{V_{xx} - V_{yy}}{V_{zz}}$$

Either q or V_{zz} is referred to as the field gradient. The *EFG* tensor has nine cornponents.

The potential at the Mössbauer nucleus (located at the origin) due to point charge q at (x,y,z) a distance $r = (x^2 + y^2 + z^2)^{1/2}$ from the origin is given by

$$V = q/r \tag{3}$$

The negative gradient of this potential, $-\vec{\nabla}V$, is the electric field, $\vec{E}$, at the nucleus, with components

$$E_x = -\frac{\delta V}{\delta x} = qx\ r^{-3}, \quad E_y = -\frac{\delta V}{\delta y} = qy\ r^{-3}, \quad E_z = -\frac{\delta V}{\delta z} = qz\ r^{-3} \tag{4}$$

the gradient of the electric field at the nucleus, $\vec{\nabla}\vec{E}$, is given by

$$\vec{\nabla}\vec{E} = -\vec{\nabla}\vec{\nabla}V = (\mathrm{EFG}) = -\begin{vmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{vmatrix}, \quad V_{xx} = \frac{\delta^2 V}{\delta x^2},\ V_{xy} = \frac{\delta^2 V}{\delta x\ \delta y}, \quad V_{xz} = \frac{\delta^2 V}{\delta x\ \delta z},\ \text{etc} \tag{5}$$

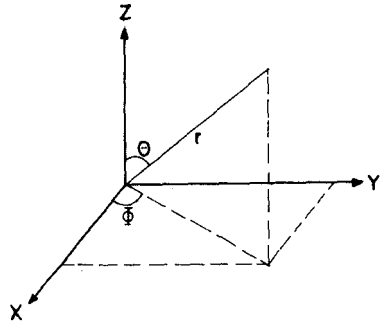
the second partial derivative tensor components are

$$\begin{aligned} V_{xx} &= q(3x^2 - r^2)r^{-5}, \\ V_{YY} &= q(3y^2 - r^2)r^{-5}, \\ V_{zz} &= q(3z^2 - r^2)r^{-5}, \\ V_{xy} &= V_{yx} = 3\,qxy\ r^{-5}, \\ V_{xz} &= V_{zx} = 3\,qxz\ r^{-5}, \\ V_{Yz} &= V_{zx} = 3\,qyz\ r^{-5}. \end{aligned} \tag{6}$$

The EFG cornponents can be expressed in spherical coordinates as

$$r = (x^2 + y^2 + z^2)^{1/2}, \quad \Theta = \cos^{-1}(z/r), \quad \Phi = \tan^{-1}(y/x),$$
$$x = r\sin\Theta\cos\Phi, \quad y = r\sin\Theta\sin\Phi, \quad z = r\cos\Theta$$

$$
\begin{aligned}
V_{xx} &= q(3\sin^2\Theta\cos^2\Phi - 1)r^{-3} \\
V_{yy} &= q(3\sin^2\Theta\sin^2\Phi - 1)r^{-3} \\
V_{zz} &= q(3\cos^2\Theta - 1)r^{-3} \\
V_{xy} &= V_{yx} = 3qr^{-3}\sin^2\Theta\sin\Phi\cos\Phi \\
V_{xz} &= V_{zx} = 3qr^{-3}\sin\Theta\cos\Theta\cos\Phi \\
V_{yz} &= V_{zy} = 3qr^{-3}\sin\Theta\cos\Theta\sin\Phi
\end{aligned}
\tag{7}
$$



The total contribution to each EFG components is obtained by simply adding the individual contributions. If the coordinate axes are properly chosen, the above tensor can be reduced to diagonal form so that the EFG can be completely specified by the three components V_{XX}, V_{YY} and V_{zz}. These components are also not independent and are related by Laplace's equation

$$V_{xx} + V_{yy} + V_{zz} = 0 \tag{8}$$

reducing the number of independent parameter to two, V_{zz} and η where

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \tag{9}$$

The value of EFG tensor components obviously depend upon the choice of the coordinate axes. For this reason a standard form of EFG tensor is expressed by defining a unique set of axes known as the principal axes of the EFG tensor. This unique coordinate system is the one for which the off-diagonal components are zero and diagonal components are ordered, such that

$$|V_{zz}| \geq |V_{yy}| \geq |V_{xx}| \tag{10}$$

this restricts $0 \leq \eta \leq 1$. Now, only two of the five independent parameters of the EFG tensor seem to be left. Actually, however, three independent off-diagonal elements have been replaced by the Euler angles (α,β,γ) necessary to describe the relative orientation of the principal and initial axes. The orientation parameters affect the line intensities in single crystal spectra.

Many properties of the EFG tensor can be deduced from the symmetry properties of the molecule or crystal. Often the Z axis of the EFG coincides with the highest symmetry axis of the molecule or crystal. The Z axis of EFG, and the X and Y axes, do not always coincide with metal - ligand bond directions. In such cases, it is necessary to choose an arbitrary set of axes, work out the EFG components, diagonalise the tensor, and then choose $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$.

If the electronic configuration has a symmetry lower than cubic, electrons about the Mössbauer atorn also contribute to the EFG tensor.

