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Reinterpretation of the Fe-57 Mössbauer Effect of 1-1′-Diacetylferrocene in 4-4′-Bis(heptyloxy)azoxybenzene[†]

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Samples were prepared for Mössbauer analysis by incorporating 0.25- 10% (by weight) of an iron bearing compound in the form of a ferrocene derivative in various liquid crystals possessing both smectic and nematic phases. The samples were ordered in a 4-9 kg magnetic field in the nematic phase and cooled to the smectic phase for the Mössbauer experiments. Analysis of the resulting Mössbauer spectra showed that a non-zero effect was present only when the iron containing constituent occurred as a solid component. This conclusion was verified by X-ray diffraction studies of the samples. The systematic variation of both the percent effect and the ratio of the areas of the two quadrupole split peaks as a function of the angle between the aligning magnetic field and the gamma beam provided evidence that the solid crystals were small enough to be ordered by the smectic structure. The percent effect data were fit by assuming that the variation was due to the anisotropy of the liquid crystal lattice restorative forces and required knowledge of the planar orientation and the characteristic tilt angle of the smectic *C*. The dependence of the area ratio of the two quadrupole split peaks on the angle was found to be a function of the strength of the aligning field. This was explained qualitatively by assuming a direct dependence of the order parameter on the magnetic field.

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INTRODUCTION

The observation of the Mössbauer effect in liquid crystals was first reported in 1970 by Uhrich, Wilson, and Resch.[1] Seven per cent by weight of 1-1′-diacetylferrocene (DAF) had been added to 4-4′-bis(heptyloxy)azoxybenzene (HAB) in order to provide a sample suitable for Mössbauer spectroscopy. The per cent effect declined gradually as the sample temperature was increased until the transition from the solid to the smectic *C* was attained. At this point the per cent effect dropped discontinuously to a new value and remained roughly constant until the nematic phase was reached, where the effect disappeared. A systematic variation of the ratio of the areas of the two quadrupole split peaks was observed as a function of the angle (θ) between the magnetic field used to align the sample and the direction of the gamma beam.

The data of Ref. 1 were thought to be the result of a solution of DAF in HAB. This was based on both microscopie evaluation and on differential thermal analysis, which both indicated a true solution. However, we have found via X-ray measurements of the DAF–HAB system that the DAF was present as a solid component in the samples used for the Mössbauer measurement. As a result, it is our purpose in this paper to reinterpret the data of Ref. 1 in terms of an ordered suspension of single crystallites. The fact that both the Mössbauer area ration (A_π/A_σ) and the recoil-free fraction are reproducible functions of the experimental angle (θ) between the aligning magnetic field and the Mössbauer γ-direction establishes that the suspension of DAF crystallites was ordered. Further, we attempt to account for the data theoretically. We show that in principle as much information can be obtained from an ordered suspension as from an ordered solution provided the angle (ξ) between the *z*-principal axis of the electric field gradient (EFG) tensor and the long axis of the microcrystallite is known. Our explanation, however, assumes that the angle ξ is the same for all the DAF molecules in each crystallite.

In the following sections, a discussion of the data of Ref. 1 and new corroborative data is given in terms of the theory presented in Refs. 2 and 3.

PROCEDURES AND RESULTS

Several samples were prepared for Mössbauer spectroscopy by attempting to dissolve either 1-1′-diacetylferrocene or di-*n*-octanoylferrocene (ONF) in liquid crystals which possess a smectic phase such as 4-4′-bis(heptyloxy)azoxybenzene, 4-pentoxybenzylidene-4′-propylaniline (PBPA) and 4-butyloxybenzylidene-4′-ethylaniline (BBEA). Ref. 1 describes the constant acceleration spectrometer and the procedures used. The Co-57 in Cu or Pd Mössbauer sources were purchased from International Chemical and Nuclear Corporation. Both normal DAF and DAF enriched in Fe-57 were used to keep the Fe-57 content constant in absorber samples with DAF concentrations ranging from 0.25% to 10%.[4] We then used the magnitude of the sum of the peak heights as a measure of the per cent effect as a function of the DAF concentration. The effect decreased and eventually disappeared as the concentration of the DAF was reduced. For samples with a DAF concentration of less than 1% the effect was not present. This suggested that the effect observed for the higher concentration samples was due to a suspension of small crystals of DAF in the liquid crystalline smectic state. Further work with DAF and ONF in PBPA and BBEA revealed that after cooling to the smectic phase in the magnetic field, the effect would not appear until 3-6 hs after cooling. It would gradually increase for the next several hours, finally stabilizing itself after 12-24 hs. This indicated that a solid component was crystallizing out slowly. However, it could not be seen via microscopic evaluation.

