Molecular Crystals and Liquid Crystals

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A Mössbauer Temperature Study of 1,1′-Diacetylferrocene in a Cold Smectic A Liquid Crystal

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Fe-57 Mössbauer Effect (ME) measurements were obtained from a 0.2% (by weight) solution of 1,1′- diacetylferrocene in the liquid crystalline material 4-n-octyloxyphenyl-4′-n-nonylbenzoate ($\overline{8}$09). The ME parameters were determined as a function of temperature for the temperature range 110–290K in the crystalline solid phase and 110–240K in the cold smectic A liquid crystalline solution. The "cold smectic A" is defined as the smectic A glass and the supercooled smectic A phase. The ME spectrum was composed of two quadrupole split doublets. The outer doublet was the usual DAF resonance. For $T < 200$ the ln recoil-free intensity (f) vs T data for this doublet yielded a Mössbauer-Debye temperature (θ_{LC}) of 45 ± 3K which was about 5K lower than for the crystalline phase. Further, it was independent of the direction of a 9KG aligning magnetic field. The smectic A glass-supercooled smectic A transition was determined to be 210K via the deviation of the ln f vs. T data from linear behavior. The inner doublet was much less intense than the outer doublet. The angular dependence of the intensity ratios from the two doublets yielded low order parameters (S) of opposite sign. $S = 0.08$ for the outer doublet and $S = -0.14$ for the inner doublet. The negative value of S suggests that the DAF molecules which contributed to the inner doublet intensity had interacted chemically with the host $\overline{8}$09 molecules.

1. INTRODUCTION

Mössbauer Effect (ME) measurements were obtained from a 0.2% (by weight) solution of 1,1′-diacetylferrocene (DAF) in 4-n-octylox-yphenyl-4′-n-nonylbenzoate ($\overline{8}$09) or (8.09). The measurements spanned the temperature range of 110–290K for DAF in the crystalline solid

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phase of $\overline{8}09$ and 110–240K for DAF in the cold liquid crystal. The cold liquid crystal encompasses both the smectic A liquid crystalline glass and the supercooled smectic A liquid crystalline phase. It is well known that only the lowest temperature liquid crystalline phase of a given material will supercool and form a glass.[1,2]

For $\overline{8}09$ the lowest temperature cold liquid crystalline phase is a smectic A. The molecules are in a layered structure, with the layer thickness approximately equal to the full length of the molecules. The centers of gravity of the molecules in a given layer show no long range order, and may be considered to reside in a two-dimensional liquid. This phase is optically uniaxial. The optic axis is normal to the plane of the layers and there is complete rotational symmetry around this axis.[3,4] The $\overline{8}09$ liquid crystalline material has the following transitions:

$$\text{Solid} \xleftrightarrow{\ 325K\ } \text{Smectic A} \xleftrightarrow{\ 341K\ } \text{Nematic} \xleftrightarrow{\ 345K\ } \text{Isotropic Liquid}$$

The ME spectrometer, the sample preparation and alignment, and the data analysis are discussed in the following sections.

2. EXPERIMENTAL

A standard constant acceleration spectrometer was employed to procure the Mössbauer data. A 30 mCi source of Co-57 on a Rhodium matrix served as the ME source[5] and it was purchased from Amersham/Searle.

The ME sample was prepared by dissolving 0.2% (by weight) DAF (Fe-enriched to ~50% Fe-57) into the liquid crystalline material ($\overline{8}09$). The sample was heated in vacuum to 8–10K above the nematic-isotropic liquid transition and maintained at this temperature for a period of 20 hours. The integrity of the resulting solution was checked by both microscopic observation and x-ray analysis.

The aligned glass was formed by cooling the disc-shaped sample (1.0 cm diam. × 0.3 cm thick) from the isotropic phase to 1 to 2 Kelvins below the isotropic-nematic transition in the presence of a 9KG magnetic field. After holding this temperature for ~30 min it was cooled to the ME run temperature at an average of 17K/min. This cooling was accomplished via a helium heat leak chamber surrounded by liquid nitrogen. The temperature was controlled to ±0.5K for the entire period of the ME experiment. The alignment angle θ is defined as the angle between the preferred direction as

determined by the magnetic field and the gamma ray direction which was coincident with the normal to the sample disc. Here, "unoriented" refers to cooling the sample in the absence of an aligning magnetic field. In the unoriented sample the molecules experienced alignment due to the surfaces of the sample container.