2. CORE POLARISATION

The field gradient which is finally produced at the Mössbauer nucleus, say iron, is modified by the presence of the inner closed-shell electrons. While these core electrons themselves do not contribute to the field gradient, they are polarisec by the field gradient of the lattice and valence electrons. This eff'ect is accounted for by the Sternheimer[5] antishielding parameters. The total field gradient at the nucleus is expressed[6] as

$$\frac{V_{zz}}{e} = q = (1 - R)q_{\text{valence}} + (1 - \gamma_\infty)q_{\text{lattice}}$$
$$\frac{V_{xx} - V_{yy}}{e} = \eta q = (1 - R)_{\text{ion}}\, q_{\text{ion}} + (1 - \gamma_\infty)q_{\text{lattice}} \qquad (11)$$

The subscript 'ion' and 'lattice' stand for the charge distribution of the spherical $3d$ valence electroris belonging to the fer-

rous ($5D\ 3d^6$) and the neighbouring ion in the crystalline lattice respectively. (I-R) and ($1-\gamma_\infty$) are the Sternheimer factors which have been introduced to correct for the polarisation of the ferric like ($6S_2\ 3d^5$) core by the EFG of the ion and the lattice charge distribution. For Fe^{2+} R = 0.32[7], γ_∞ = - 10.6[8] and for Fe^{3+} γ_∞ = - 9.1[9]. The other distribution to the EFG tensor consists of the uncompensated $3d$ electrons. In octahedral symmetry[10], the 3d electrons are split into two groups. Those transforming as T_{2g} are largely unaffected, since these do not ordinarily participate in bonding to ligands. These are usually termed as dxy, dxz and dyz and represent electric charge concentrated in regions other than along the ligand directions. The E_g electrons, dz^2 and dx^2-y^2, couple with ligand orbitals produce antibonding wavefunctions. These concentrate the charge along the bond directions. As a result, these E_g electrons occupy a higher energy level than T_{2g} electrons.

The magnitude of splitting of these groups of electrons has a profound effect on the magnetic and Mössbauer properties of these compounds. Weak ligands, such as OH^-, H_2O, NH_3 and the halogens produce relatively small splitting. The five or six $3d$ electrons of ferric or ferrous compounds fill by Hund's rule for maximum multiplicity. Strong liyands such as CN, pyridine or - 0 - phenanthroline cause a greater splitting and lead to the fitting of T_{2g} Shell.

For an electron in a state Ψ the electric field gradient has the expectation value.

$$< q > = - \frac{<3\cos^2\Theta - 1>}{<r^3>} \qquad (12)$$

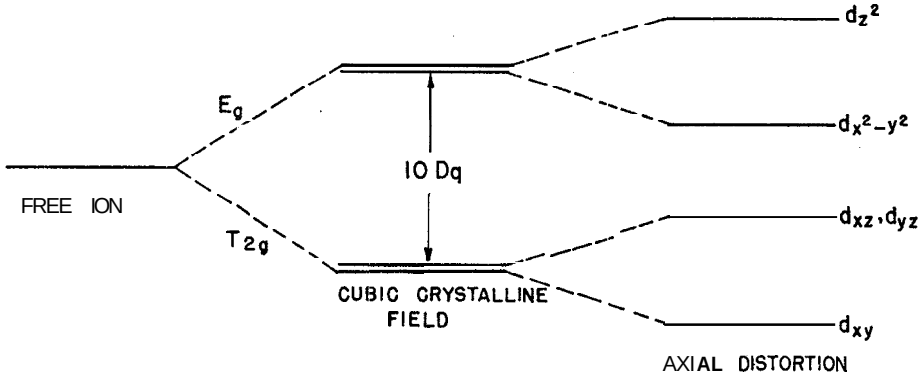
These expectation values have been calculated using $\Psi_{3d} R(r) Y_\ell^m (\Theta,\Phi)$. The values of $<3\cos^2\Theta - 1>$ are independent of $R(r)$ and are easily found[11] from various p, d - orbitals.

TABLE

Expectation values of $q_{valence}$ for p and d electrons

Wave function	$\frac{V_{zz}}{e} = q_{valence}$	Wave function	$\frac{V_{zz}}{e} = q_{valence}$	Symmetry representation
p_x	$+\frac{2}{5}\langle r^{-3}\rangle_p$	d_{z^2}	$-\frac{4}{7}\langle r^{-3}\rangle_d$	
p_y	$+\frac{2}{5}\langle r^{-3}\rangle_p$	$d_{x^2-y^2}$	$+\frac{4}{7}\langle r^{-3}\rangle_d$	E_g
p_z	$-\frac{4}{5}\langle r^{-3}\rangle_p$	d_{xy}	$+\frac{4}{7}\langle r^{-3}\rangle_d$	T_{2g}
		d_{xz}	$-\frac{2}{7}\langle r^{-3}\rangle_d$	
		d_{yz}	$-\frac{2}{7}\langle r^{-3}\rangle_d$	

It is clear from symmetry considerations that as long as d-orbitals are degenerate, $\langle q\rangle_{valence} = 0$. Even under the influence of a cubic crystalline field, the field gradient at the nucleus will vanish since the degenerate T_{2g} and E_g states both retain spherical symmetry. Distortions from cubic symmetry, however, remove the degeneracy of the states and if the non-degenerate d-orbitals one unequally populated, a field gradient is produced.



The two situations which can produce a non zero $< q >_{valence}$ are spin free Fe^{2+} (six d-electrons) and spin paired Fe^{3+} (five d-electrons) in an axially distorted octahedra field (with negative ligands). At $0^{o}K$ the electrons populate only the lowest possible states and one obtains the limiting field gradient for these two cases. Ingalls[11] has treated the field gradient in spin - free ferrous complexes in much more detail. He obtains a reduction factor to include the effects of finite temperature (Boltzman distribution) and of spin - orbit coupling. Now

$$q \simeq (1 - R)q_{valence} = - (1-R) <3\cos^2\Theta - 1><r^{-3}>_{3d} \qquad (13)$$

since $(1-R) > 0$ and $<r^{-3}>_{3d} > 0$ the sign determining factor is $<3\cos^2\Theta - 1>$, which may be positive or negative depending on the manner in which the electrons are distributed among the d-orbitals.