Both PBPA and BBEA exhibit a smectic *H* phase[5] which is the most viscous of all the smectic phases; yet DAF and ONF did not show a Mössbauer effect in either of these phases while in solution. In particular, the effect would appear or disappear as the BBEA was cycled through the transition from smectic to solid and back to smectic. The PBPA doesn't exhibit this crystal-smectic transition above room temperature.[6]

X-ray diffraction pictures taken of the samples disclosed that there was indeed a solid component crystallizing in the smectic that exactly corresponded to those cases in which the Mössbauer effect was present.[7] This evidence conclusively shows that at room temperature and above the existence of the Fe-57 Mössbauer effect in liquid crystals is dependent upon the presence of a solid component.

Fortunately, the systematic variation of both the recoil-free fraction and the ratio of the areas of the quadrupole split peaks as a function of the angle (θ) between the gamma direction and the aligning magnetic field confirmed that the DAF crystallites were ordered by the liquid crystal. Further investigations of our earlier work with high concentrations of DAF in HAB were undertaken. Eight per cent by weight of DAF was added to HAB. A magnetic field of 9 kG was applied while the sample was in the nematic phase. When the sample had cooled to 75°C in the smectic *C* phase, the field was removed and a Mössbauer spectrum taken. The magnitude of the asymmetry of the quadrupole split peaks was increased at both zero and ninity degrees in comparison with our earlier data. It ranged from 0.82-1.59 (Figure 1) as compared with 0.92-1.30 (Figure 2) found previously.[1]

In the following theory, we consider smectic liquid crystals which possess molecular alignment along a single preferred direction. In particular, this includes tilted smectics such as smectic *C* (e.g., HAB) and smectic *H* (e.g., PBPA and BBEA) in which the planar normals are either all parallel or uniformly

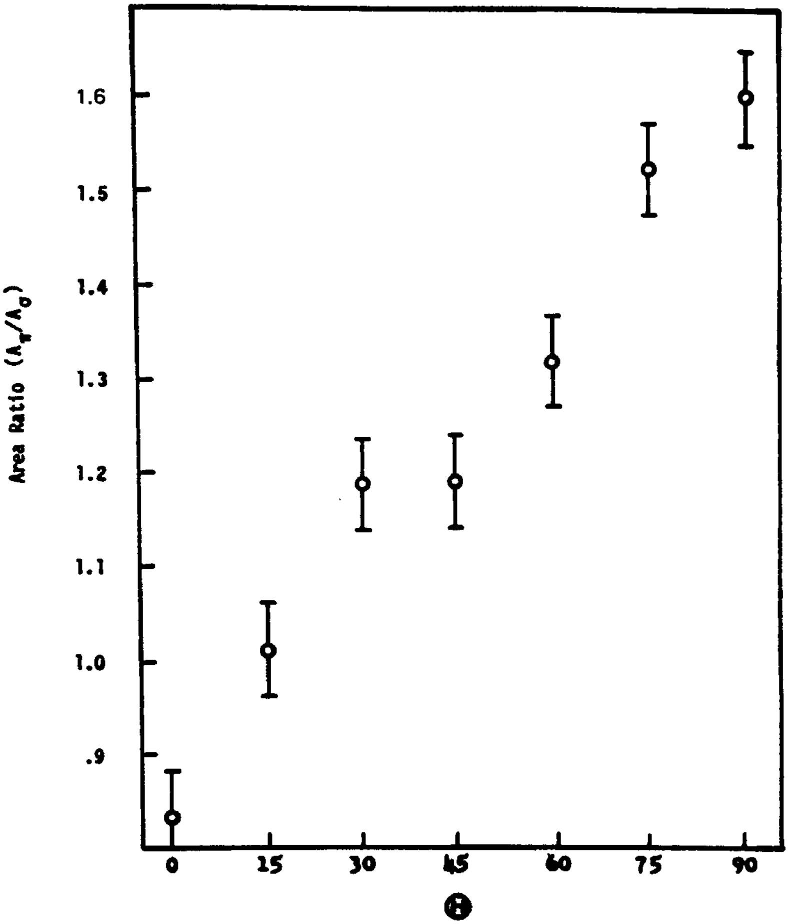

FIGURE 1 The ratio of the areas of the two quadrupole split peaks (A_π/A_σ) as a function of angle between the aligning 9 kG magnetic field and the γ-direction.

