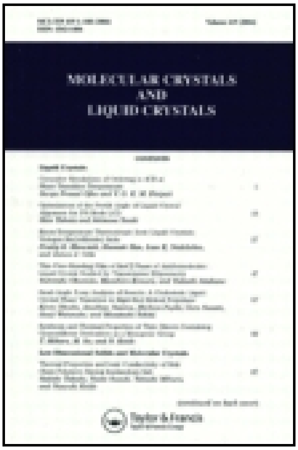

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A MÖSSBAUER TEMPERATURE STUDY OF 1,1'-DIACETYLFERROCENE IN A COLD SMECTIC C LIQUID CRYSTAL

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The Fe-57 Mössbauer effect (ME) was used to study a solution (0.2% by weight) of 1,1'-diacetylferrocene (DAF) in the liquid crystalline material 4-n-pentylphenyl-4'-n-heptyloxythiobenzoate (7S5). The ME parameters were determined for the temperature range 110-300K in the crystalline solid phase and 110-240K in the cold smectic C phase of 7S5. Here "cold" means the smectic glass and the supercooled smectic phase. The ln recoil-free intensity (f) vs T data exhibited linear Debye behavior for the solid phase over the entire temperature range. The low temperature (T<215) portion of the cold smectic ln f vs T data also exhibited Debye behavior, and the smectic glass gave a Mössbauer-Debye temperature (θ_{LC}) about 10K lower than the crystalline phase. The smectic glass - supercooled smectic transition was determined to be T_g = 215K from the deviation of the ln f vs T data from linear behavior. Above T_g, the deviation from linear Debye behavior followed a $(T-T_g)^2$ dependence. The intermolecular contribution to the vibrational ellipsoid (ε_L) declined linearly with increasing temperature below T_g. The smectic C glass yielded an order parameter of S = 0.12 for the DAF molecules at 110K. Rotational and translational diffusion were not observed for the cold smectic C phase.

1. INTRODUCTION

Mössbauer Effect (ME) measurements were obtained from a 0.2% (by weight) solution of 1,1'-diacetylferrocene (DAF) in 4-n-pentylphenyl-4'-n-heptyloxythiobenzoate ($\bar{7}S5$). The measurements spanned the temperature range of 110-300K for DAF in the crystalline solid phase of $\bar{7}S5$ and 110-240K for DAF in the cold liquid crystal. The cold liquid crystal encompasses both the smectic C liquid crystalline glass and the supercooled smectic C liquid crystalline phase. It is well known that only the lowest temperature liquid crystalline phase of a given liquid crystalline material will supercool and form a glass[1,2].

For $\bar{7}S5$ the lowest temperature cold liquid crystalline phase is a smectic C, the molecular centers of gravity form a layered structure in which there is no translational order within the layers and the long molecular axes are tilted with respect to the planar normals. This smectic C phase is also optically biaxial[3]. The $\bar{7}S5$ liquid crystalline material has the following transitions:

$$\begin{tikzcd}
\text{Solid} \arrow[r, "328K"] & \text{Nematic} \arrow[r, leftrightarrow, "355K"] \arrow[d, "309K"] & \text{Isotropic Liquid} \\
& \text{Smectic C} \arrow[ul, "296K"] &
\end{tikzcd}$$

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 Mossbauer data. A 30mCi source of Co-57 on a Rhodium matrix served as the ME source 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 ($\overline{7}$S5). 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 (1.0cm diam. x 0.3cm 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 rate of 17K/min. The temperature was controlled to ±0.5K for the entire period of the ME experiment[4]. 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 is 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, however, 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 C 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 C phase of $\overline{7}$S5 exhibited particularly difficult behavior at high temperatures. For example, at 230K crystallization occurred within fifteen minutes after the sample was prepared for the ME run. For T > 240K $\overline{7}$S5 crystallized so fast that ME measurements in the cold smectic C were impossible to obtain, even though the sensitivity limits of the ME spectrometer had not been reached. 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 two Lorentzian lineshapes using a Burroughs 6800 computer. The area ratio of the quadrupole split doublet ($A\pi/A\sigma$), f, ΔE_Q, the linewidth (Γ), and the chemical shift (δ) were all obtained from the computer fits to the data.