The relative magnitude of these two effects, ligand disposirion and uncompensated $3d$ electrons change completely with ligand strength. Ligands, sufficiently weak that the Fe^{3+} high spin electron configuration is obtained, do not cause observable EFG. The uncompensated $3d$-electron in Fe^{2+} high spin compounds causes a large quadrupole splitting. The mixed strong - weak ligand case, Fe^{3+} (O-phenthroline)$_2Cl_3^{-3}$ which has no $3d$ electron contribution to the EFG does not yield a resolved doublet. The cyanides lie at the other extreme, $K_3|Fe^{2+}(CN^-)_6|$, has a zero splitting in consequence of its balanced ligands and filled T_{2g} structure. $K_3|Fe^{3+}(CN^-)_6|\ 3\ H_2O$ has one T_{2g} electron missing, but yields only a small splitting (0.3 mm/sec). This illustrates the nephelauxetic effect of strong ligands, in which the ligands force the T_{2g} electrons away from the nucleus where the $<r^{-3}>$ is considerably smaller. The effect of ligand symmetry is correspondingly enhanced. Consider two diamagnetic ferrous compounds in which no odd $3d$ electrons affect the EFG tensor. The very strong (greater than$_{12}$ CN^-) ligand NO^+ causes a splitting of 1.70 mm/sec. in sodium nitroprusside.[12] In $Na_4|Fe(CN)_5NO_2|.2H_2O$ the weaker ligand (NO_2) results in a splitting of 0.86 mm/sec.

The choice of basis for $3d$ electrons is normally either dz^2, dx^2-y^2, dxy, dxz, dyz or d_0, $d_{\pm1}$, $d_{\pm2}$. Each of the wave functions in

these alternate bases has zero asymmetry parameter. There exists, however, other $3d$ - wavefunctions with asymmetry parameter differing from zero and even attaining the values of unity. Consider the wavefunction

$$\psi = (d_{xz} + i\lambda d_{yz})/(1 + \lambda^2)^{1/2}$$

where λ is a real number, the EFG tensor is

$$\text{EFG} = -\frac{2}{7}\begin{pmatrix} 1 - 2\lambda^2 & 0 & 0 \\ 0 & -2 + \lambda^2 & 0 \\ 0 & 0 & 1 + \lambda^2 \end{pmatrix} \frac{q\langle r^{-3}\rangle}{1 + \lambda^2} \qquad (14)$$

The mixing coefficient λ depends on the details of the distribution and the nature of metal - ligand interaction. It might be supposed that such a wave function are idle speculation. However, the EFG tensor in ferrous ammonium sulphate has been explained only by recourse to such a wavefunction by Collins et *al.*[14].

3. QUADRUPOLE SPLITTING

The principal relation giving the hyperfine splitting of nuclear energy due to electric quadrupole interaction is given by

$$E_Q = \frac{e^2qQ}{4I(I-1)}\left[3I_z^2 - I(I+1) + \eta(I_x^2 - I_y^2)\right]$$
$$= \frac{e^2qQ}{4I(I-1)}\left[3I_z^2 - I(I+1) + \frac{\eta}{2}(I_+^2 + I_-^2)\right] \qquad (15)$$

where $I_\pm = I_x \pm I_y$. Now, eigenvalues E_Q^* and E_Q appropriate to the nuclear excited state and the ground state must be calculated.

$$E_Q^* \pm \frac{3}{2} = \frac{e^2qQ}{2}\left[1 + \eta^2/3\right]^{1/2}$$
$$E_Q \pm \frac{1}{2} = -\frac{e^2qQ}{2}\left[1 + \eta^2/3\right]^{1/2} \qquad (16)$$

The resonance energies are now given by the difference between the eigenvalues

$$\Delta E_Q = \frac{e^2qQ}{2}\left[1 + \eta^2/3\right]^{1/2} \qquad (17)$$

4. SIGN OF EFG AND REASONS FOR MEASURING IT

Sinse the electric field gradient is actually a second rank tensor, what really is meant by the sign of V_{zz} or of q? The various theoretical methods employed in calculating the electric field gradients all suffer because of inadequacies of the wavefunctions available for iron ions. Therefore, theoretical estimates of the field gradients are usually not very reliable. However, the sign of EFG is completely determined by the angular part of the wavefunction. The angular part of the wavefunctions is much more reliable than the radial part, and hence, calculations of the sign can be made with some confidence if a realistic method is chosen. Thus the experimental determination of the sign of V_{zz} is reliable for differentiating between two theoretical models when they lead to different signs.

5. MAGNETIC PERTURBATION

One of the difficulties in studying quadrupole effects in Fe^{57} is the presence of only one measurable parameter in powdered, zero magnetic field samples. Ruby and Flinn[15] first suggested an interesting possibility of applying an external magnetic field in order to display more information in the Mössbauer spectrum. It was called magnetic perturbation and its theory was worked out by Collins[16], and Gabriel and Ruby[17]. Theoretical studies, analytical by Collins[16] and numerical by Gabriel and Ruby[17], verified that two normally identical lines become markedly different in presence of external magnetic field. By identifying the lines means that the sign of V_{zz} may be measured in this way. In addition, the fine structure of the perturbed spectra may be examined to yield rough values of asymmetry parameter, within limits deter-

mined by magnetic anisotropy in paramagnetic compounds and by vibrational isotropy of the sample[14]. For the limit of zero asymmetry parameter and for applied magnetic fields of about 25 Koe or more, in the Fe^{57} $m_I = \pm \frac{3}{2}$ lines appear as triplet and the $m_1 = \pm \frac{1}{2}$ lines appear as doublet. For determining the sign of V_{zz} of Fe^{57} doublet occurrs at the more positive velocity indicating V_{zz} positive and vice-versa. As the asymmetry parameter increases, the lines begin to look more alike to the point of becoming identical triplets for an asymmetry parameter of unity, although the exact appearence of the lines depends on whether the magnetic field is parallel or perpendicular to the experimental axis, the direction of the incident radiation.