Two Mössbauer parameters distinguished the cold liquid crystalline glass from the crystal phase. At a given temperature, the recoil-free intensity (f) of the cold smectic was significantly less than f for the crystalline phase. Also, the magnitude of the quadrupole splitting (ΔE_Q) at a given temperature depended on the state of the system. Since f and ΔE_Q are different for the two states, crystallization could be monitored during the ME run by noting whether f and ΔE_Q changed with time.

The supercooled smectic A phase of $\overline{8}09$ exhibited particularly difficult behavior at high temperatures. For example, at 225K crystallization occurred within fifteen minutes after the sample was prepared for the ME run. For $T > 240K$ $\overline{8}09$ crystallized so fast that ME measurements in the cold smectic A were impossible to obtain. At temperatures where crystallization occurred (215 ↔ 240K), several individual spectra from separate runs were added together to form a composite spectrum. For each component of the composite spectrum, the sample was heated to the isotropic and cooled to the ME run temperature according to the procedure previously described, and the data were collected over a time period that was less than the crystallization time.

The ME spectra were fit with Lorentzian line-shapes using a Burroughs 6800 computer. The area ratio (A_π/A_σ), f, ΔE_Q, the linewidth (Γ), and the chemical shift (δ) were all obtained from the computer fits to the data. Two quadrupole doublets were observed (Figure 1). The outer doublet was more intense than the inner doublet and it corresponded to the expected DAF spectrum. The smaller inner doublet will be discussed later.

3. RESULTS AND DISCUSSION

3.1.1. Mössbauer-Debye temperature (θ_l)

Four plots of ln f *vs* T data for the outer double of $\overline{8}09$ are presented in Figures 2 and 3. The four experimental situations presented are as follows: the crystalline solid, unoriented cold liquid crystal, and the cold liquid crystal oriented at 0° and 90°. The crystal data show a linear temperature dependence for the entire temperature range
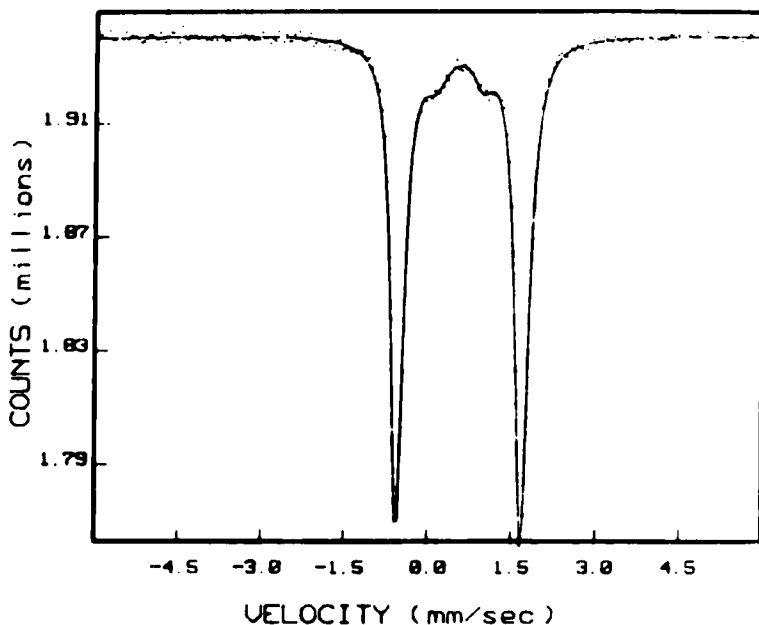
FIGURE 1   A typical spectrum showing the two quadrupole doublets. This spectrum
is for the 809 glass at 140K and θ = 90°.