3. RESULTS AND DISCUSSION

3.1 Recoil-free Intensity

3.1.1 Mössbauer-Debye Temperature (θ_L)

Four plots of ln f *vs* T data for $\overline{7}$S5 are presented in Figures 1 and 2. The four experimental situations presented are as follows: the crystalline solid, unoriented cold liquid crystal, and the cold liquid crystal oriented

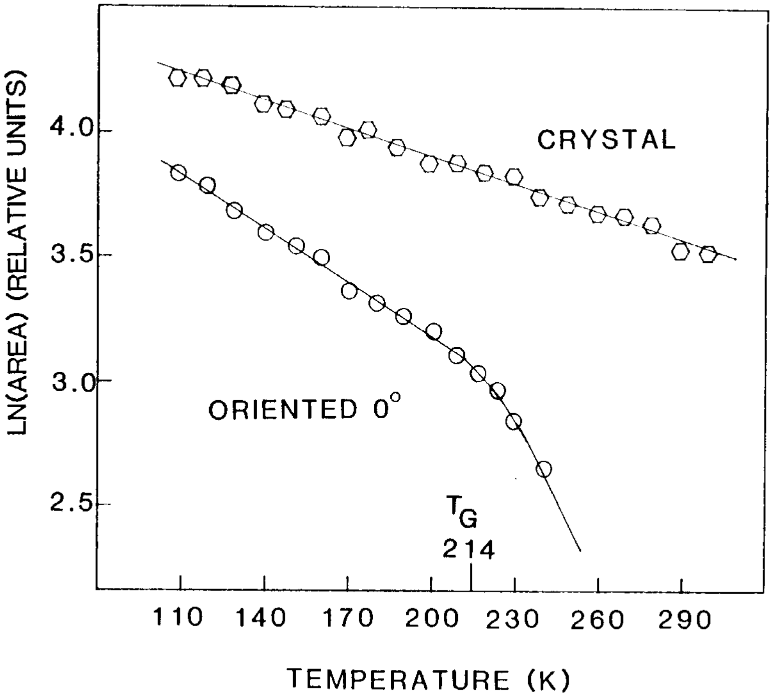


FIGURE 1

Plot of the ln f vs T data for DAF in both crystalline $\overline{7}S5$ and the cold smectic C of $\overline{7}S5$ which was oriented at $\theta = 0°$ in 9KG. For the crystal and for $T < T_g$ for the cold smectic C, the solid line represents a fit of Eq. (2) to the data. For $T > T_g$ in the cold smectic C, the solid line is a fit of Eq. (4) to the data.