Collins[16] applied this magnetic pertiirbation to determine the sign of ferrocene at 4.2K. The sign of q in some ionic ferrous compounds has also been determined[18]. It must be remarked that this method is applicable to powder samples and most samples are powders rather than single crystals.

6. GOLDANSKII-KARYAGIN EFFECT

The intensities for a single crystal absorber are generally not equal. Occasionally in powder sample absorbers also there is asymmetry in the two lines of a Fe^{57} quadrupole split spectrum. The most obvious reason for intensity asymmetry in powdered samples is simply the preferential orientation. This sort of preferential orientation in powdered samples may be reduced or eliminated by improving sample grinding and or mixing with noninterfering powder such as chalk dust, sugar etc. If still the sample shows the intensity asymmetry it may be due to Goldanskii Karyagin effect.

Karyagin[19] has derived an expression for the ratio of two lines as a function of the difference of the mean - square vibrational amplitudes of the nucleus along and perpendicular to the V_{zz} axis. Since the recoilless fraction is related to the mean square vibrational amplitude in the direction of the incident gamma, the contribution of each microcrystal in the sample is dependent upon its orientation,

yielding a preferential intensity having an effect similar to preferential orientation. The Goldanskii - Karyagin effect may, sometimes, be employed to deduce the sign of V_{zz}. The reported[20] dependence of intensity ratio upon ($\langle Z^2 \rangle - \langle X^2 \rangle$) may be employed to identify the lines and hence the sign of V_{zz} or conversely sign of vibrational anisotropy can be determined if the sign of V_{zz} is known. In iron and tin, the $m_I = \pm \frac{3}{2}$ line is more intense for negative values of the anisotropy parameter ($\langle Z^2 \rangle - \langle X^2 \rangle$) and is less intense for positive values.

7. IMPORTANCE OF EFG INFORMATION

Generally, the quadrupole splitting has been used in the literature as a sort of measure of distortion of a system from spherical symmetry. Same quadrupolesplittingcould be shared by two compounds, for exarnple, iron sulphide, (pyrite) and iron sulphide (marcasite); but their strength would differ.

Ingalls[11] has shown that the ligand and valence contributions to V_{zz} invariably have opposite sign for some systems. Thus at the low temperature limit, where the valence contribution depends neither on distortion nor temperature, increased ligand distortion would decrease V_{zz} and hence the quadrupole splitting, since the valence contribution would be doininant. At the high temperature limit, the problem would be ligand only and be subject to the difficulties, but would, within those splitting indicates increased distortion. In the intermediate temperature range, where the valence contribution is both temperature and distortion sensitive the story becomes very complicated. The splitting of the d - orbitals, which determine the valence contribution of distortion, whereas the ligand contribution to the EFG corresponds to q/r^3 type of distortion. Since both contributions increase, in opposite senses in response to two different types of distortion, the meaningful assignment of a distortion - quadrupole splitting relationship for such system at intermediate ternperatures require some prior assumptions.

8. SINGLE CRYSTAL METHOD FOR EFG DETERNIINATION

From the discussion of 'Goldanskii Karyagin effect' it is apparent that peak intensity area ratio may also be a measurable parameter (of iron and tin) of compounds by the use of single crystals. However, to obtain accurate values of EFG parameters it is essential to find a theoretical expression for the area in term of these parameters.

Following Lang[21], let us introduce the rate fS_0, the number of recoilless 14 4 Kev photons emitted per second into the solid angle subtended by the detector; $(1-f)S_0$ being the non-recoilless rate. Since the emitted recoilless photons are not actually monoenergetic, but show a distribution of energies centered about $E_0 \simeq$ '14.4 Kev, we introduce the function $S(E-E_0)$, the number recoilless photons emitted per second per unit energy interval into the same detector ang'le. If the source is moving with velocity V relative to absorber, then recoilless photon distribution is actually centered about $E_0 + (V/C)E_0 = E_0 + \varepsilon$ and $S(E-),E \rightarrow S(E - E_0 - \varepsilon)$. $S(E - E_0 - \varepsilon)$ is a resonance type function with Γ(FWHM) = $10^7 \hbar$, therefore

$$\int_0^\infty S(E - E_0 - \varepsilon)dE = fS_0 \tag{18}$$

the photon arrival rate $R(\varepsilon)$ at the detector is

$$R(\varepsilon) = e^{-\sigma e^m} S(E - E_0 - \varepsilon) \exp\left[f' \sigma(E) W\right] + (1-f') S_0 e^{-} e^m \tag{19}$$

where e = average surface density of atom

m = surface density of nuclei capable of resonance

f' = recoilless absorption probability

$\sigma(E)$ = energy dependent resonance absorption cross section per nucleus in the presence of EFG when no perturbing fields are present; the resonance when no perturbing fields are present, cross section is given by[22]

$$\sigma(E) = \sigma_0 \Gamma_0^2/4 \left[(E - E_0)^2 + \Gamma_0^2/4\right]^{-1} \tag{20}$$

where

$$\sigma_0 = \frac{2\Pi \lambda^2 \cdot (2I' + 1)}{1 + \alpha(2I+1)}$$

σ_0 = natural linewidth of the excited state

a = internal cross-section coefficient

However, in the solid, the resonance cross-section becornes more complicated due to energy dependent splittings, shifts and broadenings. Since the actual resonance is strictly a nuclear process, the condition

$$\int_0^\infty \sigma(E)dE = \sigma_0 \Gamma_0 \frac{\Pi}{2} \tag{21}$$

is always fulfilled. Consequently $\sigma(E)$, in general, may be written in the form

$$\sigma(E) = \frac{\Pi}{2} \sigma_0 \Gamma_0 K(E) \tag{22}$$

where

$$\int_0^\infty K(E)\, dE = 1$$

If the nuclear energy levels are split by H or/and EFG fields so that the various energy transitions can be resolved in a Mössbauer type experirnent, then $K(E)$ may be written in the form,

$$K(E) = \sum_n K_n(E_n, \Theta, \Phi)$$
$$= \sum_n P_n(\Theta, \Phi) K_n(E-E_n)$$

where $K_n(E-E_n)$ = a resonance type function which is chosen to have normalisation

$$\int_0^\infty K_n(E - E_n)dE = 1 \tag{23}$$

$P_n(\Theta)$ = relative angular dependent absorption probability satisfying the condition

$$P_n(\Theta,\Phi) = 1 \quad \text{since} \quad \int K(E)dE = 1 \tag{24}$$

The directional dependence of P_n has its origin in the fact

that H and/or EFG interaction destroys the spherical symmetry of the nuclear environment.