(110–300K), and it is in accord with the expectations of the Debye
model of a solid.[6]
   The expression for f is:

$$\ln f = - k^2 \langle x^2 \rangle, \tag{1}$$

where $k = 7.31 \times 10^{10}$ m^{-1} is the gamma ray wave vector and $\langle x^2 \rangle$
is the mean square displacement which is a sum of the displacements
arising from vibration, diffusion, configurational fluctuations and lat-
tice disorder of the Mössbauer nucleus. In the high temperature limit,
the result of the Debye model is:

$$\ln f = \frac{-3 \, E_r^2 \, T}{Mc^2 \, K_B \, \theta_L^2} \quad T \geqslant \left(\frac{\theta_L}{2} \right), \tag{2}$$

here E_r = 14.4 kev is the energy of the gamma ray, T is the sample
run temperature, M is the mass of the vibrating unit (thus for DAF
$Mc^2 = 2.515 \times 10^8$ kev), K_B is Boltzmann's constant and θ_L is the
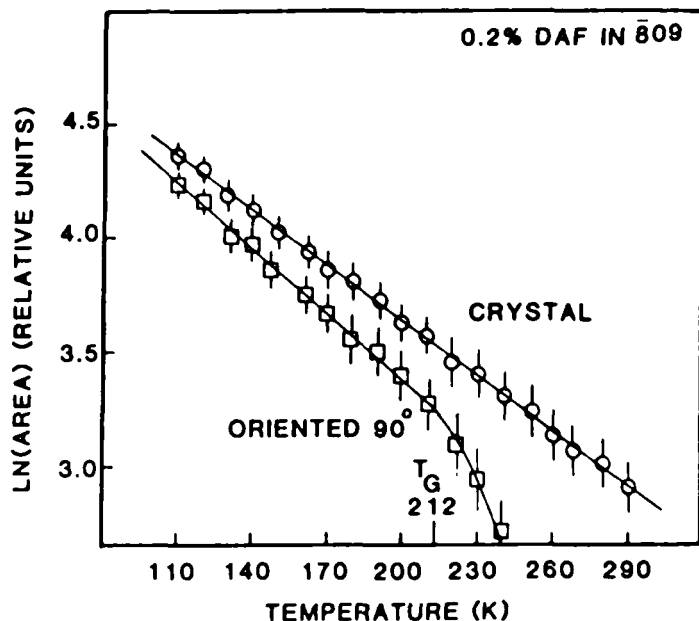Mösbauer-Debye temperature for the material. To obtain the Möss-

FIGURE 2   Plot of the ln f vs T data for DAF in both crystalline $\overline{8}09$ and the cold smectic A of $\overline{8}09$ which was oriented at $\theta = 90°$ in 9KG. For the crystal and for $T < T_g$ for the cold smectic A, the solid line represents a fit of Eq. (2) to the data. For $T > T_g$ in the cold smectic A, the solid line is a fit of Eq. (4) to the data.

bauer-Debye temperature for the host (θ_{LC}) (either the liquid crystalline solid or the smectic A glass) the following expression must be used:[6]

$$\theta_{LC} = \left(\frac{M_{\text{probe}}}{M_{LC}}\right)^{1/2} (\theta_L), \qquad (3)$$

here M_{probe}/M_{LC} is the ratio of mass of the probe molecule to the mass of the host molecule.

For the cold smectic A there is a deviation from the linear behavior described by Eq. (2). The temperature at which this deviation from linear behavior begins is taken to be the glass transition temperature. The increased $\langle x^2 \rangle$ is attributed to additional relaxation experienced by the DAF solute molecules as the systems enters the supercooled liquid state.

