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A Mössbauer Study of a Sn-119 Bearing Solute in an Ordered Smectic Liquid Crystal, at 77 °K†‡

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Abstract—An ordered solute "monocrystal" was obtained by dissolving 3.5–7.0% (by weight) of triethyltin palmitate (3EtSnPalm) into 4-*n*-hexoxybenzylidene-4′-*n*-propylaniline and cooling from 90 °C to room temperature through the nematic and smectic *A* phases to the smectic *H* phase ($T < 60$ °C) in a magnetic field of 9000 Gauss. The disc-shaped sample was then removed from the magnetic field and cooled to 77 °K at which temperature the Mössbauer measurements were made. From the variation of the area ratio of the two quadrupole split Mössbauer absorption peaks as a function of the angle θ between the orienting magnetic fields and the γ-ray beam we have determined the sign of the axial electric field gradient (V_{zz}) at the tin site in 3EtSnPalm to be positive. Further, the theoretical fit to the data yielded the solute order parameter, $S = 0.17$ and the molecular contribution to the nuclear vibrational anisotropy for the tin atom in the 3EtSnPalm molecule, $\epsilon_M = -0.8$. An independent value of $\epsilon_M = -1.50$ was obtained from the orientational dependence of the recoil-free fraction (as percent effect). The difference is attributed to the lattice contribution to the recoil-free fraction in the latter case. A field dependent study of the area ratio showed that the surface oriented the molecules perpendicular to the surface normal.

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1. Introduction

Mössbauer effect spectroscopy has become a very useful way of studying the interaction between the nuclear quadrupole moment and the electric field gradient (efg) at the sites of the heavy metal Mössbauer nuclei in solids. Unfortunately, only a small portion of the useful information about this interaction is usually obtained in the typical Mössbauer experiment which involves an $I = 3/2 - I = 1/2$ transition as in Fe-57 and Sn-119. In particular, the sign of the principal component of the efg tensor (V_{zz}) cannot be obtained from normal powder pattern spectroscopy,[1] and even the magnitude cannot be obtained for nuclei which are in sites of less than axial symmetry.[2] This is easily seen from the expression for the quadrupole splitting energy

$$E_Q = \tfrac{1}{2}eQV_{zz}(1 + \tfrac{1}{3}\eta^2)^{1/2} \tag{1}$$

where e is the proton charge, Q is the quadrupole moment of the $I = 3/2$ state, and $\eta \equiv (V_{xx} - V_{yy})/V_{zz}$ which is the anisotropy parameter of the efg tensor.

Zory has shown how to obtain both the magnitude and sign of V_{zz} by making use of single crystal absorbers.[3] However, the availability of single crystal platelets cut at precise angles with respect to the crystallographic axes for any one compound is severely limited. In fact, there are several classes of compounds, such as the metal organics, for which suitable single crystals cannot be grown, much less cut and oriented. The basic problem in Fe-57 and Sn-119 spectroscopy is the identification of the two quadrupole split lines. For single crystals Zory[3] shows that whether the ratio of the intensity of the $m = 3/2$ transition (π-transition) to the $m = 1/2$ transition (σ-transition) is greater or less than one for a particular orientation depends on the sign of V_{zz}, thus allowing identification of the lines. There are two other methods which allow the determination of the sign of V_{zz} for axial molecules. The first method was reported by Collins[1] and then by Collins and Travis.[4] Their classic work involved the measurement and calculation of the consequences of applying a large external magnetic field (20–40 kg) to iron compounds which exhibited a relatively large quadrupole splitting. By comparing the calculated effect of the external Zeeman

field on the quadrupole split doublet with experiment, they were able to identify the π and the σ transition lines and, therefore, determine the sign of V_{zz} for several iron compounds. The second method makes use of X-ray diffraction data to determine whether the equivalent ellipsoid of electronic charge about the Mössbauer nuclide has a prolate (V_{zz} negative) or an oblate (V_{zz} positive) shape. The X-ray data have been used to identify the transition lines in some Mössbauer experiments whose object is the nuclear vibrational anisotropy of the Mössbauer nuclide in some molecular crystals. Herber *et al.*, have used the above method in discussing the Godanskii–Karyagin effect in triethyltin cyanide, for example.[5] Also, if the anisotropy is known from other methods, the Mössbauer lines can then be identified from their intensity ratio, thus yielding the sign of V_{zz}.

In this report we have determined the sign of the principal component of the efg tensor (V_{zz}) to be positive for the axially symmetric molecule triethyltin palmitate (3EtSnPalm). Furthermore, we have determined the value of the molecular contribution to the nuclear vibrational anisotropy parameter which is defined as follows:

$$\epsilon_M = (\langle x_\parallel^2 \rangle - \langle x_\perp^2 \rangle)/\lambda^2 \qquad (2)$$

where $\langle x_\parallel^2 \rangle$ and $\langle x_\perp^2 \rangle$ are the mean square vibrational amplitudes parallel and perpendicular to the molecular axis of the 3EtSnPalm molecule and λ is the reduced wavelength of the Mössbauer γ-ray.

We obtained an ordered solute " monocrystal " by dissolving $\sim 5\%$ (by weight) of 3EtSnPalm into 4-*n*-hexoxybenzylidene-4′-*n*-propylaniline (HBPA). HBPA is a liquid crystalline material possessing the following phase transitions: isotropic-nematic at 85 °C, nematic-smectic *A* at 68 °C and smectic *A*-smectic *H* at 66 °C. The smectic *H* phase is very viscous and exhibits a characteristic tilt angle (τ) between the planar normal and the preferred molecular direction. In addition there is a regular relation (probably hexagonal) between the molecular axes within the layer.[6]

The experimental method employed is similar to that described by Uhrich *et al.*[7] The disc-shaped sample was heated to 90 °C in a magnetic field of 9000 Gauss and then cooled in the field to room temperature. At this temperature the sample existed in the smectic *H* phase and could be removed from the magnetic field without disturbing the molecular alignment. At this point, the sample was

inserted into a liquid nitrogen Mössbauer absorber dewar and cooled to 77 °K where the smectic H order remained. This procedure could be repeated several times so data could be obtained for the whole range of $\theta(0° \leqslant \theta \leqslant 90°)$. Here θ is the angle between the normal to the disc face (and therefore, the γ-beam direction) and the preferred molecular direction as determined by the magnetic field. The significant difference between this work and that of Ref. 7 is that the Mössbauer measurements were made at 77 °K which is required for most Sn-119 spectroscopy. Orientation data for the area ratio of the π-transition relative to the σ-transition and the percent effect of the two lines were obtained. From the former we were able to identify the two transition lines using the theory of Wilson and Uhrich.[8] Further, in order to fit the area ratio data, the above theory had to be modified to include the anisotropy of the molecular contribution to the recoil free fraction. As a result the area ratio data also yielded the anisotropy parameter ϵ_M for the 3EtSnPalm molecule and the molecular order parameter for the solute molecules in the supercooled liquid crystalline matrix. The anisotropy parameter found differed from the value of ϵ_M found using the orientation dependence of the recoil-free fraction of the quadrupole split doublet due to lattice effects in the latter.