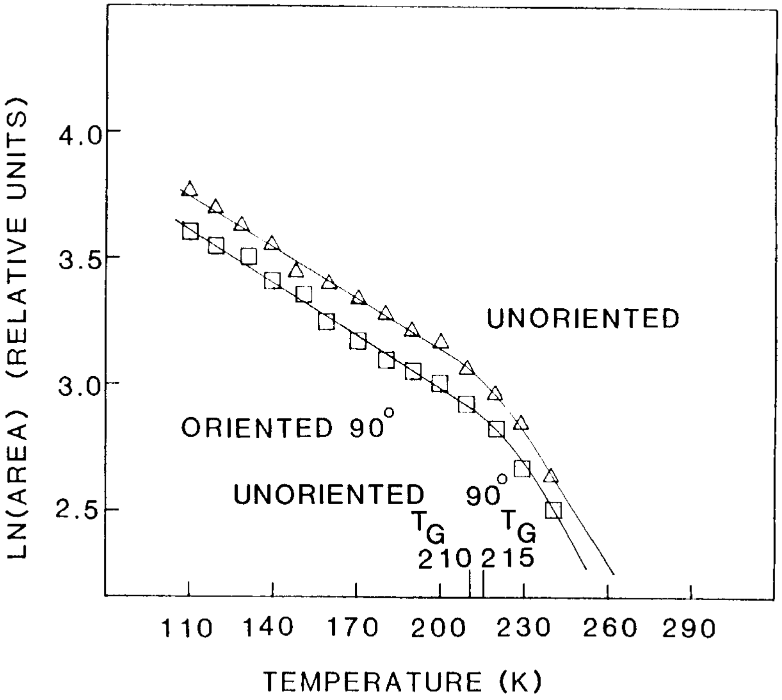


FIGURE 2

Plot of the ln f *vs* T data for DAF in the cold smectic C of $\overline{7}S5$ for both the unoriented sample and for the sample oriented with θ = 90° in 9Kg. For $T < T_g$, the solid lines represent 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.

at 0° and 90°. The crystal data show a linear temperature dependence for the entire temperature range (110-300K), and it is in accord with the expectations of the Debye model of a solid[5].

The expression for f is:

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

where k is the gamma ray wave vector and $\langle x^2 \rangle$ is the mean square vibrational displacement of the Mössbauer nucleus along k. In the high temperature limit, the result of the Debye model is:

$$\ln f = \frac{-3E_\gamma^2 T}{Mc^2 k_B \theta_L^2} \qquad T \geq \left(\frac{\theta_L}{2}\right), \tag{2}$$

here E_γ is the energy of the gamma ray, T is the sample temperature, M is the mass of the vibrating unit, k_B is Boltzmann's constant and θ_L is the Mössbauer-Debye temperature for the material. To obtain the Mössbauer-Debye temperature for the host (θ_{LC}) (either the liquid crystalline solid or the smectic C glass) one must use the expression[5]

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

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 C 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 an increase in the vibrational degrees of freedom as the system enters the supercooled liquid state.

Table I lists the Debye temperatures as obtained from the linear regions of the ln f _vs_ T data. θ_{LC} for each glass orientation is less than the θ_{LC} obtained for the corresponding crystalline phase. The expectation that the glass is less rigid than the crystal is, therefore, confirmed.

Table I

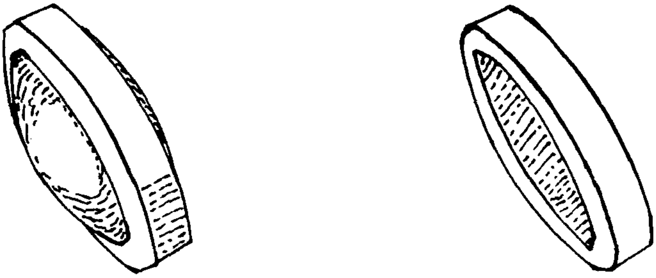
Mössbauer-Debye temperatures obtained from a best linear fit of ln f _vs_ T data for $\overline{7}$S5.

		Orientation		
Crystal	Liquid Crystalline Glass	0°	90°	Unoriented
65.4	$\overline{7}$S5 Smectic C (T < 210K)	58.5	55.6	59.4
74.7	BBOA Smectic B (T < 175K)	40	48	52

The aligned smectic C has the following structure. The liquid crystal molecules are aligned in a distribution about the magnetic field direction. As a result, the smectic planes are tilted with a random azimuthal distribution of the planar normals about the aligning magnetic field direction[6-8]. Previous ME orientation data for several substituted ferrocene derivatives have shown that the DAF molecule resides in the end-chain region of the liquid crystalline material[4,9,10].