distributed about the preferred molecular direction, such that, a unique tilt angle (τ) is maintained between the preferred molecular direction and the normal to each layer. We assume that the liquid crystal molecules are distributed about the preferred direction according to Saupe's distribution function which results in the following definition of the orientational order parameter:

$$S = \frac{\int_0^\pi \tfrac{1}{2}(3\cos^2\delta - 1)\, e^{-(q/kT)(\sin^2\delta)} \sin\delta \, d\delta}{\int_0^\pi e^{-(q/kT)(\sin^2\delta)} \sin\delta \, d\delta} \qquad (1)$$

where q is a measure of the orientational order, k is Boltzmann's constant, T is the absolute temperature and the angle δ is the angle between the preferred direction and the long molecular axis of the liquid crystal molecule. Solute molecules and needle shaped crystallites may also be ordered, but their S parameters will not in general be the same as the S of the liquid crystal molecules because of their different lengths and shapes. For the cases of ordered crystallites, δ becomes the angle between the long axis of the crystallite and the preferred direction which in this paper is that of the external magnetic field. For the case of an ordered suspension of crystallites, the area ratio of the quadrupole split doublet has been determined to be:[2,3]

$$\frac{A_\pi}{A_\sigma}=\frac{\tfrac{1}{2}+[1/16(1+\eta^2/3)^{\frac{1}{2}}][3\cos^2\theta-1][3\cos^2\xi-1+\eta\sin^2\xi\cos2\mu]S}{\tfrac{1}{2}-[1/16(1+\eta^2/3)^{\frac{1}{2}}][3\cos^2\theta-1][3\cos^2\xi-1+\eta\sin^2\xi\cos2\mu]S} \tag{2}$$

where θ is the experimental angle, ξ and μ are, respectively, the polar and azimuthal angles of the crystallite in the EFG coordinate system of each DAF molecule, and η is the asymmetry parameter of the EFG tensor which is defined as $\eta=(V_{xx}-V_{yy})/V_{zz}$. Eq. (2) has been derived under the assumption that the contribution of the unit housing the Mössbauer nuclide (in the present case, this is the DAF crystallite) to the recoil anisotropy is isotropic. Furthermore, it has been assumed that the liquid crystal lattice contribution to the recoil anisotropy is dependent only on the layered structure. This latter assumption causes the

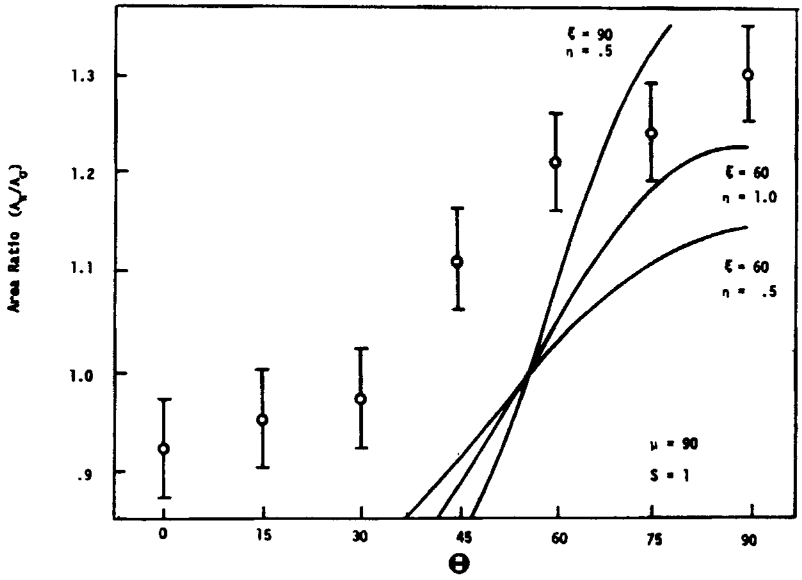

FIGURE 2 Fits of Eq. (1) to the area ratio data taken using a 4 kG field.

liquid crystal lattice contribution to the recoil anisotropy to cancel out of the expression for A_π/A_σ.[2,3]

Qualitatively the increase in the area ratio asymmetry with increasing field is just what one would predict from Eq. (2) by just increasing the order parameter, S. Thus, the higher aligning field appears to produce a higher order parameter.