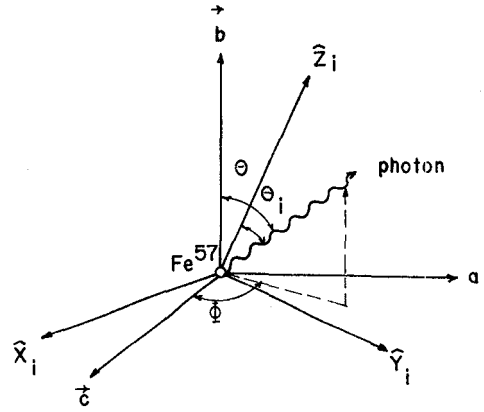
If β is the detector efficiency for 14.4 Kev protons and R_B, some velocity independent background counting rate, then $M(\varepsilon) = \beta R(\varepsilon) + R_B$ the experimental data of interest is actually $M(\varepsilon)/c$ where c is the count rate independent of source velocity. The area under the n^{th} peak is for $t_n << 1$ and $(\frac{1}{c})\, f\, \beta_0\, S_0 \exp(-\sigma e^m) = D$ given by

$$A_n = \int_0^\infty f'\, w\, \sigma_n(E)\, dE = D\, \Gamma_0\, (\tfrac{\Pi}{2}) D\, \Gamma_0\, \sigma_0\, w\, f'(\Theta,\Phi) P_n(\Theta,\Phi) \qquad (25)$$

where P_n = relative absorption probability for transition

f' = recoilless absorption probability.

If X, Y and Z are the principal axes of the EFG at an iron nucleus in the absorber both P_n and f' will vary with the orientation angle of the incident photon beam relative to the axes. The angular dependente of f' results from an anisotropy in the mean square displacement of the vibrating nucleus.



For a single crystal absorber with two or more possible orientations for EFG'S relative to the incident beam, the area ratio is given by

$$\frac{A_n}{A_m} = \frac{\sum_i P_n(\Theta_i,\Phi_i) f'(\Theta_i,\Phi_i)}{\sum P_m(\Theta_i,\Phi_i) f'(\Theta_i,\Phi_i)} \qquad (26)$$

In case the absorber is a powder, the expression for the ratio of the area is

$$\frac{A_n}{A_m} = \int_{4\Pi} P_n(\Theta,\Phi) f'(\Theta,\Phi) d\Omega \Big/ \int_0^{4\Pi} P_m(\Theta,\Phi) f'(\Theta,\Phi) d\Omega \qquad (27)$$

The importance of the Debye-Waller factor (or Mössbauer fraction) in determining the intensities of the absorption lines was pointed out oy Goldanskii et *al*. (G.K.E).

Zory[23] and Hien[24] have discussed the analysis of EFG in single crystal absorbers containing Fe^{57}, while Karyagin[25,26] has discussed the more general case of a nuclear transition of arbitrary multipolarity, all in the thin absorber limit. Zory[23] applied his analysis to $FeCl_2.4H_2O$ and evaluated all the EFG parameters, while Danon and Iannareila[27] used the same analysis to confirm their expectations concernino the field gradient parameters in sodium nitroprusside, $Na_2|Fe(CN)_5NO|.2H_2O$. Ingalls, Ono and Chandler[28] and Chandra and Puri[29] have also applied a similar analysis for the deterrnination of EFG as a function of temperature in Ferrous ammonium sulphate. Chandra and Puri[29] also analysed $FeSO_4.7H_2O$. There are reports, in the literature, of EFG using similar analysis for $Fe(KSO_4)_2.6H_2O$ [30], $FeSO_4.4H_2O$ [31-33], $FeSO_4$ [34], $FeSiF_6.6H_2O$ (Ref.35-37), $FeTiO_3$ [38], FeS_2(p) [39], FeS_2(m) [40], KfeS$_2$41-42, Fe_2O_3 [43,44], Ferrocene[16], Siderite[45] etc.

In order to use the above equation let it be expressed in nuclear EFG parameters. Considering the crystal areas $\vec{a}$, $\vec{b}$, and $\vec{c}$ as mutually orthogonal, the unit vectores $(\hat{X}_i, \hat{Y}_i, \hat{Z}_i)$ locate the principal axes of EFG of i^{th} site, the three Euler angles $(\alpha_i, \beta_i, \gamma_i)$ designating their orientations relative to $(\vec{a},\vec{b},\vec{c})$ being unknown. Angles (Θ_i, Φ_i) are the orientation angles of the incident beam relative to (X_i, Y_i, Z_i). Let us introduce (Θ,Φ) the polar and azimuthal angles of the incident photon beam relative to $(\vec{a},\vec{b},\vec{c})$ axes.