Table I lists the Debye temperatures observed from the linear regions of the ln f vs T data. The expectation that the glass is less rigid than the crystal is confirmed.
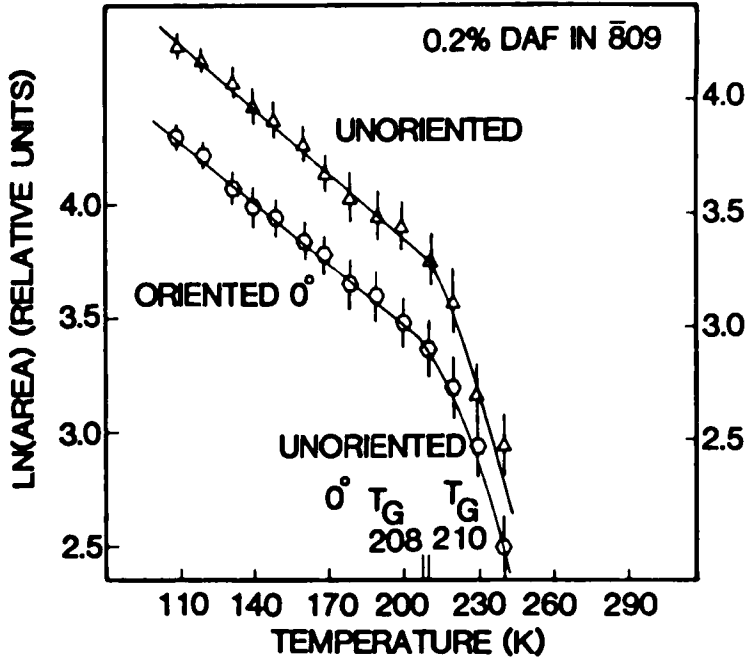
FIGURE 3   Plot of the ln f vs T data for DAF in the cold smectic A of $\bar{8}$09 oriented at $\theta = 0°$ in 9KG and for DAF in the unoriented sample. The data from the unoriented sample have been shifted with respect to the 0° data to allow a clearer presentation in the figure. The right scale is for the unoriented data and the left scale is for the 0° data. For $T < T_g$, the solid line represents the best fit of Eq. (2) to the data. For $T > T_g$, the solid line corresponds to the best fit of Eq. (4) to the data.

The aligned smectic A phase consists of an ordered stack of molecular layers in which the long molecular axes are distributed about the planar normal. For the 0° orientation, the γ-ray direction is parallel to the planar normal for $\bar{8}$09 and for the 90° orientation the gamma ray is directed within the layers. Table I shows that the ex-

TABLE I

Mössbauer-Debye temperature in Kelvins (K) obtained from the best linear fit of ln f vs T data for $T < T_g$ in the $\bar{8}$09 smectic A glass and in the $\bar{8}$09 crystalline state. Data for the cold smectic B of $\bar{4}$08 are given for comparison

| Crystal | Liquid crystalline glass | Orientation | | |
		0°	90°	Unoriented
50.4	$\bar{8}$09 Smectic A ($T < 208$)	45 ± 3	45 ± 3	45 ± 3
74.7	$\bar{4}$08 Smectic B ($T < 175$)	40 ± 3	48 ± 3	53 ± 3

pected anisotropy of θ_{LC} for the above orientations was not detected.

Of interest is the comparison of the θ_{LC}'s for the $\overline{8}09$ smectic A glass to those of the smectic B glass of $\overline{4}08$ (4-n-butoxybenzylidene-4'-octylaniline).[7] Table I compares θ_{LC} values for $\overline{8}09$ to corrected[8] values of θ_{LC} for $\overline{4}08$. θ_{LC} for the crystal state of $\overline{4}08$ is greater than θ_{LC} for $\overline{8}09$ (74.4K $>$ 50.4K) indicating a larger force constant between the DAF and $\overline{4}08$ than between DAF and $\overline{8}09$.

Table I gives the θ_{LC} values for DAF in the smectic A glass of $\overline{8}09$ and also those for DAF in the smectic B glass of BBOA. This comparison shows that the θ_{LC}'s are all between 40K and 53K but the smectic A glass does not exhibit the anisotropy of the smectic B glass. That is surprising, because the structure of the aligned smectic A glass is very similar to that of the aligned smectic B glass.

3.1.2. Glass transition temperature (T_g)

The glass transition temperature is taken to be the temperature where the $\ln f$ vs T plot starts to deviate from Debye-like behavior. This non-Debye behavior many be associated with an increase in the number of relaxations experienced by the DAF molecule. These relaxations occur because of the increase in free volume and configurational entropy which occur at this temperature.

Table II lists the values of T_g obtained for the oriented and unoriented smectic A glass. Note that T_g in $\overline{8}09$ is essentially independent of orientation.

T_g was determined by fitting the $\ln f$ vs T data to the following equation

$$\ln f = aT + b(T - T_g)^2 + c \qquad (4)$$

where a, b, and c are constants and a was determined from the linear portion of the curve. Ruby, Zabransky and Flinn first proposed the $(T - T_g)^2$ dependence for isotropic glasses.[9,10] They attributed this dependence to a shift of the Debye-like vibrational modes to lower energy at the glass transition; that is, one can think of the lattice as "softening" at T_g.