Therefore, without single crystals, without the use of superconducting magnets, and without the need of supplementary data from other sources, e.g., X-rays, we have found that for 3EtSnPalm, V_{zz} is positive, $\epsilon_M = -0.80$ and that the liquid crystal order parameter for the solute molecules is $S = 0.17$. Further, all the measurements can be made at a single temperature (77 °K) and with a single sample. The experimental technique used in this work is extremely simple and routine and really only requires that the molecule which contains the Mössbauer nuclide have a unique long axis and that it dissolve in the appropriate liquid crystalline material. As more and more low temperature smectic phases are discovered any solubility problems for iron and tin bearing molecules should be minimized. In addition with a few modifications the asymmetry parameter η of the efg tensor can be obtained from experiments of this type. In fact, the theory of Ref. 8 already includes it and slight modification would allow its determination for non-axially symmetric molecules.

In the following sections we will give the details of the experiment,

the modifications of the theory of Ref. 8 required for the data of this paper and the experimental results and the calculated fits of the theory to the experiment.

2. Experiment

Sample Preparation

The triethyltin palmitate was prepared by standard techniques from the starting materials bis(trimethyl tin) oxide and palmitic acid.[9] The 4-*n*-hexoxybenzylidene-4′-*n*-propylaniline (HBPA) was prepared using the following synthetic route. A mixture of 4-*n*-hexoxybenzaldehyde (20 g. 0.1 m) and 4-*n*-propylaniline (13.5 g. 0.1 m) in ethanol (80 ml) was refluxed for 5 h. The resulting solution was cooled and the precipitate filtered. Recrystallization from absolute ethanol four times gave 4-*n*-hexoxybenzylidene-4′-*n*-propylaniline (22.7 g, 0.07 m, 70%) DTA 29 (C-Sm*H*) 65.7 (Sm*H*-Sm*A*), 68° (Sm*A*-N), 85.6 (N-I), mass spectrum (70 eV) *m/e* (rel. intensity) 324 (16), 323 (*m* +, 100), 295 (10), 294 (47), 239 (7), 211 (13), 210 (85), 180 (5), 91 (13), 90 (18), 89 (6), 77 (10), 65 (14). Elemental analysis C (cal: 81.69%; found: 81.86%), H(Cal: 9.04%; found: 9.02%), N(Cal: 4.33%; found: 4.20%). The HBPA when first prepared showed a crystal to smectic *H* phase transition at 29 °C upon heating. Further heating yielded the following behavior:

$$\text{Smectic } H \xrightarrow{66\,^\circ\text{C}} \text{Smectic } A \xrightarrow{68\,^\circ\text{C}} \text{Nematic} \xrightarrow{85\,^\circ\text{C}} \text{Isotropic Liquid.}$$

Upon cooling the material from the isotropic, a smectic *H*-solid transition was not found down to 77 °K. Even repeated heating and cooling failed to cause crystallization. The phases were classified via microscopic observation of the textures through crossed polarizers. Of particular interest was the smectic *H* phase which exhibited a beautiful mosaic texture. Transition temperatures were verified by means of differential thermal analysis. Both the microscope (Reichert Thermopanmicroscope equipped with a Köfler Hotstage) and the differential thermal analysis equipment (Du Pont thermograph model 920) are discussed elsewhere.[10]

The Mössbauer experiments were performed on four separate samples of 3EtSnPalm dissolved in HBPA. They contained 3.5%,

5%, 5% and 7% of 3EtSnPalm by weight, respectively. Within experimental error the Mössbauer experiments on all four samples yielded data which were indistinguishable. The solutions were made by heating weighed portions of the two components in vacuum to 90 °C and allowing the solution to stand at this temperature for about three hours. Microscopic evaluation of the product showed that the smectic *H* and nematic had maintained their integrity with the only effects being the suppression of the nematic-isotropic transition by several degrees and the loss of the short smectic *A* range. The latter resulted in a nematic-smectic *H* transition temperature of 60 °C. This was verified by differential thermal analysis. The resulting solution appeared to be completely homogenous and free of particles and extra phases. The samples were particularly stable and were used for at least one set of orientation runs each and after several weeks showed no signs of deterioration.

Mössbauer Spectometer

All the Mössbauer experiments employed a standard constant acceleration spectrometer based on an electromechanical feed back system.[11] The data were stored in a Victorian PiP 400A multichannel analyzer which was operated in the time mode. All spectra were fit with two Lorentzian lines via a Burroughs 5500 computer. All of the area ratios, splittings, isomer shifts, linewidths, and intensities used in this work are from the computer fit data. Typical spectra are provided in Fig. 1. The spectrometer was calibrated by using a Co-57 in Cu source on the back end of the shaker and a National Bureau of Standards standard metallic iron absorber. The Co-57 source was purchased from International Chemical and Nuclear Corporation. The Sn-119 Mössbauer source employed was 5 mCi of Sn-119 as $BaSnO_3$. All isomer shifts were with respect to the room temperature $BaSnO_3$ source. This source was obtained from the New England Nuclear Corporation. The K X-ray was filtered out by using a 2 mil thick palladium foil.