The expressions for relative transition probabilities P_3 and P_1 were derived utilizing the fact that 14.4 Kev gamma rays is a magnetic dipolar radiation and given by

$$P_3(\Theta,\Phi) = 4(1 + \eta^2/3)^{1/2} + (3\cos^2\Theta_i - 1 + \eta \sin^2\Theta_i \cos 2\Phi_i)$$
$$P_1(\Theta,\Phi) = 4(1 + \eta^2/3)^{1/2} - (3\cos^2\Theta_i - 1 + \eta \sin^2\Theta_i \cos 2\Phi_i) \quad (28)$$

Expressing $\cos^2\Theta_i$ and $\sin^2\Theta_i \cos 2\Phi_i$ in terms of known experimental angles (θ,ϕ) and the known Euler angles relating site to axes $(\vec{a},\vec{b},\vec{c})$, from equations (above) assuming isotropy of $f'(\Theta,\Phi)$ one gets

$$\frac{a_3}{a_1} = \frac{\sum_{\text{sites}} \{4(1 + \eta^2)^{1/2} + (3K - 1 + K')\}}{\sum_{\text{sites}} \{4(1 + \eta^2)^{1/2} + (3K - 1 + K')\}} \quad (29)$$

where

$$K = \sin^2\theta[(\cos^2\phi)Z_{a'}^2 + (\sin^2\phi)Z_c^2] + (\cos^2\theta)Z_b^2 + (\sin^2\theta \sin 2\phi)Z_a Z_c$$
$$+ \sin 2\theta[(\sin\phi)Z_c Z_b + (\cos\phi)Z_a Z_b]$$
$$K' = \sin^2\theta[(\cos^2\phi)(X_{a'}^2 - Y_a^2) + (\sin^2\phi)(X_c^2 - Y_c^2)] + (\cos^2\theta)(X_b^2 - Y_b^2) +$$
$$+ \sin^2\theta(\sin 2\phi)(X_a X_c - Y_a Y_c) + \sin 2\theta[(\cos\phi)(X_a X_b - Y_a Y_b)$$
$$+ (\sin\phi)(X_c X_b - Y_c Y_b)]$$

The symbols $X_{a'}$, X_b etc denote the directioti cosines $\hat{X}.\vec{a}$, $\hat{Y}.\vec{b}$ etc. These direction cosines can be expressed as a function of the same Euler angles (α,β,γ). The schematics of the absorption of 14.4 Kev gama rays be Fe^{57} in single crystals in shown in the figure.

In the above analysis, unfortunately, it has been necessary to use samples of sufficient thickness that the thin absorber analysis can not be completely justified; because the saturation effects can not be neglected. Therefore, it is necessary to have a method of analysis in which saturation is taken into account. Because of polarization dependente of the individual nuclear cross sections the intensities[46] or areas[47] of the absorption lines can not be calculated in the thin absorber approximation. Polarization effects must also be taken into account in making a detailed interpretation of spectra obtained by applying a

magnetic field to a thick, randomly oriented powder of a material exhibiting a quedrupole doublet[15]. Blume and Kistner[48] calculated the intensities transmitted through an absorber of arbitrary thickness in the case where all parameters describing the individual cross sections are known. Housley; Grant and Gonser[49] generalised the Blume and Kistner[48] treatment, for more than one resonant site per unit cell by introducing an average scattering amplitude per unit cell obtained by summing the properly weighted scattering amplitudes from all sites, all scattering amplitude matrices being expressed in terms of same basis polarisations. Housley *et al*[49] obtained formulas relating absorptions as a function to the individual nuclear cross sections for radiation propagating along special directions in the monocrystal which are predictable from crystal symmetry considerations. In these cases the gamma ray beam canbe thought of as consisting of two orthogonal intensities each of which propagates through the crystal with its own index of refraction. Housley et *al*[50-52] has shown by means of several exarnples, the importance of polarisation effect in analysis of data on single crystals or magnetised materials and determination[53] of the sign of the magnetic hyperfine field. Housley, Gonser and Grant[45] determined the Debye Waller factor in Siderite taking into consideration the polarisation terms. Siderite has been of considerable interest and there exist many reports[45].

9. FINITE THICKNESS ANALYSIS

The complex index of refraction for the material is given by[53]

$$n = 1 + \frac{2\Pi N}{k^2} F(k,k') \qquad (30)$$

where k and k' are the wave vectors of the incident the scattered radiation, respectively, N is the number of resonant nuclei per unit volume, and $F(k,k')$ is the coherent scattering amplitude for a single nucleus. The quantities F and n may be replaced by a 2x2 matrix. Generalising, for a complicated crystal having several resonant nuclear sites per unit cell,

$$n = 1 + \frac{2\Pi}{k^2} \sum_j N_j F_j(k,k) \equiv 1 + \frac{2\Pi}{k^2} F_r(k,k) \quad . \qquad (31)$$

Sum runs over all the sites. It is assumed that the electromagnetic interaction is so weak that the index of refraction has a negligible influence on an incident beam in a distance of order of the unit cell dimensions. Now expressing n in terms of the density matrix rotation.

$$n = 1 + i\frac{\sigma_0}{2k}\sum_{ij}\begin{pmatrix}\rho_{11}^{ij} & \rho_{12}^{ij}\\ \rho_{21}^{ij} & \rho_{22}^{ij}\end{pmatrix}\frac{N_j f_j'}{(x-x_{ij})^2+1} - \frac{\sigma_0}{2k}\sum_{ij}\begin{pmatrix}\rho_{11}^{ij} & \rho_{12}^{ij}\\ \rho_{21}^{ij} & \rho_{22}^{ij}\end{pmatrix}\frac{N_j f_j'(x-x_{ij})}{(x-x_{ij})^2+1} \qquad (32)$$

here j and i represent sites and hyperfine coniponents. The quantity x is related to the energy E by $x = \frac{2E}{\Gamma}$ and x_{ij}'s correspond to the resonant energies at the different sites. The Debye - Waller factors are no longer assumed isotropic but are the ones appropriate for the direction k.