TABLE II

Glass transition temperature for $\overline{8}09$. The units are Kelvins (K)

Liquid crystal	Orientation	T_g
$\overline{8}09$	Unoriented	210
$\overline{8}09$	0°	208
$\overline{8}09$	90°	212

3.1.3. Vibrational Anisotropy (ϵ_L)

From Figures 2 and 3 it can be seen that $\overline{8}$09 does exhibit a very small anisotropic f. For the case when the intramolecular contribution to the vibrational anisotropy is small and the orientational order parameter is small, the angular dependence of f is given by[11]

$$\frac{f(\theta)}{f(\theta = 0)} = \text{EXP} \ (\epsilon_L \ \sin^2\theta) \tag{5}$$

$\epsilon_L = k^2 \ (\langle x_\perp^2 \rangle_L - \langle x_\parallel^2 \rangle_L)$ is the intermolecular contribution to the nuclear vibrational ellipsoid. The intramolecular contribution to the nuclear vibrational anisotropy, ϵ_m, is similary defined. For DAF ϵ_m = 0.15.[5] Figure 4 shows the temperature dependence of ϵ_L for DAF in $\overline{8}$09, and from Eqs. (2) and (5) it is easily shown that Figure 4 exhibits the expected behavior of ϵ_L for materials which are described by an anisotropic Debye temperature.
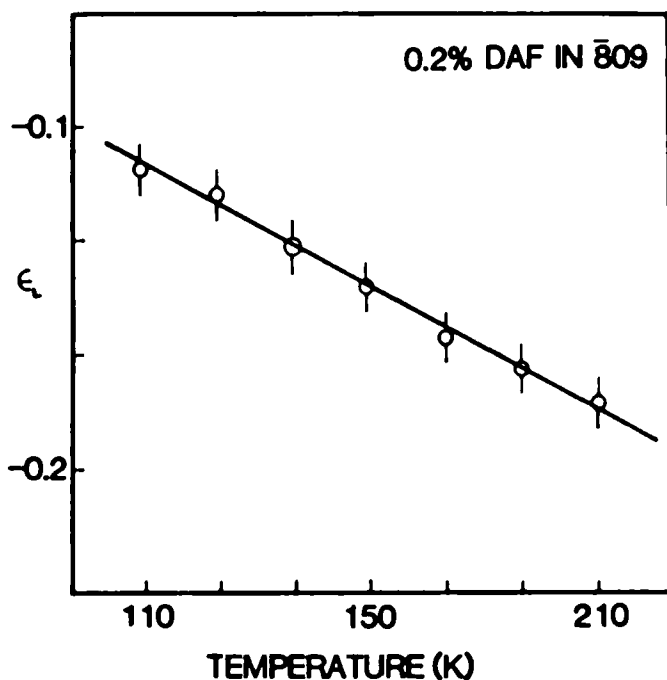

FIGURE 4   The intermolecular contribution to the vibrational anisotropy (ϵ_L) for DAF in the smectic A glass of $\overline{8}$09 is plotted as a function of temperature. The plot results from the difference in the linear least-squares fits to the ln f vs T data for $\theta = 0°$ and $\theta = 90°$.

3.2. Intensity ratio of the quadrupole split lines

To obtain the glass phase, the DAF-liquid crystal system was cooled at a rate of ~17K/min. At this cooling rate crystallization was avoided and any ordering of the DAF molecules by the $\overline{8}09$ host molecules was preserved.

The π and σ transition probabilities depend on θ and if there is any orientational alignment, an asymmetric absorption results. The area ratio for $\overline{8}09$ is independent of temperature and exhibits a small angular dependence as shown in Figure 5. The theoretical expression for the θ-dependence of A_π/A_σ for DAF for small ϵ_m is as follows:

$$A_\pi/A_\sigma(\theta) = \frac{8 - (3\cos^2\theta - 1)S}{8 + (3\cos^2\theta - 1)S} \qquad (6)$$