The area ratios and recoil-free fractions (as percents of the background counts) recorded in this paper are the average values taken from multiple runs (at least four) on the four samples prepared for this study. The average deviation for the area ratios is slightly less

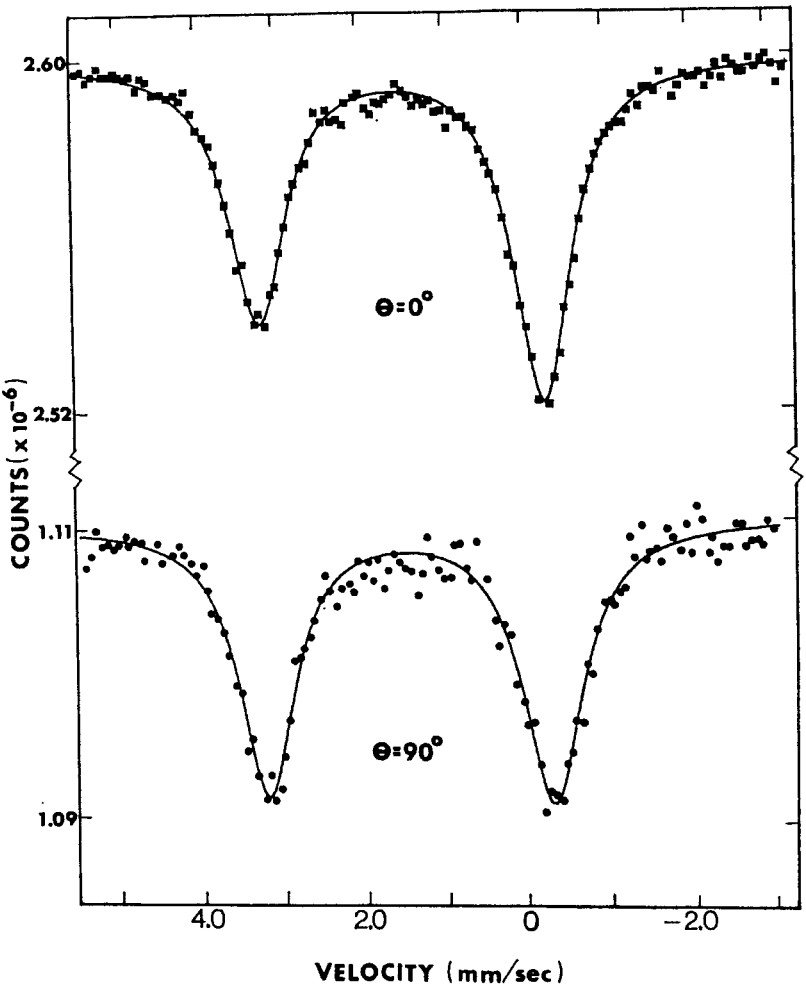

Figure 1. The Mössbauer transmission spectra for 3.5% (by weight) of 3EtSnPalm in HBPA at 77 °K is shown for $\theta = 0°$ and $\theta = 90°$, where θ is the angle between the molecular preferred direction as determined by the external magnetic field (H = 9000 g) and the gamma beam from a $BaSnO_3$ source. The solid lines are the best fits of two lorentzian lines to the data.

than ± 0.05. The average deviation for the normalized percent effects is also slightly less than ± 0.05. We estimateth is to be the maximum error possible. Because there was no trend in the linewidths the percent effect was used as a measure of the recoil-free fraction. From the rather smooth variation of our data points with θ in Figs. 2, 6 and 7, we think our above claims for accuracy are somewhat conservative.

The peak positions and the resulting isomer shifts and quadrupole splittings were obtained to within ± 0.02 mm/sec. The uncertainty in the fitted linewidths was ± 0.03 mm/sec.

Mössbauer Absorber Alignment

The solution of the 3EtSnPalm in HBPA was heated to the isotropic phase (85 °C) in a nitrogen atmosphere and then poured into a teflon washer of thickness 0.125 in. and diameter 0.50 in. Either 10 mil mylar or 10 mil beryllium discs were used to form a sandwich to contain the disc shaped sample. Teflon tape was used to hold the sandwich intact. The absorber samples met the criterion of " thin " absorbers because the number of Sn-119 nuclei presented to the beam was $n \lesssim 10^{18}/\text{cm}^2$.

The sandwich was placed into a brass holder which could be inserted into a small brass alignment oven. The oven was positioned in the air gap of a 10-in. Magnion magnet and it could be oriented such that the face of the sample disc would make an angle θ with the magnetic field ($0 \leqslant \theta \leqslant 90$). The error in the measurement of the angle θ is estimated to be $\pm 2°$. The sample was then heated to the isotropic liquid (90 °C) in the magnetic field and cooled through the nematic phase to the smectic H phase ($T < 60$ °C) at room temperature. The total cooling process took about two hours with the isotropic to smectic H portion comprising about 45 min. The brass holder which contained the aligned sample was then removed from the oven and the magnetic field and inserted into the Andonian absorber cyrostat. The absorber was actually cooled from room temperature to 77 °K almost instantaneously by immersing it directly into liquid nitrogen. This, however, is probably not necessary for maintaining the molecular alignment but was just convenient in our experimental setup. This procedure was repeated several times for

each sample so that we could obtain the area ratio and the recoil-free fraction as a function of θ and also the magnetic field strength. Orientation data were reproducible even after periods of two or three weeks for the same sample and were independent of the concentrations of 3EtSnPalm which were used.

The quadrupole splitting ($\Delta = 3.54$ mm/sec) and the isomer shift ($\delta = 1.42$ mm/sec) were independent of orientation and solute concentration, as expected. Further, the solution values are the same as the values which we obtained for the pure 3EtSnPalm in the solid state at 77 °K. This indicates that the tin molecule maintains the same configuration in the solid and in the liquid crystal solution. As a result, the solid cannot polymerize as was found in trimethyltin-acetate, for example.[12] The reason is that polymerization requires the tin atom to lie in the plane of the three ethyl (or methyl) groups. This, however, could not possibly be the minimum energy configuration in solution and since the Mössbauer parameters do not change from solid to solution the threefold pyramidal symmetry of the molecule must be present in the solid state as well.[13,14] This agrees with the observation that as the length of the R or R′ chain increases in $R_3SnOCOR'$ the polymer type structures break down.[15]

3. Theory

The 3EtSnPalm molecule has axial symmetry and it is assumed that the long molecular axis is coincident with the z-principal axis of the efg tensor. For the case of an axial molecule dissolved in a smectic liquid crystal with complete planar alignment the theory of Ref. 8 predicts the area ratio to be:

$$\frac{A_\pi}{A_\sigma} = \frac{(1/2) + (1/8)(3\cos^2\theta - 1)\langle(1/2)(3\cos^2\delta - 1)\rangle}{(1/2) - (1/8)(3\cos^2\theta - 1)\langle(1/2)(3\cos^2\delta - 1)\rangle} \tag{3}$$

where θ is the angle between the preferred molecular direction as determined by the magnetic field and the γ-ray beam, and $\langle(1/2)(3\cos^2\delta - 1)\rangle$ is the spatial order parameter S which was first defined by Saupe[16] and δ is the polar angle that a particular molecule makes with the preferred direction. As is obvious from Eq. (3), the ratio of the intensity of the π-transition (A_π) to the intensity of the σ-transition (A_σ) is required to be unity for $\theta = 55°$. The experimental

data of this paper while yielding a curve of the general form of Eq. (3) show that the ratio A_π/A_σ never is equal to unity and only approaches unity for $\theta = 90°$ (see Fig. 2). This difference between theory and experiment can be accounted for by including in the theory the molecular contribution to the nuclear vibrational anisotropy which appears in the Mössbauer recoil-free fraction. Here we assume that a