The value of the quadropole splitting in DAF ($\Delta E_Q = 2.2$ mm/sec) is only about 10% different than in ferrocene itself. Since η in ferrocene is identically zero due to the axial symmetry, then in DAF we can assume that η is very small. Therefore, assuming that $\eta = 0$ in DAF should not affect the theoretical prediction for A_π/A_σ.

For the case of $\eta = 0$ the quadrupole splitting in Fe-57 is given by

$$E_{3/2} - E_{1/2} = eQV_{zz}/2 \tag{3}$$

For iron the quadrupole moment, eQ, is positive,[8] and for DAF the z-component of the electric field gradient, V_{zz}, is also positive.[9] Therefore, the 3/2 level will be at a higher energy than the 1/2 level. Our data consistently show that an angle (θ) of zero degrees between the γ-beam and the magnetic field, the lower energy transition, which corresponds to the 1/2 level (σ-transition), has the larger intensity. In this case (i.e., $\theta = 0$, $\eta = 0$ Eq. (2) becomes

$$\frac{A_\pi}{A_\sigma} = \frac{(1) + (1/4)\,[3\cos^2\xi - 1]S}{(1) - (1/4)\,[3\cos^2\xi - 1]S} \tag{4}$$

The theory yields the same result as the experiment only if the polar angle (ξ) of the long axis of the crystallite in the EFG principal axis system is larger than fifty-five degrees. This also assumes that ξ will be identical for each DAF molecule in all the crystallites.

Equation (2) cannot be brought into quantitative agreement with the data for any choice of parameters, ξ, $S(\leqslant 1)$, μ, and $\eta(\leqslant 1)$ because the theory predicts a value of unity at $\theta = 55°$ while the data cross unity near $\theta = 30°$. Figure 2 shows the fit of Eq. (2) to the data in the four kG case for several choices of the parameters. Theoretical curves for $\eta \ll 1$ and $S < 1$ give much poorer fits. We attribute the lack of agreement between theory and experiment to the following sources: (1) ξ may not be the same for all DAF molecules in all the crystallites; (2) The assumption that only the layered structure determines the liquid crystal contribution to the recoil anisotropy may be in error for crystallites which extend through many layers; (3) When crystallites are present wall effects may be important; and (4) The contribution of the crystallites to the recoil-free fraction may not be isotropic because there will be a distribution in the size of the suspended particles. The relatively large particles will exhibit the angular dependence characteristic of solid DAF which would in general be different from the anisotropy imposed by the smectic layered structure. The former would contribute to Eq. (2) while the latter does not. In addition, the distribution of particle sizes will affect the observed recoil anisotropy which is discussed below.

The dependence of the percent effect on θ for DAF in HAB at the four and nine kG aligning fields exhibits the same functional form to within the experimental error. Figure 3 illustrates the averaged normalized values of the percent effect and the theoretical fit. If we assume that *only* the smectic layered structure is important in determining the liquid crystal lattice contribution to the recoil free fraction, we can represent it as follows:

$$f_L = C e^{-\epsilon_L \cos^2 \rho} \tag{5}$$

where $\epsilon_L = K^2(\langle x^2{}_{\parallel}\rangle - \langle x^2{}_{\perp}\rangle)_L$ is a measure of anisotropy of the binding forces with respect to the smectic normal; $\langle x^2 \parallel\rangle$ and $\langle x^2 \perp\rangle$ are the mean squared vibrational amplitudes parallel and perpendicular to the smectic normal, respectively, and K is the wave vector of the Mössbauer γ-beam.[10] Here ρ is the angle between the smectic normal and the gamma direction. Transforming ρ into the laboratory coordinant system yields

$$f_L = C e^{-\epsilon_L (\sin\tau \cos\beta \sin\theta + \cos\tau \cos\theta)^2} \tag{6}$$

where θ is the angle between the magnetic field and the γ-beam, and τ and β are the polar and azimuthal angles of the normal to the smectic plane in the coordinant system determined by the magnetic field along the z-axis and the

