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Mössbauer studies of DNF and FMA in a smectic B liquid crystal

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The FE-57 Mössbauer effect (ME) was used to study two solutions 0.4 wt% of ferrocenyl-4'-methoxyaniline (FMA) in the liquid crystalline material 4-*n*-butoxybenzylidene-4'-*n*-octylaniline (4O.8) and 0.4 wt% of 1,1'-dinononyl-ferrocene in 4O.8. The ME parameters were determined for the temperature range 40–300 K in the crystalline solid phase and 40–220 K in the cold smectic B phase of 4O.8 for both samples. The 'cold smectic B' is defined as the smectic B glass and the supercooled smectic B phase. For $T < 60$ K the DNF-4O.8 system exhibited a ME spectrum that was composed of two quadrupole split doublets. This four-line spectrum was observed for both the crystal phase and the smectic B glass phase of the DNF-4O.8 system. The FMA-4O.8 system exhibited a single quadrupole doublet. The \ln (recoil-free intensity f) versus T data exhibited linear Debye behaviour for the solid phase over the entire temperature range. The cold smectic $\ln f$ versus T data also exhibited Debye behaviour for this system. The smectic B glass gave a Mössbauer-Debye temperature (θ_{1c}) about 23 K lower than the crystalline phase for the FMA-4O.8 system and about 25 K for the DNF-4O.8 system. The intermolecular contribution to the vibrational ellipsoid (ϵ_{1c}) declined linearly with increasing temperature for both systems.

1. Introduction

The Mössbauer effect (ME) was used to study two different solutions 0.4 wt% of ferrocenyl-4'-methoxyaniline (FMA) in 4-*n*-butoxybenzylidene-4'-*n*-octylaniline (BBOA or 4O.8) and 0.4 wt% of 1,1'-dinononyl-ferrocene (DNF) in 4O.8. The measurements spanned the temperature range of 40–300 K for both FMA and DNF in the crystalline phase of 4O.8 and 40–220 K for FMA and DNF in the cold liquid crystal. The cold liquid crystal encompasses both the smectic B liquid crystalline glass and the supercooled smectic B liquid crystalline phase. Only the lowest liquid crystalline phase of a given liquid crystalline material will supercool and form a glass [1, 2]. The lowest temperature cold liquid crystalline phase for 4O.8 is a smectic B [3].

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 used which is identical to and described in [4].

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The two ME samples were prepared by dissolving 0.4 wt% FMA and DNF independently into the liquid crystalline material (4O.8). For a complete discussion of the sample preparation and the aligned glass, consult the experimental section of [5].

The ME spectra were fit with Lorentzian line shapes using an IBM 3090 computer.

3. Results and discussion

3.1. Temperature dependencies

3.1.1. Mössbauer-Debye temperature (θ_{1c})

The plots of $\ln f$ versus T data are presented in figures 1 to 4 (see figures 1 and 2 for FMA in 4O.8 and figures 3 and 4 for the outer doublet of DNF in 4O.8), where f is the recoil free intensity which is equal to the normalized area of the quadrupole doublet and T is the temperature of the run. The normalized area is given by \rightarrow (per cent effect \times ($\frac{1}{2}$ width) of the peaks. 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 (40–300 K) for both samples, and it is in accord with the expectations of the Debye model of a solid [6].

The expression for f is

$$\ln f = -k^2 \langle x^2 \rangle, \quad (1)$$

where $k = 7.31 \times 10^{10} \text{ m}^{-1}$ is the gamma ray wavevector and $\langle x^2 \rangle$ is the mean square displacement which is a sum of the displacements arising from vibration, diffusion, configurational fluctuations and lattice disorder of the

Mössbauer nucleus. In the high temperature limit, the result of the Debye model is

$$\ln f = \frac{-3E_\gamma^2 T}{M^2 k_B \theta_L^2}, \quad T \gg \left(\frac{\theta_L}{2}\right) \quad (2)$$

here $E_\gamma = 14.4 \text{ keV}$ is the energy of the gamma ray, T is the sample run temperature, M is the mass of the vibrating unit (for FMA $Mc^2 = 2.99 \times 10^8 \text{ keV}$ and for DNF $Mc^2 = 3.82 \times 10^8 \text{ keV}$), k_B is Boltzmann's constant and θ_L is the Mössbauer-Debye temperature for the material.

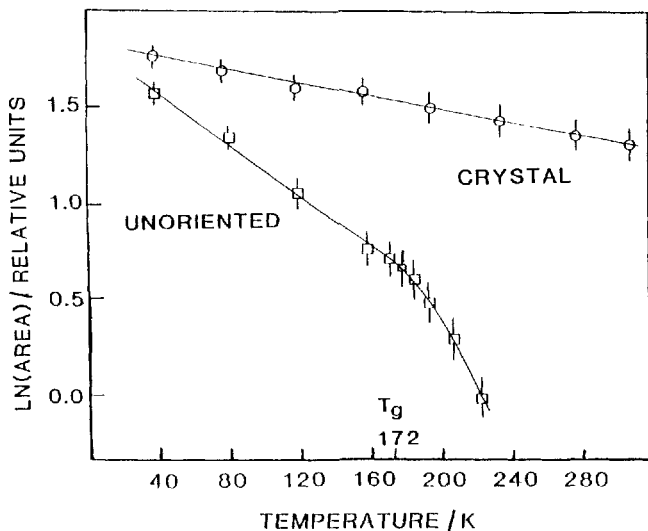


Figure 1. $\ln(\text{area})$ versus temperature for the crystal and unoriented glass phases of 0.4 wt% FMA in 4O.8. The solid line is a fit of equations (2) and (4) to the data.