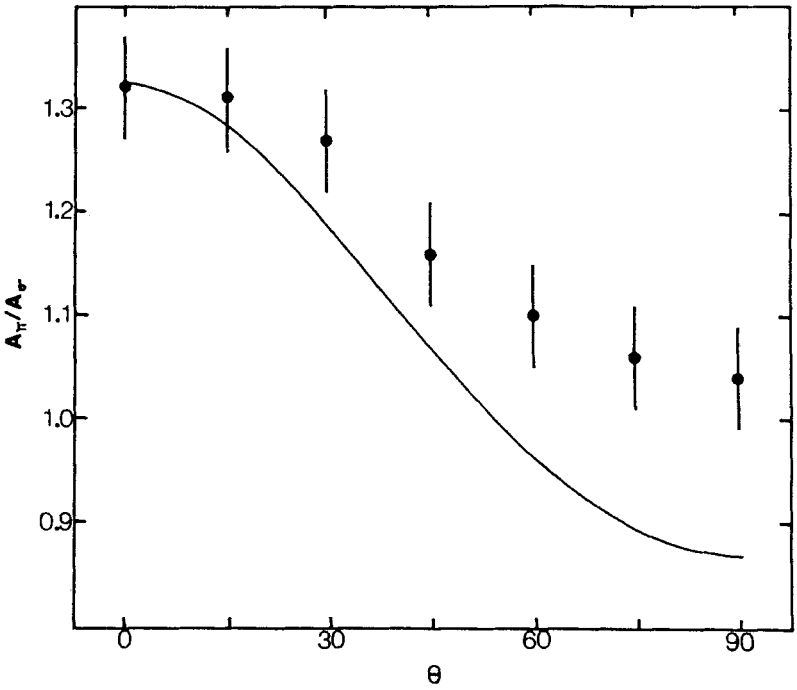

Figure 2. A plot of the area ratio (A_π/A_σ) vs. θ for 3EtSnPalm in HBPA at 77 °K. The solid line is a fit of Eq. (3) to the data with $S = 0.28$.

principal axis of the nuclear vibrational ellipsoid is parallel to the long axis of the molecule and, therefore, coincident with the z efg axis. The contribution of the anisotropy of the lattice restorative forces of the smectic layers has been shown not to contribute to the area ratio for smectics with complete planar alignment.[8] In fact it is accounted for in the derivation of Eq. (3). Flinn, Ruby and Kehl have determined the dependence of A_π/A_σ on the nuclear vibrational anisotropy parameter ϵ for a polycrystalline sample.[17]

They find that the net effect is to make the value of the area ratio deviate from unity depending on the sign of ϵ. Therefore, if one were to naïvely guess that incorporating this into the area ratio calculation would just raise or lower the entire A_π/A_σ vs. θ curve, then it is seen that the desired effect of moving the $A_\pi/A_\sigma = 1$ point along the θ axis is accomplished.

Zory has calculated the angular dependent absorption probabilities for the two quadrupole split transitions for unpolarized incident (magnetic dipole) radiation.[3] His result for an axially symmetric molecule whose long axis is coincident with the z-axis of the efg tensor and for which the asymmetry parameter vanishes is:

$$\begin{aligned} P_\pi(\gamma_i) &= 1 + (1/4)(3\cos^2\gamma_i - 1) \\ P_\sigma(\gamma_i) &= 1 - (1/4)(3\cos^2\gamma_i - 1) \end{aligned} \tag{4}$$

where $P_\pi(\gamma_i)$ and $P_\sigma(\gamma_i)$ are the transition probabilities from the ground state ($I = 1/2$) to the split excited states with $m = \pm 3/2$ and $m = \pm 1/2$, respectively; and γ_i is the angle between the long molecular axis and the γ-ray direction for the ith molecule. The ratio of the total intensities (or absorption line areas) is related to the transition probabilities of Eq. (4) as follows:

$$\frac{A_\pi}{A_\sigma} = \frac{\Sigma_i P_\pi(\gamma_i) f(\gamma_i, \rho_i)}{\Sigma_i P_\sigma(\gamma_i) f(\gamma_i, \rho_i)} \tag{5}$$

where $f(\gamma_i, \rho_i)$ is the recoil-free fraction as a function of γ_i and ρ_i and the sum over i takes into account the different nuclear sites due to the orientational distribution of the molecules. Here ρ_i is the angle between the smectic layer normal and the gamma direction for the ith molecule. The recoil-free fraction can be approximated by a product of the molecular and liquid crystalline lattice contributions and is:

$$f(\gamma_i, \rho_i) = f_M(\gamma_i) f_L(\rho_i) = B \exp(-\epsilon_M \cos^2\gamma_i) \exp(-\epsilon_L \cos^2\rho_i) \tag{6}$$

where B is a constant, $\exp(-\epsilon_M \cos^2\gamma_i)$ is the molecular contribution and ϵ_M is defined in Eq. (2), and $\exp(-\epsilon_L \cos^2\rho_i)$ is the lattice contribution for a smectic.[18] Since all the molecules in a smectic with a perfect planar arrangement will experience the same angle ρ, the

dependence on ρ will cancel out of Eq. (5). As a result Eq. (5) takes the following form:

$$\frac{A_\pi}{A_\sigma} = \frac{\Sigma_i[1 + (1/4)(3\cos^2\gamma_i - 1)]\exp(-\epsilon_M \cos^2\gamma_i)}{\Sigma_i[1 - (1/4)(3\cos^2\gamma_i - 1)]\exp(-\epsilon_M \cos^2\gamma_i)}. \tag{7}$$

Now we consider the laboratory coordinate system (Fig. 3) where δ_i and α_i are the polar and azimuthal angles of the ith molecule in the coordinate system whose z-axis is defined by the external magnetic field (H) and in which the Mössbauer gamma direction lies in the x-z plane. Then the result of transforming from the molecular system to the laboratory system yields:

$$\cos^2\gamma_i = [\sin\delta_i \sin\theta \cos\alpha_i + \cos\theta \cos\delta_i]^2. \tag{8}$$

