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Theory of Mössbauer Spectral Asymmetry of Quadrupole Split Lines in Liquid Crystals†

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Abstract—We have extended the theory for the intensity asymmetry of Fe-57 quadrupole split lines to iron bearing solutes in particular liquid crystalline systems. An expression for the area ratio is obtained for solutions (or suspensions) in smectic liquid crystalline systems with complete planar alignment and also for nematic solutions (or suspensions) which have been frozen so as to preserve their liquid crystalline order. The theory will allow determination of the order parameter of the Mössbauer impurity and the asymmetry parameter of the electric field gradient at the site of the resonant nucleus.

Introduction

The interaction of the quadrupole moment of the nuclear excited state ($I = \frac{3}{2}$) of Fe-57 with the electric field gradient (*efg*) at the iron site splits the observed Mössbauer resonance spectrum into two lines. In 1965, P. Zory(1) showed that the *efg* tensor could be determined from the dependence of the intensity ratio of the two spectral lines on the direction of the γ-ray beam with respect to the *efg* principal axes in a single crystal. More recently, the spectral asymmetry of the quadrupole split lines of an Fe-57 bearing solute has been observed in an aligned liquid crystalline system.(2) In this latter case the intensity ratio of the two lines was observed to depend on the angle between the γ-ray beam and the preferred molecular direction as determined by an external magnetic field. In this report we have extended Zory's result to apply to an ordered solute monocrystal in

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a liquid crystalline solution. In particular, our result is applicable to both a smectic liquid crystalline system with complete planar alignment and to a nematic system frozen so as to preserve the molecular alignment of the mesophase.(3) This theory will also account for the spectral asymmetry of oriented suspensions of rod-like crystallites in the above liquid crystal matrices.(4,5)

The main intent of this paper is to show that the asymmetry parameter of the *efg* tensor which is present in a particular compound can be determined without requiring data from solid single crystals of that compound. We show that for an ordered liquid crystalline system as described above that the Mössbauer intensity ratio for the Fe-57 quadrupole split doublet is dependent on the *efg* asymmetry parameter, the impurity order parameter(6) (defined below), the polar and azimuthal angles (β and μ, respectively) of the long molecular or crystallite axis in the principal axis system of the *efg*, and the experimental angle between the radiation direction and the preferred molecular direction.

Theory

The 14.4 keV nuclear excited state of Fe-57 is a spin (I) $\frac{3}{2}$ state. It is split into a doublet ($m = \pm\frac{3}{2}$ and $m = \pm\frac{1}{2}$) via the interaction of the nuclear quadrupole moment with the *efg* seen by the nucleus. Zory(1) has calculated the relative angular dependent absorption probabilities for the two transitions for unpolarized incident (magnetic dipole) Mössbauer radiation. His result is:

$$P_3(\theta_i, \phi_i) = \tfrac{1}{2} + \frac{1}{8(1+\eta^2/3)^{1/2}}[3\cos^2\theta_i - 1 + \eta\sin^2\theta_i\cos 2\phi_i] \quad \text{(1a)}$$

$$P_1(\theta_i, \phi_i) = \tfrac{1}{2} - \frac{1}{8(1+\eta^2/3)^{1/2}}[3\cos^2\theta_i - 1 + \eta\sin^2\theta_i\cos 2\phi_i] \quad \text{(1b)}$$

where $P_3(\theta_i, \phi_i)$ and $P_1(\theta_i, \phi_i)$ are the transition probabilities from the ground state ($I = \frac{1}{2}$) to the split excited states with $m = \pm\frac{3}{2}$ and $m = \pm\frac{1}{2}$, respectively; η is the asymmetry parameter of the *efg* tensor and θ_i and ϕ_i are the polar and azimuthal angles of the γ-ray direction in the *efg* principal axis system of the *i*th site. The experimentally relevant parameter, however, is the ratio of the total intensities (or absorption line areas) which is related to the transition probabilities of Eq. (1) as follows:

$$\frac{A_3}{A_1}=\frac{\sum_i P_3(\theta_i,\phi_i)f'(\theta_i,\phi_i)}{\sum_i P_1(\theta_i,\phi_i)f'(\theta_i,\phi_i)} \tag{2}$$

where A_3/A_1 is the area ratio for the two transition lines and $f'(\theta_i, \phi_i)$ is the recoil-free fraction as a function of θ_i and ϕ_i and the sum over the index i accounts for the different nuclear sites. For powdered samples where all values of θ and ϕ are present then the sums of Eq. (2) must be replaced by integrals. If the single crystal is such that the *efg* experienced by all the resonant nuclei is of the same magnitude and has the same orientation relative to the incoming gamma beam then each sum in Eq. (2) reduces to one term and the recoil free fraction anisotropy cancels out leaving:

$$\frac{A_3}{A_1}=\frac{P_3(\theta,\phi)}{P_1(\theta,\phi)} \tag{3}$$

Kaplan and Glasser⁽⁷⁾ have predicted the recoil free fraction in a smectic liquid crystal to be:

$$f_i = B\exp(-c\sin^2\rho_i) \tag{4}$$

where B is a constant, c is a measure of the anisotropy of the restorative forces parallel and perpendicular to the smectic direction (normal to the layers), and ρ_i is the angle between the smectic direction and the γ-beam direction for the ith molecule. Since the orientation of the molecules relative to the planar normal does not affect the value of the recoil free fraction, a smectic with *perfect* planar alignment ($\rho_i=\rho$ for all i) will provide the same resonant probability for all of the Mössbauer nuclei. As a result, for complete planar alignment Eq. (2) becomes:

$$\frac{A_3}{A_1}=\frac{\sum_i P_3(\theta_i,\phi_i)B\exp(-c\sin^2\rho)}{\sum_i P_1(\theta_i,\phi_i)B\exp(-c\sin^2\rho)} \tag{5}$$

because f_i depends only on ρ_i and for perfect planar alignment $\rho_i=\rho$ for all i. Consequently, Eq. (5) reduces to:

$$\frac{A_3}{A_1}=\frac{\sum_i P_3(\theta_i,\phi_i)}{\sum_i P_1(\theta_i,\phi_i)} \tag{6}$$

which is independent of the recoil free fraction as is Eq. (3). Equation (6) should also be applicable to a frozen nematic solution where one can reasonably expect that the anisotropy of the recoil free fraction will be small and therefore not contribute significantly to the area ratio.

A more useful way of writing Eq. (6) is in terms of the angle between the preferred molecular direction (as determined by an external magnetic field) and the radiation direction. This angle is the measurable experimental commodity. The problem then is to transform Eqs. (1a) and (1b) to the laboratory system accounting for the properties of a liquid crystal. The theory will apply to extended solute molecules which retain their identities in solution and to small rod-like crystallites⁽⁴⁾ which form a suspension in the liquid crystalline matrix. In both cases it is assumed that the impurity will experience the alignment characteristic of the liquid crystal molecules, themselves.

Consider a molecule which has an asymmetric *efg* tensor such that none of the *efg* principal axes coincide with the long molecular axis. Figure 1 illustrates the situation for this molecule. The angles Θ and Φ are the orientation angles of the γ-ray direction with respect to the molecular axes (a, c, b) and the angles θ and ϕ relate the radiation direction to the *efg* principal axes (x, y, z). The three Euler angles relating the orientation of the *efg* system with the molecular system are designated by (μ, β, α).⁽⁸⁾ To be noted is the fact that because of the rotational freedom of the molecule about its long axis in the liquid crystal the angle α is completely unspecified and will therefore not appear in the area ratio expression.

The angular terms in Eq. (1) can now be written in terms of the molecular coordinate system as follows⁽¹⁾:

$$\begin{aligned}
\sin^2\theta\cos^2\phi &= [\sin\Theta\cos\Phi(\hat{a}\cdot\hat{x})+\sin\Theta\sin\Phi(\hat{c}\cdot\hat{x})+\cos\Theta(\hat{b}\cdot\hat{x})]^2\\
\sin^2\theta\sin^2\phi &= [\sin\Theta\cos\Phi(a\cdot\hat{y})+\sin\Theta\sin\Phi(\hat{c}\cdot\hat{y})+\cos\Theta(\hat{b}\cdot\hat{y})]^2 \qquad (7)\\
\cos^2\theta &= [\sin\Theta\cos\Phi(\hat{a}\cdot\hat{z})+\sin\Theta\sin\Phi(\hat{c}\cdot\hat{z})+\cos\Theta(\hat{b}\cdot\hat{z})]^2.
\end{aligned}$$

Each of the direction cosines $(\hat{a}\cdot\hat{x})$, $(\hat{c}\cdot\hat{y})$, etc., is easily expressed in terms of the components of the Euler matrix and therefore (μ, β, α). P_3 and P_1 for this molecule can then be written in terms of μ, β, α, Θ, and Φ. Because of a molecule's rotational freedom around its long axis in a liquid crystal, one must average over the angle Φ in the computation of the area ratio. As a result, for complete parallel alignment of the molecules (as well as the previous requirement of