In the special case where n is diagonal, an incident radiation beam may be decomposed into two components with polarisations corresponding to the basis polarisations in which n is diagonal. Each of these beams may be regarded as separately propogating through the crystal with its own index of refraction.

An effective thickness matrix σ may be defined from the equation (32) and will be diagonal when n is diagonal

$$\sigma = \begin{pmatrix}\sigma_{11} & \sigma_{12}\\ \sigma_{21} & \sigma_{22}\end{pmatrix} = \sigma_0\sum_{ij}\begin{pmatrix}\sigma_{11}^{ij} & \sigma_{12}^{ij}\\ \sigma_{21}^{ij} & \sigma_{22}^{ij}\end{pmatrix}\frac{n_i f_i'}{(x-x_{ij})^2+1} \qquad (33)$$

where n_i are the number of resonant nuclei of type j per unit area. When

n is diagonal, the matrix elements of σ can be extracted from experimental line intensities, if the spectra are well resolved.

Assuming that the γ ray beam can be described as a plane wave incident on a slab of homogeneous absorbing material of uniform thickness and that the absorption may be described without dispersion. Describing the polarisation and intensity of the unshifted component of the source radiation at any energy by a density matrix

$$S = \frac{I}{2\Pi} \sum_{k,\ell} \begin{pmatrix} \rho_{11}^{k\ell} & \rho_{12}^{k\ell} \\ \rho_{21}^{k\ell} & \rho_{22}^{k\ell} \end{pmatrix} \frac{r_\ell f_\ell}{(x - x_{k\ell} - v) + 1} \qquad (34)$$

where I is the total intensity due to the transition of interest and r is the fraction of the emitting nuclei in site ℓ. The source resonance energies $x_{k\ell}$ and site positions ℓ will not generally correspond to those the absorber. The quantity v describes the Doppler shift in the resonance energies due to relative motion of the source and absorber. The general expression for the transmitted intensity at a particular energy x when radiation from a source described by Eq. (34) is incident on an absorber described by equation (33) can easily be found since S_{11} gives the projection of the transrnitted source intensity on one of the basis polarizations and S_{22} that of the other.

$$I(x,v) = \frac{I}{V} \left[S_{11} e^{-\sigma_{11}} + S_{22} e^{-\sigma_{22}} \right] \qquad (35)$$

This expression is similar to the corresponding expression foi- the unpolarised radiation except For containing two terms instead of one on the right. It may be substracted from the incident intensily $S_{11}+S_{22}$ and the result integratea over x to obtain the fractional absorption dip at an Doppler velocity V. Integrating over v to obtain the dimensionless areai the absorption spectrum.

The unknown parameters of the experiment are contained in the o's and hopefully can be extracted from measurements made in different direction and/or with different thickness absorbers. If the absorption1i

nes are well resolved individual areas can be defined. Assuming source and absorber resonance lines to be of natural width, then after Bykov and Hein[47], for the overlap of the k^{th} source line from site with the i^{th} absorber line from site j, this gives

$$A_{ij}^{k} = S_{11}(x_{k\ell})\sigma_{11}(x_{ij}) \exp\left[\frac{\sigma_{11}(x_{ij})}{2}\right]\left\{I_0\left[\frac{\sigma_{11}(x_{ij})}{2}\right] + I_1\left[\frac{\sigma_{11}(x_{ij})}{2}\right]\right\}$$

$$+ S_{22}(x_{k\ell})\sigma_{22}(x_{ij}) \exp\left[\frac{\sigma_{22}(x_{ij})}{2}\right]\left\{I_0\left[\frac{\sigma_{22}(x_{ij})}{2}\right] + I_1\left[\frac{\sigma_{22}(x_{ij})}{2}\right]\right\} \quad (36)$$

where I_0, and I_1 are zeroth and first - order Bessel functions of imaginary arguments. When different absorber lines have same energy, their contributions are added in the arguments of functions of equation above.

The dimensionless area $A_{ij}^{k\ell}$ is related to the bõckground corrected experimental area B by

$$A_{ij}^{k\ell} = 2B/\Pi\Gamma \quad (37)$$

For relatively thin absorbers, power series expansions in equation (36) are useful. If we restrict ourselves for simplicity to a single line unpolarised source $S_{11} = S_{22} = f/2$ and we define the average cross section on resonance

$p = |\sigma_{11}(x_{ij}) + \sigma_{22}(x_{ij})|/2$ and the fractional polarisation

$a = \dfrac{\sigma_{11} - \sigma_{22}}{\sigma_{11} + \sigma_{22}}$ of the absorption we may write

$$A = p - \frac{1}{4}(1 + a^2)p^2 + \frac{1}{16}(1 + 3a^2)p^3 - \frac{5}{384}(1 + 6a^2 + a^4)p^4 + \ldots$$

on inverting

$$p = A + \frac{1}{4}(1 + a^2)A^2 + \frac{1}{16}(1 + a^2 + 2a^4)A^3 + \frac{5}{384}(1 + a^4 + 6a^6)A^4 \ldots$$

here

$$A = A_{ij}/f \tag{38}$$

Therefore for a relatively thin absorber, the effects of polarisations may be quite small unless fractional polarisations become large.

Equations for the area ratios which have been previously used in analysing the experimental data can be obtained by dropping all but the first term in equation (38).

Grant, Housley and Gonser[12] applied the above corrections to determine the electric field gradient and the mean square displacement tensor parameters at the Fe sites in sodium nitroprusside and found that the principal axes of two tensor do not coincide. Similar analysis was also applied in the case of $FeSO_4.4H_2O$ [33] in the temperature range of 300 -77K.