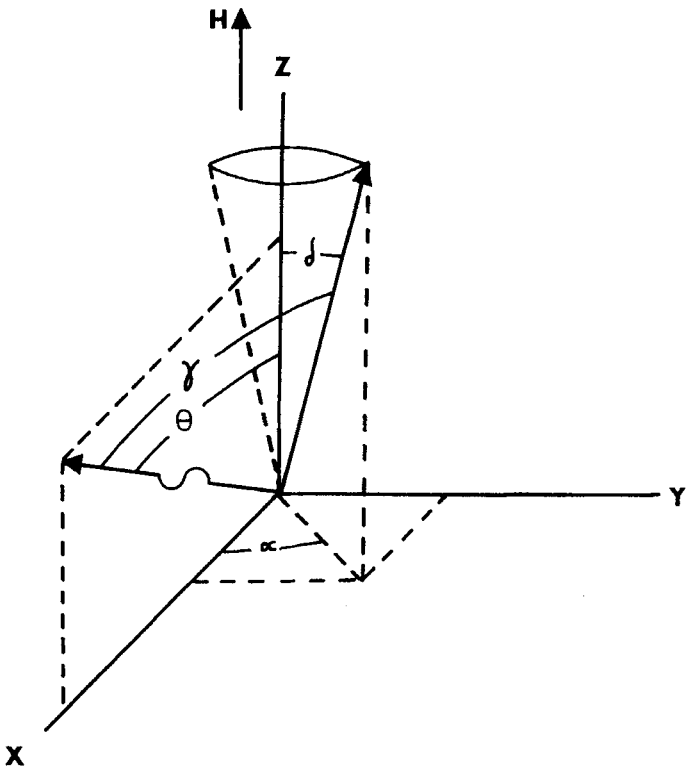

Figure 3. The polar and azimuthal angles of the molecular direction in the laboratory coordinate system are given by δ and α, respectively. The angle θ is the experimental angle between the preferred molecular direction and the gamma beam direction.

For a continuous distribution of molecules the sums in Eq. (7) become integrals. The spatial distribution of the molecules about the magnetic field is given by Saupe's angular distribution function:

$$F = C \exp[-(q/kT)(\sin^2 \delta)] \tag{9}$$

where q is a measure of the orientational order, T is the absolute temperature and k is Boltzmann's constant.[19] Therefore, the integration is over the spherical angle (4π) of the molecular orientations weighted according to the distribution function of Eq. (9). This cylindrically symmetric distribution function is not strictly correct and the anisotropy inherent in the highly ordered smectic H phase should really be accounted for. For our purposes, however, we will assume that the anisotropy in the plane perpendicular to the molecular axis is small compared to the anisotropy described in Eq. (9). Eq. (7) then becomes:

$$\frac{A_\pi}{A_\sigma} = \frac{\int_0^{2\pi}\int_0^{\pi}[1+(1/4)(3\cos^2\gamma-1)]\exp[-(\epsilon_M\cos^2\gamma)] \cdot \exp[-(q/kT)\sin^2\delta]\sin\delta\,d\delta\,d\alpha}{\int_0^{2\pi}\int_0^{\pi}[1-(1/4)(3\cos^2\gamma-1)]\exp[-(\epsilon_M\cos^2\gamma)] \cdot \exp[-(q/kT)\sin^2\delta]\sin\delta\,d\delta\,d\alpha} \tag{10}$$

where $\cos^2\gamma$ has the form of Eq. (8). This equation must be numerically integrated and will yield the functional dependence of the area ratio on the experimental angle θ. A best fit of Eq. (10) to the experimental data points will yield both ϵ_M and q/kT. Once q/kT is known, the solute order parameter can be evaluated by computing the following integral:

$$S = \frac{\int_0^{\pi}(1/2)(3\cos^2\delta-1)\exp[-(q/kT)\sin^2\delta]\sin\delta\,d\delta}{\int_0^{\pi}\exp[-(q/kT)\sin^2\delta]\sin\delta\,d\delta}. \tag{11}$$

The functional dependence of S on q/kT is given in Fig. 4.

It is interesting to note that Eq. (10) properly predicts the area ratio for the case of a uniform distribution of planes about the preferred molecular direction for a smectic H (or a smectic C) mesophase. If we consider a coordinate system such that the tilt angle between the preferred molecular direction and the normal to the smectic plane is given by τ, then we have the situation depicted in Fig. 5. Here the z-axis is defined by the magnetic field (H), and the x-z plane houses the γ-ray direction (determined by θ). The polar and azimuthal angles

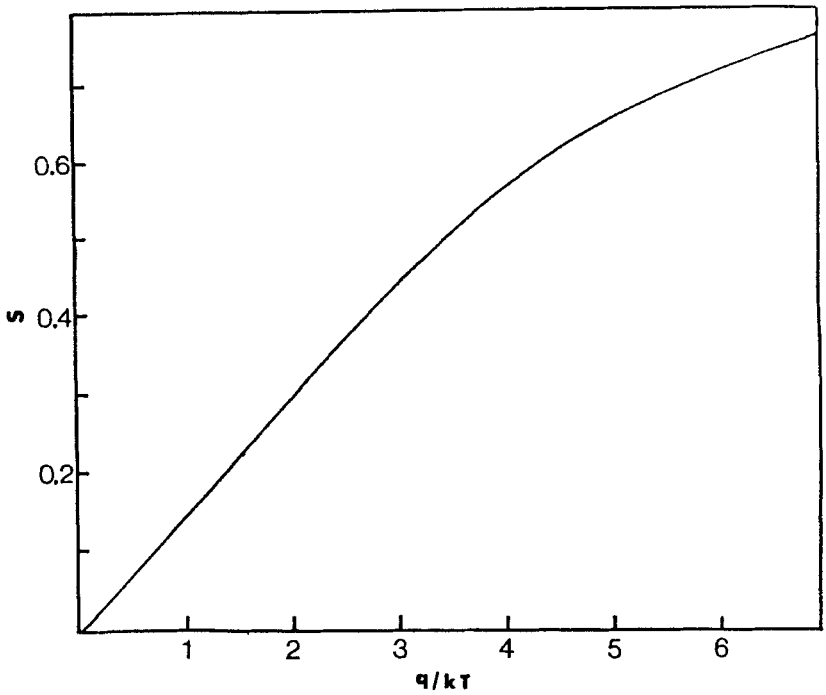

Figure 4. A plot of the functional dependence of the order parameter, S, on the value of q/kT.