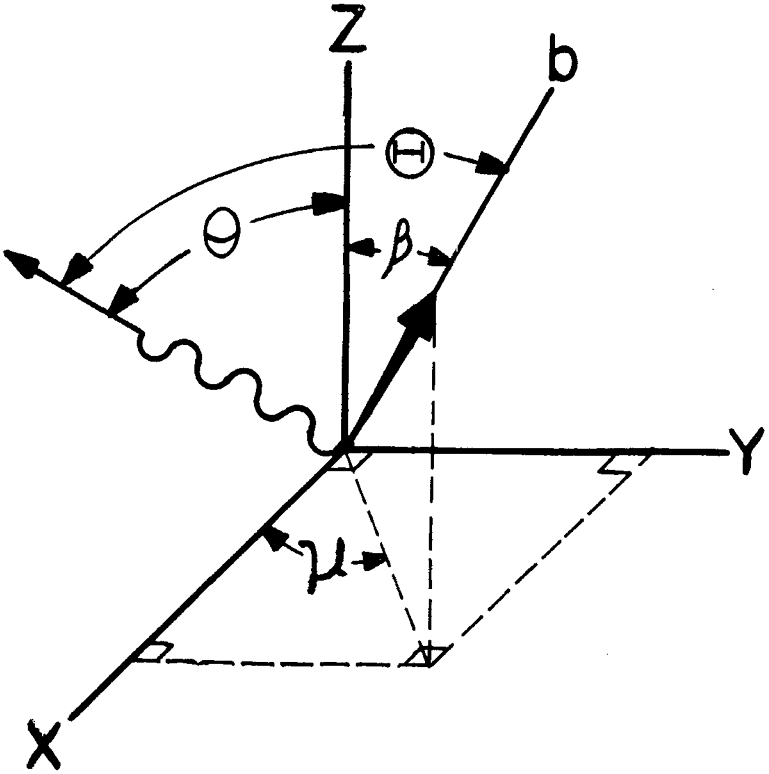

Figure 1. The polar and azimuthal angles of the molecular direction in the principal axis system of the electric field gradient are given by β and μ, respectively. Also the polar angle of the γ-beam direction is shown in each coordinate system.

complete planar alignment in the smectic) the area ratio of Eq. (6) becomes:

$$\frac{A_3}{A_1}=\frac{\frac{1}{2}+[1/16(1+\eta^2/3)^{1/2}]\,[(3\cos^2\Theta-1)\{3\cos^2\beta-1+\eta\sin^2\beta\cos 2\mu\}]}{\frac{1}{2}-[1/16(1+\eta^2/3)^{1/2}]\,[(3\cos^2\Theta-1)\{3\cos^2\beta-1+\eta\sin^2\beta\cos 2\mu\}]} \tag{8}$$

where μ and β are the previously defined Euler angles (see Fig. 1) and Θ is the polar angle of the γ-direction in the molecular coordinate system.

Unfortunately, this result does not correspond to a real situation and a further transformation is required. In order to align a nematic solution of considerable bulk one usually relies on a strong magnetic field. A smectic liquid crystal can also be aligned this way if the material possesses a higher temperature nematic phase which can be aligned with the field, because on cooling the smectic phase will retain the nematic order. The molecules, however, will not all be absolutely parallel to the magnetic field but rather, will be distributed about the field direction according to the following angular distribution function:

$$\mathrm{f}(\delta) \propto \exp\,[(b/kT)\sin^2\delta] \tag{9}$$

where b depends on the molar volume, T is the absolute temperature, k is Boltzmann's constant and δ is the angle between a particular molecule's long axis and the magnetic field.(9)

The second transformation requires an Euler matrix(8) (δ, ϵ) relating the molecular axis system to the laboratory system defined by the magnetic field direction (see Fig. 2). The angles δ and ϵ are polar and azimuthal angles of the molecule in the lab system, respectively. The total transformation relating the *efg* system to the lab system is the product of the two Euler matrices $(\mu, \beta, \alpha) \times (\delta, \epsilon)$. A new set of relations similar to Eq. (7) can now be written linking the *efg* and lab systems. In the new set of relations the angles γ and ξ which are the polar and azimuthal angles of the gamma direction in the lab system replace Θ and Φ of Eq. (7). Also, the new direction cosines can be expressed in terms of the five Euler angles $(\delta, \epsilon, \mu, \beta, \alpha)$. Then after taking the appropriate averages which account for the axial symmetry of the magnetic field and the rotational freedom of the molecule about its long axis, we find the following expression for the area ratio:

$$\frac{A_3}{A_1} = \frac{\frac{1}{2} + [1/16(1+\eta^2/3)^{1/2}]\{(3\cos^2\gamma - 1)\langle \frac{1}{2}(3\cos^2\delta - 1)\rangle \cdot [3\cos^2\beta - 1 + \eta\sin^2\beta\cos 2\mu]\}}{\frac{1}{2} - [1/16(1+\eta^2/3)^{1/2}]\{(3\cos^2\gamma - 1)\langle \frac{1}{2}(3\cos^2\delta - 1)\rangle \cdot [3\cos^2\beta - 1 + \eta\sin^2\beta\cos 2\mu]\}} \tag{10}$$

where all the parameters are as defined previously. The average value of $\frac{1}{2}(3\cos^2\delta - 1)$ appears in Eq. (10) because as stated previously the weighted average over δ must be performed using Eq. (9) as the weighting factor. This averaged quantity is commonly referred to as the molecular order (S) in a liquid crystal and is measurable by a variety of techniques including nmr, epr, dielectric

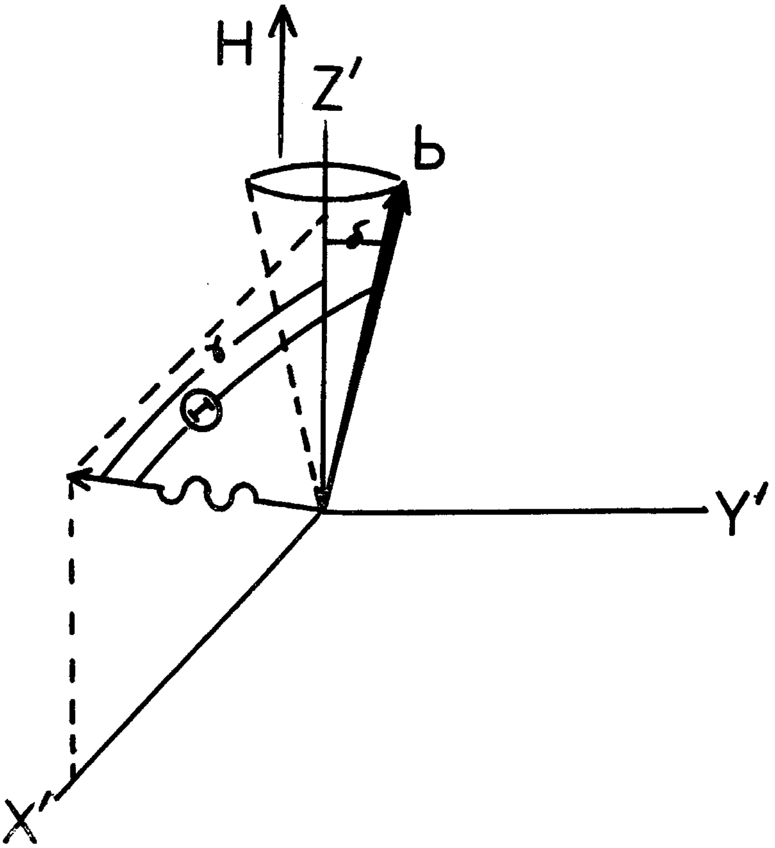

Figure 2. The polar angle of the molecule in the laboratory coordinate system (defined by the magnetic field direction, H) is shown to be δ. Also the angle between H and the γ-direction is represented by γ (the experimental angle) and the angle between the molecular axis and the γ-direction is given by Θ.

relaxation, etc.(10) Since Mössbauer experiments will be mainly on solutes or suspensions in the liquid crystal the S value will be for these rather than the liquid crystal molecules.

It is our contention, therefore, that with some crystallographic information allowing guesses of μ and β to be made, then a best fit of the data for $0° \leqslant \gamma \leqslant 90°$ will yield both S and η for the iron bearing solute or crystallite. This theory is applicable to smectics with complete planar alignment and to frozen nematics which have been aligned with an external field. It does not apply, however, to the experimental data of Ref. 2. This is because that experiment did not provide complete alignment of the smectic planes but rather provided a cone of planes about the molecular direction as determined by the orienting field. That the theory does not agree with their data is easily seen from Eq. 10 which yields $A_3/A_1 = 1$ for $\gamma = 55°$ which is not the observation of Ref. 2.

Conclusion

In conclusion, several things may be said: (1) It is possible to determine the asymmetry parameter of the *efg* tensor for molecules which are unavailable in the form of single crystals. (2) The Mössbauer effect can be used to determine the order parameter in liquid crystals. In particular, if the solute molecule has an axial *efg* then $\eta = 0$ and the only unknown in Eq. (8) is S. (3) This theory should hold not only for Fe-57 but also for Sn-119 inasmuch as the two have identical Mössbauer spin states and both experience resonance via magnetic dipole radiation.

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