where S is the orientational order parameter.[11] The solid line in Figure 5 is the best fit of equation (6) to the data. The resulting order parameter for DAF in $\overline{8}09$ is 0.08 at 110K. This low order parameter is attributed to the fact that the DAF resides in the disordered tail
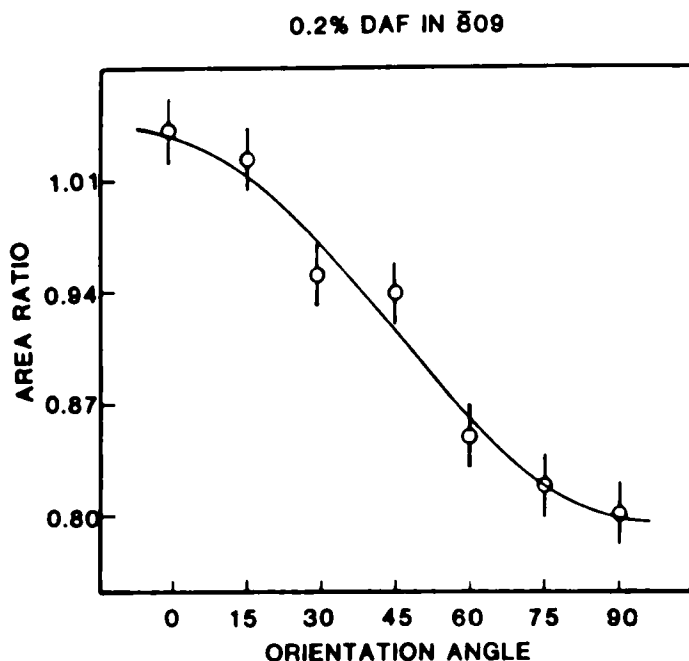
0.2% DAF IN $\overline{8}09$

FIGURE 5   Plot of the area ratio (A_π/A_σ) vs θ for DAF in the cold smectic A glass phase of $\overline{8}09$. The data were recorded at 110K.

regions of the liquid crystalline molecules. Neither line broadening nor quadrupole relaxation was observed for DAF in the cold smectic A of $\overline{8}09$. Thus, rotational and translational diffusion were not observable for the time scale of Fe-57 spectroscopy.

3.2.1. Results and discussion for the inner doublet

The data for the internal doublet are shown in Figure 6. Here the ln f exhibits a small change with temperature producing a slope which is much smaller than that exhibited by the outer doublet. This small slope produces a larger Debye temperature than that determined for the outer doublet (see Table I). (The actual numbers are probably not very significant due to the very low intensity of the inner doublet.) Therefore, the DAF molecules which contribute to the inner doublet experience a larger force constant than the DAF molecules which contribute to the outer doublet. The signal-to-noise ratio was too
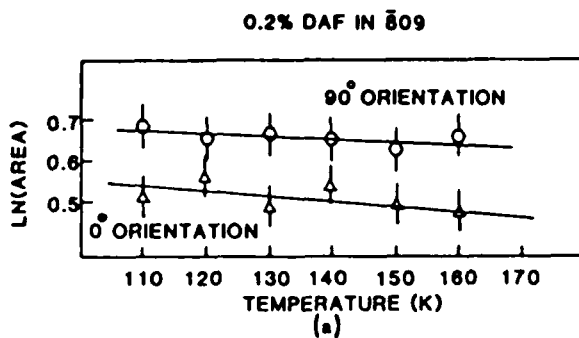
0.2% DAF IN $\overline{8}$09

FIGURE 6a.   Plot of the ln f vs T data for the inner doublet of DAF in the cold smectic A of $\overline{8}09$ oriented at $\theta = 90°$ and $\theta = 0°$ in 9KG. The solid line represents the best fit of Eq. (2) to the data.
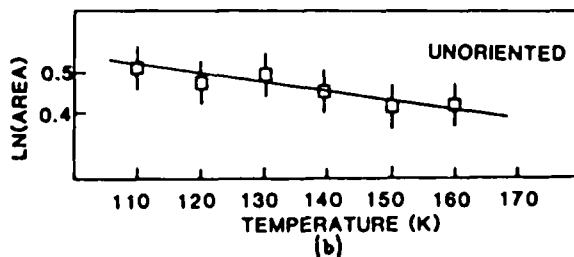

FIGURE 6b.   Plot of the ln f vs T data for the inner doublet of DAF in the cold smectic A of $\overline{8}09$ for the unoriented sample. The solid line represents the best fit of Eq. (2) to the data.

poor to extract any useful information concerning the inner doublet for run temperatures > 160K.