of the smectic normal are τ and β_i, respectively. The angle τ is the same for all the molecules while β_i will be the azimuth for a particular plane. Therefore, in terms of the experimental angle θ and the angles τ and β_i, $\cos^2 \rho_i$ (where ρ_i is the angle between the smectic normal for the ith molecule and the gamma direction) can be expressed as follows:

$$\cos^2 \rho_i = (\sin \tau \sin \theta \cos \beta_i + \cos \theta \cos \tau)^2 . \tag{12}$$

Notice tnat this equation has the same general form as Eq. (8) and is independent of both δ_i and α_i. For the purposes of the ratio calculation (after replacing the discrete sum with the continuous distribution) the term $\exp(-\epsilon_L \cos^2 \rho)$ must appear in the integrand of both the numerator and denominator of Eq. (10) and a third average (integration) is required over the azimuth β. However, because the expression for $\cos^2 \rho i$ does not include δ or α, the β integration is

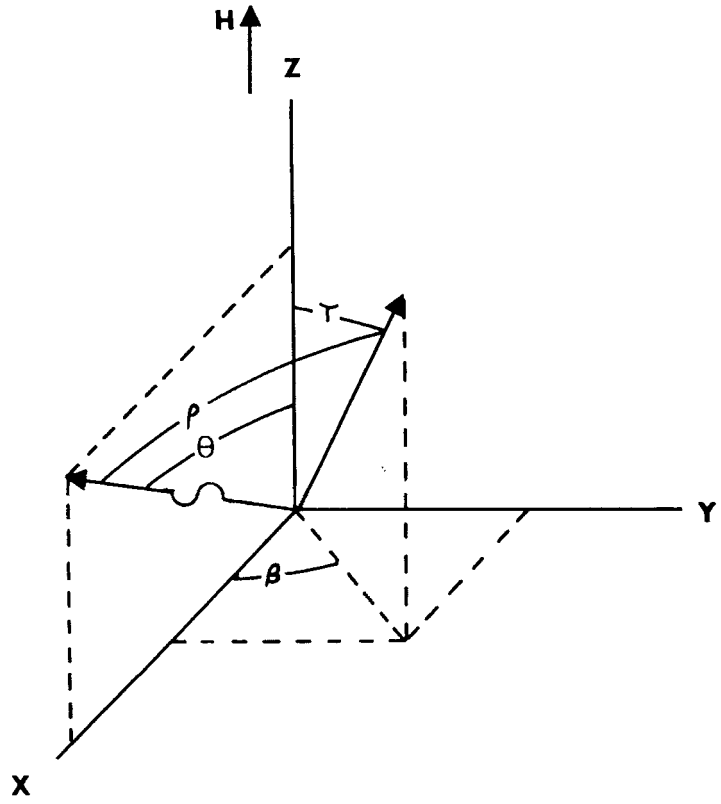

Figure 5. The polar (tilt angle) and azimuthal angles of the planar normal of the smectic H structure in the laboratory system are given by τ and β, respectively. The angle θ is the experimental angle.

separable from the other two and appears in the ratio, top and bottom, in the identical fashion. As a result these integrals cancel and the result is Eq. (10). Therefore, Eq. (10) cannot distinguish between a smectic liquid crystal with perfect planar alignment and a uniform distribution of the planes about the preferred molecular direction such that the integrity of the tilt angle τ is maintained. That is, the area ratio (A_π/A_σ) is independent of the lattice contribution to the recoil-free fraction.

Since the recoil-free fraction depends on the angle θ through Eq. (6) it is possible to obtain, independently, another value for the molecular vibrational anisotropy ϵ_M by fitting the angular dependence

of the recoil-free fraction to the following equation:

$$\frac{f(\theta)}{f(\theta=0)} = \frac{\int_0^{2\pi}\int_0^{\pi} \exp[-(\epsilon_M \cos^2\gamma)] \exp[-(q/kT)\sin^2\delta] \sin\delta \, d\delta \, d\alpha}{\int_0^{2\pi}\int_0^{\pi} \exp\{-[\epsilon_M \cos^2\gamma(\theta=0)]\} \exp[-(q/kT)\sin^2\delta] \sin\delta \, d\delta \, d\alpha} \tag{13}$$

where the expression for $\cos^2\gamma$ as a function of θ has the form of Eq. (8) and the expression has been normalized to the value of the recoil-free fraction at $\theta = 0°$. Any difference between the value of ϵ_M obtained from Eq. (10) and that obtained from Eq. (13) will then be a measure of the anisotropy of the lattice restorative forces in the smectic layered structure because this strictly speaking should not be left out of Eq. (13).

4. Results and Discussion

The area ratio data for the oriented 3EtSnPalm molecules in the smectic liquid crystal HBPA as a function of the angle θ between the preferred molecular direction as determined by the external magnetic field and the gamma beam direction are shown in Figs. 2 and 6. In Fig. 2, the theory of Wilson and Uhrich,[8] which assumes that the molecular contribution to the recoil-free fraction is isotropic, was used to fit the data. It obviously is unsatisfactory, although it does give the general shape of the experimental curve. In this fit the theory was constrained to reproduce the experimental value of the $\theta = 0°$ area ratio. The resulting value of the order parameter was $S = 0.28$. Fig. 6 shows the result of incorporating the molecular contribution to the nuclear vibrational anisotropy into the former theory as per Eq. (10). The calculated curve is a best fit of numerically integrating Eq. (10). The best fit yielded $\epsilon_M = -0.80$ and $q/kT = 1.15$ which in turn from Fig. 3 corresponds to a value of $S = 0.17$. In each case the fits require the identification of the π-transition as the lower velocity spectral line (therefore, $eV_{zz}Q$ is negative). Attempts to reverse the identification resulted in reasonably good fits to the data, but the resulting numbers were not physically tenable. In particular, the choice of the π-transition as the higher velocity component resulted in a value of $q/kT = -2.10$ and therefore in a