Of interest is the comparison of the θ_{LC}'s for $\overline{7}$S5 smectic C glass to those of the smectic B glass of BBOA (4-n-butoxybenzylidene-4'-n'-octylaniline)[10]. Table I shows that the θ_{LC} for crystal BBOA is greater than the θ_{LC} for crystal $\overline{7}$S5 (74.7K > 65.4K) indicating a larger force constant between the DAF and BBOA than between DAF and $\overline{7}$S5. Comparison of the θ_{LC} values for the glass phase is not so easily done.

Table I gives the θ_{LC} values for DAF in the smectic C glass of $\overline{7}$S5 and also those for DAF in the smectic B glass of BBOA. The BBOA values differ from those reported by LaPrice and Uhrich[10]. The original values were found to be in error because of competition between surface (in BBOA the molecules tend to line up parallel to the surface[9,11,12]) and magnetic field alignment. The curved faces (Figure 3) of the samples used by LaPrice and



a. b.

FIGURE 3

a) Sample geometry used in the LaPrice and Uhrich experiment

b) Sample geometry used in this experiment. Note the parallel sides.

Uhrich[10] have larger surface to volume ratios than the flat-sided samples of this report. The resulting misalignment caused by the curved surfaces[13,14] affected the slope of the originally reported ln f vs T plots for DAF in BBOA. By comparing the θ_{LC} values for the probe molecules ferrocenyl-4'-methoxyaniline (FMA) and ferrocentyl-4'-n-butylaniline (FBA) for both the flat-sided and curved-sided sample holders Marande[14] was able to obtain a correction factor for the θ_{LC} values for DAF in BBOA. Those corrected values are reported in Table I.

The comparison of the $\theta = 0°$ values for DAF in the smectic B of BBOA and for DAF in the smectic C of $\bar{7}S5$ yields a relatively large difference in (∿20°K) in the θ_{LC}. This comparison is unfair, however, because the DAF in the smectic B phase of BBOA at $\theta = 0°$ experiences a neat stack of layers. The DAF in the smectic C phase of $\bar{7}S5$ at $\theta = 0°$ experiences a variety of different layer configurations due to the smectic C tilt angle. The tilt also affects the $\theta = 90°$ comparison and explains the near isotropy of θ_{LC} for DAF in the smectic C glass of $\bar{7}S5$.

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 is associated with an increase in the number of vibrational relaxations which result from the increase in free volume and configurational entropy at this temperature.

Table II lists the values of T_g obtained for the oriented and unoriented smectic C glass. Note that T_g in $\bar{7}S5$ is essentially independent of orientation.

Table II

Glass transition temperature for $\overline{7}S5$.
The units are Kelvins (K).

Liquid Crystal	Orientation	T_g
$\overline{7}S5$	unoriented	210
$\overline{7}S5$	0°	214
$\overline{7}S5$	90°	215

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

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

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[15,16]. 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.

3.1.3. Vibrational Anisotropy (ε_L)

From Figures 1 and 2 it can be seen that $\overline{7}S5$ does exhibit an 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[9]

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

$\varepsilon_L = K^2(\langle X_{||}{}^2\rangle_L - \langle X_{\perp}{}^2\rangle_L)$ is the intermolecular contribution to the nuclear vibrational ellipsoid. The intramolecular contribution to the nuclear vibrational anisotropy, ε_m, is similarly defined. For DAF $\varepsilon_m = 0.15$[4]. Figure 4 shows the temperature dependence of ε_L for DAF in $\overline{7}S5$, and from