The area ratio for the unoriented and oriented configurations are temperature independent, and exhibit a small angular dependence as shown in Figure 7. Using the same procedure as in section 3.2 the inner doublet gives an order parameter of $S = -0.14$. The negative order parameter means that the principal axis of the electric field gradient tensor for the DAF molecules producing the inner doublet is oriented parallel to the long molecular axis of $\overline{8}09$. On the other hand for the DAF molecules producing the outer doublet ($S > 0$) the principal electric field gradient axis is oriented perpendicular to the long molecular axis of $\overline{8}09$.

Goldanskii[12] *et al.*, have reported an internal doublet in the ferrocene cholesterylmyristate system. Here the ferrocene was enriched to 90% of Fe-57. Goldanskii *et al.*, attributed the internal doublet to the formation of charge transfer complexes due to chemical inter-
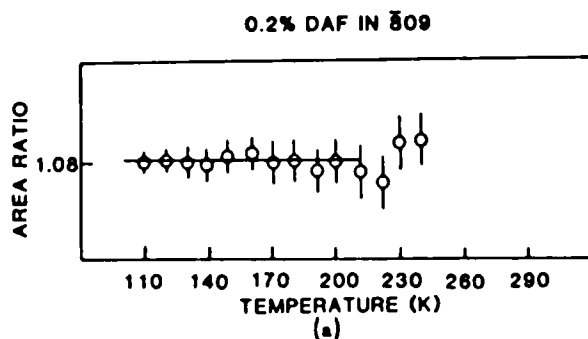
0.2% DAF IN $\overline{8}$09

FIGURE 7a. Plot of the area ratio (A_π/A_σ) *vs* temperature for the inner doublet of DAF in the cold smectic A glass phase of 809. This plot shows that the area ratio is temperature independent.
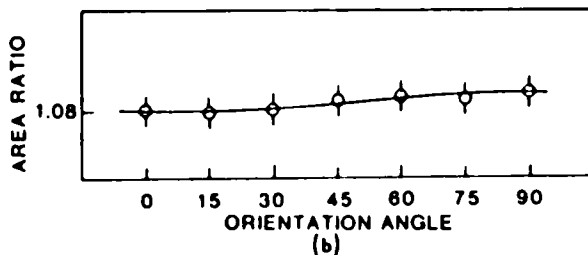
FIGURE 7b. Plot of the area ratio (A_π/A_σ) *vs* θ for the inner doublet of DAF in the cold smectic A glass phase of $\overline{8}$09. These data were recorded at 110K.

actions between ferrocene and cholesterylmyristate. Their argument was that the donor acceptor interaction between the ferrocene molecules and the matrix in such complexes may arise from transfer of an electron from the π molecular orbitals of ferrocene to cholesterylmyristate molecular orbitals. Also their inner doublet gave an order parameter of $S = 0.70$ and the area ratio was angle dependent. They regarded this as additional evidence for the formation of a complex between the label and the liquid crystal. It is believed that a similar mechanism may produce the internal doublet in the DAF-$\overline{8}$09 system.

4. CONCLUSIONS

The area ratio data for the outer doublet show that the $\overline{8}$09 host ordered the DAF solute molecules to a very small extent. The ln f vs T data deviated from Debye-like behavior via a $(T - T_g)^2$ dependence which is accounted for by relaxations which can be associated with a glass transition temperature. The smectic A glass of $\overline{8}$09 has a lower Mössbauer-Debye temperature than the crystalline phase showing that the glassy phase is less rigid. Further, the smectic A glass exhibits a θ-independent Mössbauer-Debye temperature which indicates that the DAF molecules which contribute to the outer doublet are located in the flexible end-chain region of the host $\overline{8}$09 molecules.

Finally, the inner doublet gives an order parameter of $S = -0.14$ which means that the principal axis of the electric field gradient tensor of the DAF is oriented parallel to the long molecular axis of $\overline{8}$09. Further, this inner doublet is believed to be the result of some type of complexing between the DAF and the $\overline{8}$09 molecules.

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