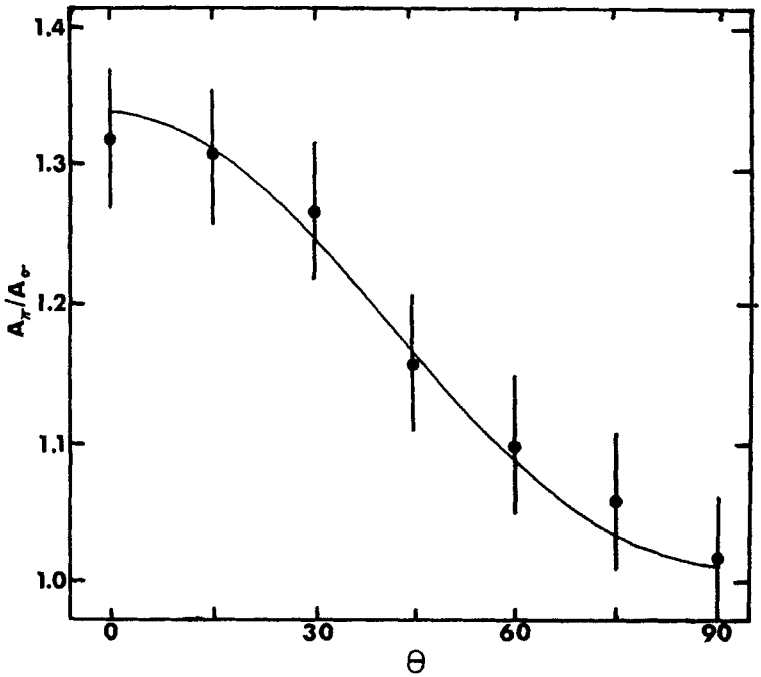

Figure 6. The best fit of Eq. (10) to the area ratio data. Here $\epsilon_M = -0.80$ and $q/kT = 1.15$.

negative order parameter ($S = -0.24$) for the 3EtSnPalm molecule. This corresponds to the solute molecule preferring to align perpendicular to the liquid crystal molecule (i.e. $\delta = 90°$ is preferred; see Fig. 2). This concept is untenable and contrary to all known experiments on solute order in liquid crystalline solutions.[19,20] Clearly, therefore, the identification of the lower velocity line as the π-transition is correct. Consequently, the sign of V_{zz} must be positive for the 3EtSnPalm molecule inasmuch as the quadrupole moment of the $I = 3/2$ state (Q) is known to be negative.[21] This in turn requires the electrostatic charge distribution in this axially symmetric molecule to have an oblate shape.

The value of ϵ_M reported above shows that the mean squared vibrational amplitude perpendicular to the long molecular axis $\langle x_\perp{}^2 \rangle$ is substantially larger than that parallel to the long axis $\langle x_\parallel{}^2 \rangle$. This agrees with solid state experiments on other molecules of this type. For example, Herber and his co-workers have found ϵ to be

negative in trimetnyltincyanide and at 77 °K its value of $\epsilon = -1.2$ is comparable to our value for the 3EtSnPalm.[5]

As stated above, the best fit of Eq. (10) to the area ratio data yielded an order parameter $S = 0.17$. This value is quite a bit lower than one would expect for a viscous low temperature smectic phase. However, this value is for a solute molecule which is not the same length or shape as the liquid crystal molecule. Furthermore, the liquid crystalline phases have been disturbed by $\sim 5\%$ (by weight) of the solute (3EtSnPalm) such that the smectic A phase is lost and leaving a rather broad (in temperature) nematic to smectic H transition. Consequently, the low order parameter probably ought to be expected for systems of this type. To be noted, however, is the fact that the low order parameter in no way limits the amount of molecular information obtained in these experiments.

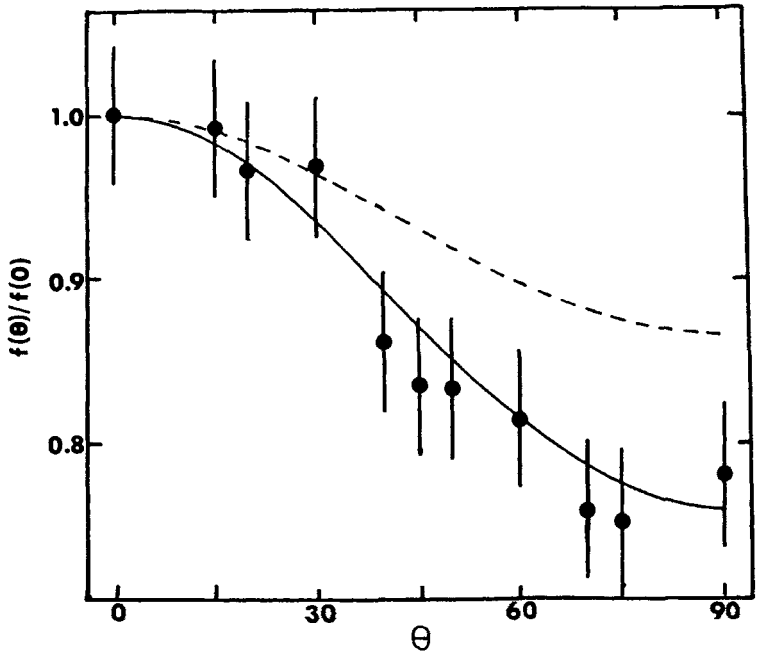

Figure 7. A plot of the recoil-free fraction (as percent of the background) vs. the experimental angle θ for 3EtSnPalm in HBPA at 77 °K. The data are normalized to the $\theta = 0$ value of the recoil-free fraction. The solid line is a best fit of Eq. (13) to the data with the q/kT constrained to be 1.15. This fit yielded $\epsilon_M = -1.50$. The dashed line is a fit of Eq. (13) to the data with the constraint that $\epsilon_M = -0.80$ and $q/kT - 1.15$ as per Fig. 6.

Figure 7 shows the best fit of Eq. (13) to the normalized recoil-free fraction data. The values $\epsilon_M = -1.50$ and $q/kT = 1.15$ were obtained from this fit. In this case the value of q/kT was constrained to have the value obtained from the fit to the area ratio data. The justification for this is that identical order parameters must be operative for each data set. Figure 7 also displays a fit of Eq. (13) to the orientation dependence of the recoil-free fraction in which ϵ_M and q/kT have