10. USING IPOLARISED RADIATION

The polarisation of γ rays has been reported[54-58] by many workers, and it can take place by the Stark and Zeeman effect that are already familiar in the optical polarisation studies[55]. If the recoilfree γ rays are brought into resonance the matching of polarisation components in the source and the absorber nuclear transitions is required in addition to the usual appropriate Doppler motion. For example, circularly polarised γ rays from a source can only be resonantly absorbed if a transition with the same helicity is offered (conservation of angular momentum). By observing the helicity of circularly polarised γ rays, the sign of magnetic hyperfine field can be determined .

Linearly polarised γ rays[60-62] are of particular interest. Some methods for producing 14.4 Kev linearly polarised γ rays are briefly described below;

One simple method is to use a magnetically source rnatrix (iron foil) and to magnetise it in a fixed direction. With iron foil it is

convenient to magnetise perpendicular to the direction of emission. The emitted radiation is then not monochromatic but consists of six individual coniponents with intensity ratios 3:4:1:1:4:3 each of which has a definite polarisation. In the case we are considering $\pm 3/2 \rightarrow \pm 1/2$ and $\pm 1/2 \rightarrow \pm 1/2$ transitions have a linear polarisation with the electric vector vihration parallel with respect to the magnetisation, and $\pm 1/2 \rightarrow \pm 1/2$ transitions are similar but perpendicularly polarised. In a single crystal absorber, of the source and absorber are directionally polarised by a magnetic field which can be internal in origin or by an electric field such as is associated with the electric field gradient tensor, the polarisation of each emission line becomes important. The relative orientation of the principal directions in the source and the absorbcr will cause variation of the line intensity. Detailed theory of the line intensities has been reported[63,64]. One of the first application of an iron foil source was in the determination of the sign of the quadrupole coupling constant in a single crystal of $FeSiF_6.6H_2O$ [65].

The assignment of hyperfine components in a complex spectrum would be easier if the source was effectively polarised and monochromatic so that the resonant absorption would only be observed in those transitions with the same polarisation. This method was first demonstrated by Housley[66] using a paramagnetic single crystalline source exhibiting a quadrupole spli: spectrum. If the V_{zz} principal axis of the EFG is perpendicular to the direction of observation the γ rays corresponding to the $\pm 3/2$ transition are totally linearly palarised and the γ rays corresponding to $\pm 1/2$ transition are partially linearly polarised. This more intense line can be selectively filtered out. The asymmetry parameter should be zero to ensure that the nuclear wavefunction are pure $|m>$ states.

An equivalent mthod which does not require a split source is to use a polariser. This was first demonstrated using iron foils magnetised perpendicular to the propagation[67] and more recently using a polycrystalline sample of Yattrium iron garnet (YIG).

When source and absorber exhibit a hyperfine interaction, the polarisation of the γ rays has to be taken into account in deriving the relative line intensities[56,69]. By analysing the line intensities ob-

tained from a source emitting linearly polarised recoilfree γ rays and a single crystal absorber cut in an arbitrary direction, one can determine the spin orientation and the principal axes of the EFG with respect to the crystal axes[6,16,17,65,70,71]. Daniels[72] has considered the problem of calculating line intensities in Mössbauer absorption using the polarised gamma rays polarised absorbers with especial reference to Fe^{57}.

The polarisation dependence has been reported in a number of theoretical studies[49,57,63,73-79] and various techniques have been used tc carry out polarimetry experiments based on transverly magnetised CO^{57}(αFe) source[51,52,58,60,61,64,68,71,74,80-88] or by filter technique[56,60,62,64,89]. Kultiplicity resulting from the six linearly polarised lines or inefficiency of the selective excitation or of the filters in terms of intensity, degree of polarisation and non Lorentzian lines are some of the disadvantages of the above methods. Sources exhibiting quadrupole hyperfine interaction will circumvent some of the problems. The utility of a quadrupole split CO^{57} source for a polarimeter depends on fulfillment of following conditions.

The material can be grown as a single crystal and cutting of thin plates in various directions is possible.

CO^{57} can be incorporated with a unique charge state and a crystallografically unique resonance site.

The lattice site should have axial symmetry with unique orientations.

The quadrupole splitting should be large or at least well resolved.

Gonser, Sakai and Keune[90] reported a qradrupole Fe^{57} polarimeter consisting of single crystal of $LiNbO_3$:CO^{57} as source (polariser) and $FeCO_3$ (siderite) as a absorber (analyser). The possibility of using two identical single crystals as polariser and analyser has been mentioned by Goldanskii *et al.*[45] and Gibb[86] used it as a means of determining tne directional data normal to the observation axis in the case of ferrous ammonium sulphate and the EFG was determined by using crystals grown on one particular face ($\bar{2}01$) so that the observation direction was nor-

mal to the b axis and at 47.3^0 to the c axis in the ac plane. This type of measurements have difficulty in measuring an accurate thickness curve and because of the large time envolved. The choice of the parameters to fit the data is also not unambiguous. Gibb[87] made further experiments on ferrous ammonium sulphate using a CO^{57}/Fe foil source magnetised in the plane of the foil and perpendicular of observation by mounting the source in between the poles of a permanent magnet. Thus, most inner and outer pair of lines were plane polarised while parallel to the applied magnetic field, and the other two lines are polarised perpendicular to the field.

Because of the self absorption in the source matrix, and, also due to incomplete polarisation of the foil in absence of the applied magnetic field is not strong enough, the predicted intensity ratios (3:4:1:1:4:3) are unlikely to be achieved. Gibb[91,92] redetermined the electric field gradient tensor in FeCl .4H O using a polarised Mössbauer source in the same method. Spiering and Vogel[93] calculated the absorption cross section for a polarised single crystal absorber of finite thickness using a intensity matrix method and applied it in the case of $FeCl_2.4H_2O$. Zimmermann[94] also made experiment on $FeCl_2.4H_2O$ using the intensity tensor method.

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