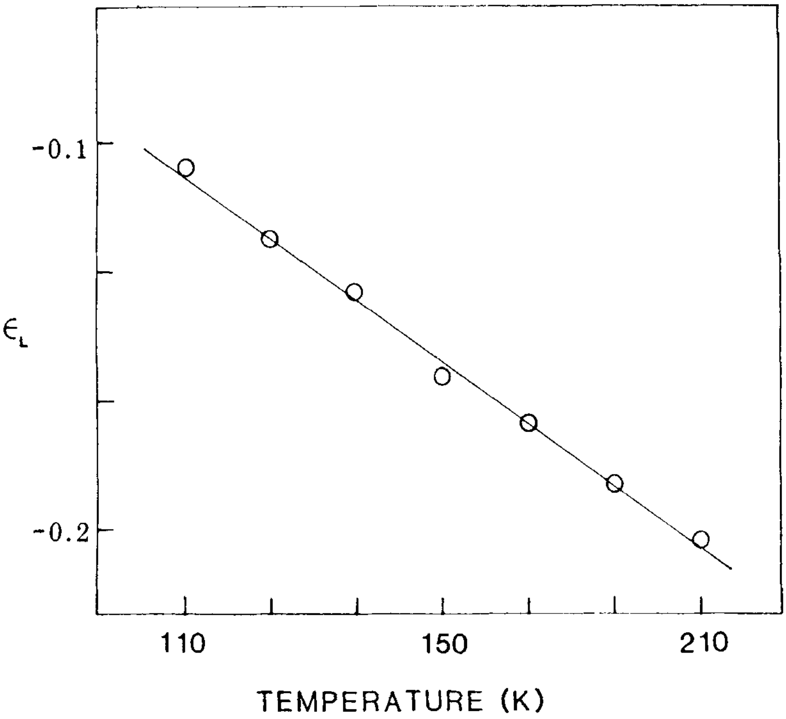


FIGURE 4

The intermolecular contribution to the vibration anisotropy (ε_L) for DAF in the smectic C glass of $\overline{7}S5$ 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 $\theta = 90°$.

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.

3.2 Intensity Ratio of the Quadrupole Split Lines

To obtain the glass phase, the DAF-liquid crystal system must be rapidly cooled ~17K/min. Any molecular ordering of the DAF by the liquid crystalline host is preserved by the rapid cooling technique.

The π and σ transition probabilities depend on θ and if there is any orientational alignment, an asymmetric absorption results. Figure 5 shows the intensity ratio ($A\pi/A\sigma$) of the π and σ transitions of Fe-57 quadrupole split doublet versus temperature. One can see a small difference between the three orientations (0°, 90°, unoriented). That is to say $A\pi/A\sigma \approx 1$ for 0°, $A\pi/A\sigma \approx 1.18$ for 90° and $A\pi/A\sigma \approx 1.07$ for unoriented. Consequently, the DAF molecules are orientationally ordered at each of the temperature points in the range of 100 to 215K.

Previously, DAF was found not to order in liquid crystalline materials[4,10]. Figure 6 shows that $A\pi/A\sigma$ versus θ at the temperature of 110K. The theoretical expression for the θ-dependence of $A\pi/A\sigma$ 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[9]. The solid line in Figure 6 is the best fit of Eq. (6) to the