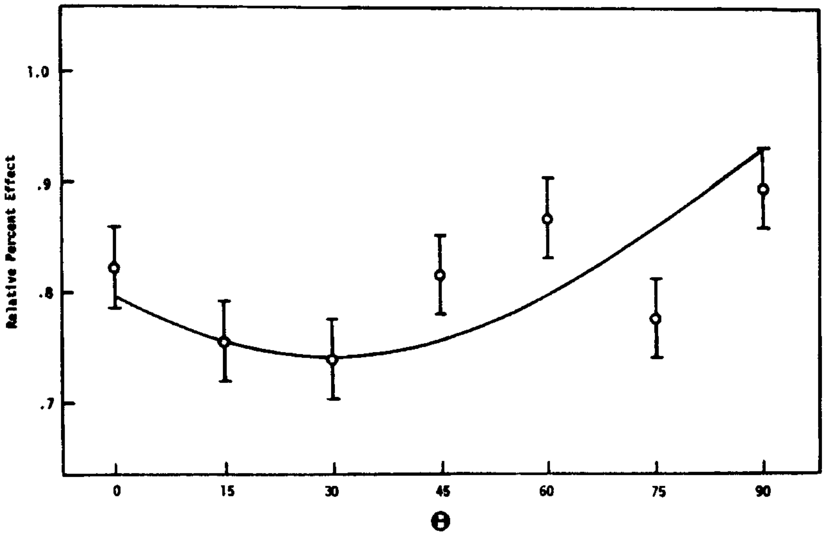

FIGURE 3 Fit of Eq. (6) to the angular dependence of the percent effect, normailzed to the $\theta = 0$ value. Here $\beta = 0$, $\tau = 30°$ and $\epsilon_L = 0.3$.

γ-beam in the x-z plane. If we assume that every angle β is equally probable (cone of planes), Eq. (6) must be averaged over β yielding a function with extrema at 0° and 90°.[11]

Because the experimental data show a minimum at $\theta = 30°$, then in this approximation the sample must not have a distribution of orientations of the normal to the smectic planes. The best fit of the Eq. (6) to the experimental data occurs for $\beta = 0$, $\tau = 30°$, and $\epsilon_L = 0.3$. This corresponds to a completely, aligned smectic C with a tilt angle of 30°. This agrees with an EPR measurement[12] of the tilt angle of HAB but disagrees with NMR[13] and optical[14] determinations which yielded $\tau = 45°$. Also, it is not in agreement with the X-ray measurement of de Vries who also reported $\tau = 45°$.[15] To be noted here is that the crystallite contribution to the recoil anisotropy has been assumed to vanish (as was assumed in the derivation of A_π/A_σ in Eq. 2) and the multi-layer penetration of the crystallites has been ignored in Eqs. (5) and (6). However, from Fig. 3, it appears that the layered structure alone is responsible for the recoil anisotropy.

CONCLUSIONS

The presence of DAF as a suspension of crystallites in HAB rather than as a true solution of DAF molecules in HAB complicates the quantitative theoretical explanation of the area ratio data. In particular, X-ray knowledge of the angle ξ between the crystallite long axis and the DAF–EFG axis is necessary to account for the data. However, the theory shows that $\xi > 55°$, if in fact it is unique for all the DAF molecules in the crystallites. As a result, if crystallographic data is available for the crystallites as much information can be obtained, via the Mössbauer technique, from ordered suspensions in liquid crystals as from ordered solutes in liquid crystals. The specifics of the latter are detailed in Ref. 3.

Liquid crystal information has been provided in that the smectic C tilt angle in HAB has been measured and is in reasonable agreement with other studies. Also, the liquid crystal phases have been shown to lack the rigidity required for Mössbauer absorption by an Fe-57 bearing molecule in solution for temperatures at or above room temperature. This, however, does not affect the applicability of the technique as has been demonstrated for supercooled liquid crystalline solutions.[3]

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