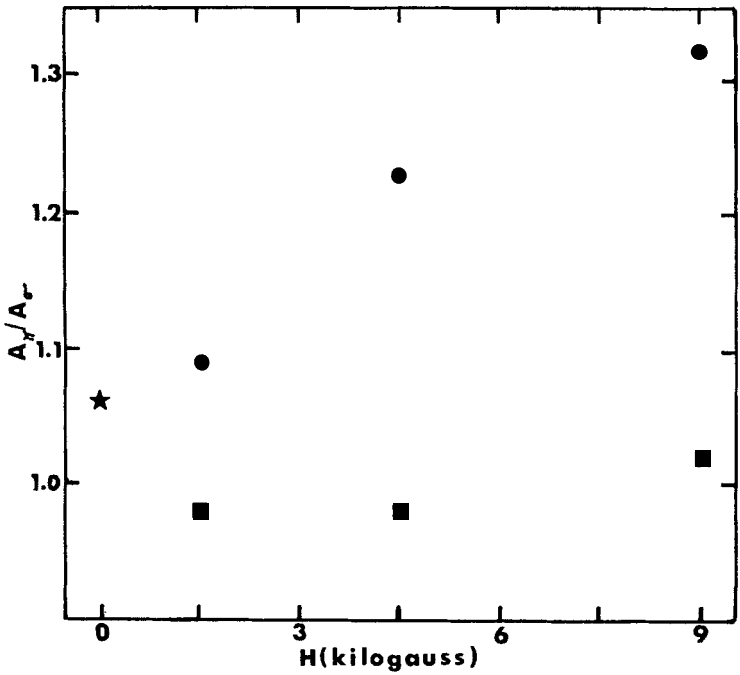

Figure 8. A plot of the area ratio (A_π/A_σ) vs. magnetic field strength for $\theta = 0°$ (dots) and $\theta = 90°$ (squares).

been constrained to be the best fit values obtained for the area ratio data. ($\epsilon_M = -0.80$ and $q/kT = 1.15$.) As pointed out previously the discrepancies arise from the fact that the lattice contribution of the smectic layers to the vibrational anisotropy has not been included in the calculation. We see from the separation of the two curves that at 77 °K the lattice contribution is of the same order as the molecular contribution. However, in order to evaluate the lattice anisotropy from these data, the tilt angle (τ) of the smectic H phase must be

known. An X-ray measurement of this angle τ in HBPA has not yet been affected.

The dependence of the area ratio for $\theta = 0°$ and $\theta = 90°$ on magnetic field strength is shown in Fig. 8. The anisotropy observed at $\theta = 0°$ declines to the $\theta = 90°$ value as the field is reduced to 1500 gauss. Furthermore, the $\theta = 90°$ area ratio is unaffected by the field strength. Figure 9 shows the field dependence of the recoil-free

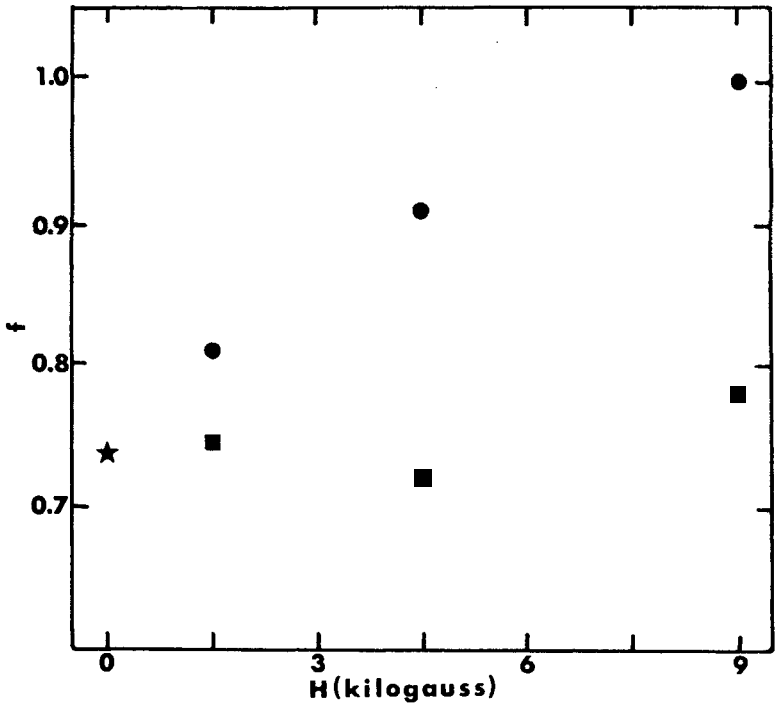

Figure 9. A plot of the normalized recoil-free fraction as a function of magnetic field strength for $\theta = 0°$ (dots) and $\theta = 90°$ (squares).

fraction for both the 0° and 90° orientations. Interestingly, the sample exhibits area ratios and recoil-free fractions corresponding to the $\theta = 90°$ values for unoriented runs. This shows that the effect of the surface is to align the molecules parallel to the boundary. In zero field, the surface alignment penetrates the bulk and, therefore, aligns the entire sample. It is quite likely that the order parameter is somewhat lower for the unoriented sample than the oriented one

because of the competition between the rim and the faces of the disc-shaped sample holder. The possibility that the unoriented sample is similar to a polycrystalline sample with a random distribution of molecular axes has been discounted because of the recoil-free fraction results. If the alignment were random, as an area ratio of near unity might indicate, then the recoil-free fraction (percent effect) for the zero field runs should be midway between the 0° and 90° values (that is, on the order of 0.85 on Fig. 7). This is definitely not the case (see Fig. 9) and as a result surface alignment is needed to explain the experiment.

5. Conclusions

The method reported herein of using an ordered liquid crystalline matrix to form a solute " monocrystal " for Sn-119 (and Fe-57) bearing molecules provides the Mössbauer spectroscopist with a new weapon. We have determined the sign of the principal value of the efg tensor (V_{zz}) at the tin site in 3EtSnPalm and the nuclear vibrational anisotropy of the tin in this molecule. This is the first time one method has been employed to extract these Mössbauer parameters in non-single crystal spectroscopy. Furthermore, the method can be employed to evaluate the asymmetry parameter of the efg tensor for non-axial molecules. An added bonus is the determination of two properties of the aligned liquid crystalline matrix, namely, the lattice vibrational anisotropy and the direction of molecular alignment by the container walls. The most stringent constraint on the technique at present is the solubility of Sn-119 and Fe-57 bearing molecules in suitable liquid crystals. Here suitable means that the liquid crystal must have a nematic phase to facilitate ordering with a magnetic field and a lower temperature smectic phase which persists to 77 °K. Further the character of the phases must remain firm upon dissolution of the impurity molecules. We expect that besides HBPA that other suitable liquid crystalline materials will become available in the near future. Once a compatible solute–solvent system is found the technique described in this work is relatively simple and cheap.

The experimental data are adequately accounted for by the theory which is based on the known properties of liquid crystals. As a

result, the theory should be generally applicable to ordered solvent–solute problems. It can also be used to treat the problem of an ordered suspension of crystallites. The recent work on 1, 1′ diacetylferrocene in the smectic *C* liquid crystal, 4, 4′ heptyloxyazoxybenzene, which is reported in Ref. 7 is an example of an ordered suspension. An explanation of the data of Ref. 7 using in part the theory of this paper will be published shortly.[22]

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