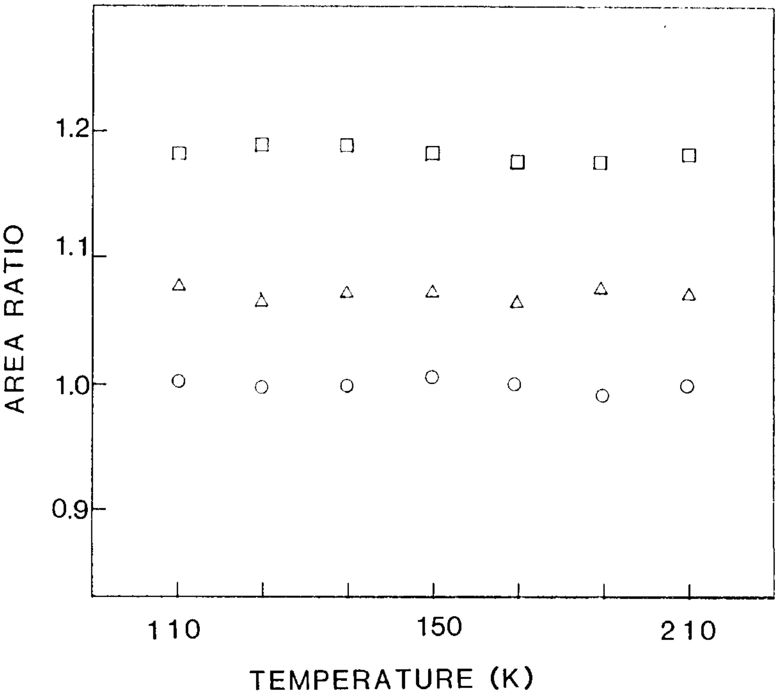


FIGURE 5

The intensity ratios ($A\pi/A\sigma$) are plotted versus temperature for the cold smectic C of $\overline{7}S5$. The points at a given temperature represent averages of three or more runs. Unoriented (△), θ = 0° (○), and θ = 90° (□) data are all presented.

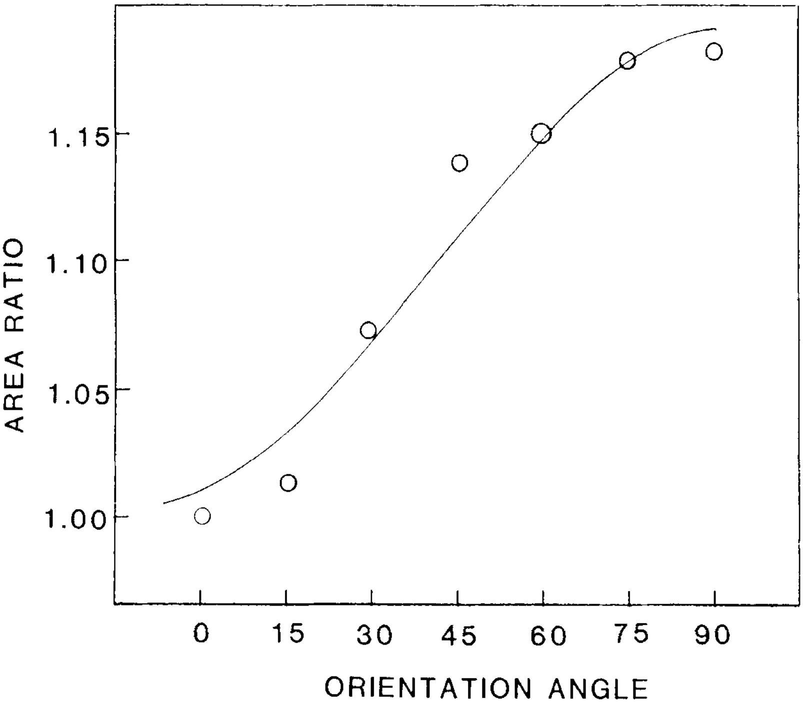


FIGURE 6

Plot of the area ratio (Aπ/Aσ) versus θ for DAF in the cold smectic C glass phase of $\bar{7}S5$. The data were all recorded at 110K (see Ref. 14).

data. The resulting order parameter for DAF in $\bar{7}S5$ is 0.12 at 110K. The low order parameter is attributed to the fact that the DAF resides in the disordered tail regions of the liquid crystalline molecules. Neither line broadening nor quadrupole relaxation was observed for DAF in the cold smectic C of $\bar{7}S5$. Thus, rotational and translational diffusion were not observable for the time scale of Fe-57 spectroscopy.

3. CONCLUSIONS

The area ratio data show that the $\overline{7}S5$ host ordered the DAF solute molecules to a small extent. The ln f vs T data deviate from Debye-like behavior via a $(T-T_g)^2$ dependence which illustrates a structural relaxation which can be associated with a glass transition temperature.

Finally, the smectic C glass of $\overline{7}S5$ has a lower Mössbauer-Debye temperature than the crystalline phase showing that the glassy phase is less rigid. Further, the smectic C glass exhibits a small anisotropic Mössbauer-Debye temperature showing that the θ = 0° orientation is the most rigid.

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