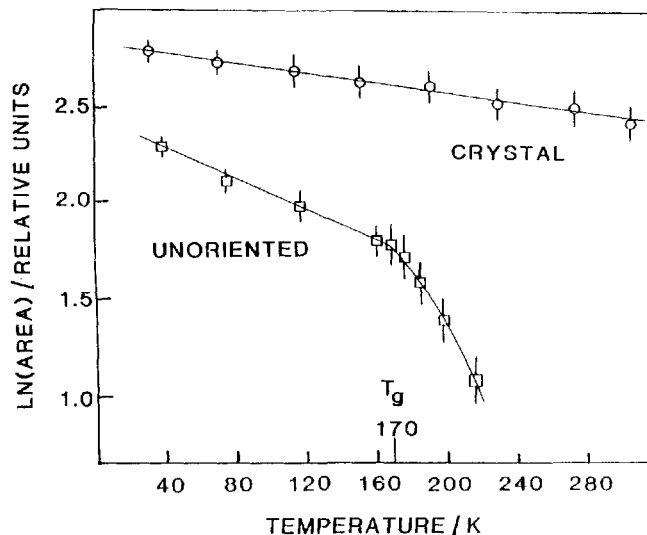


Figure 3. $\ln(\text{area})$ versus temperature for the crystal and unoriented glass phases of 0.4 wt% DNF in 4O.8. The solid line is a fit of equations (2) and (4) to the data.

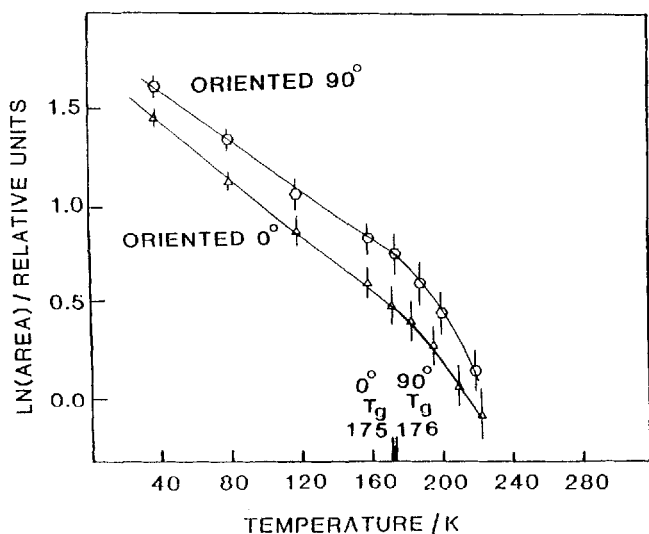


Figure 2. $\ln(\text{area})$ versus temperature for the 0° and 90° orientations of the glass phase of 0.4 wt% FMA in 4O.8. The solid line is a fit of equations (2) and (4) to the data.

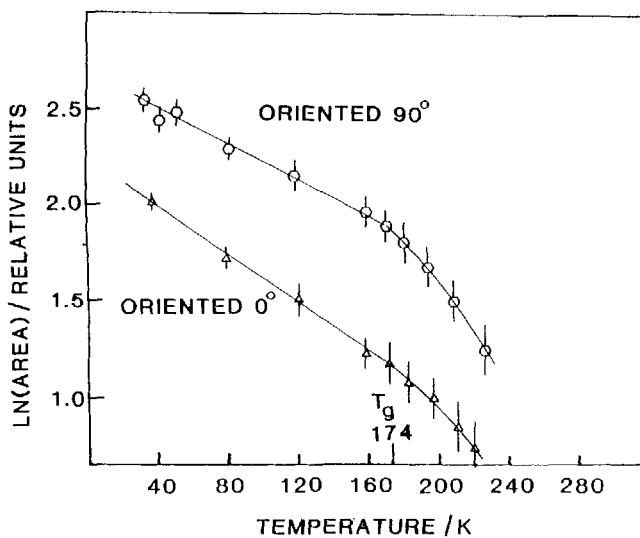


Figure 4. $\ln(\text{area})$ versus temperature for the 0° and 90° orientations of the glass phase of 0.4 wt% DNF in 4O.8. The solid line is a fit of equations (2) and (4) to the data.

Table 1. Compares θ_{LC} s values for FMA and DNF in 4O.8.

Cold liquid crystalline glass	θ_{LC} 's			
	Orientation			
	Crystal	Unoriented	90°	0°
0.4% FMA in 4O.8	54.2	30.6	33.9	28.7
0.4% DNF in 4O.8	64.6	35.0	37.0	30.3
0.4% DNF in 4O.8 inner doublet	46.8	44.5	44.5	44.5

To obtain the Mössbauer–Debye temperature for the host (θ_{LC}) (either the liquid crystalline solid or the smectic B glass) the following expression must be used [6]:

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

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 B there is a deviation from linear behaviour described by equation (2). The temperature at which this deviation from linear behaviour begins is taken to be the glass transition temperature. The increased $\langle x^2 \rangle$ is attributed to additional relaxation experienced by the FMA and DNF solute molecules as the systems enter the supercooled liquid state.

Table 1 lists the Debye temperature observed from the linear regions of the $\ln f$ versus T data. The expectation that the glass is less rigid than the crystal is confirmed.

The aligned smectic B phase consists of an ordered stack of molecular layers in which the long molecular axes are distributed about the planar normal [3]. For the 0° orientation the gamma ray direction is along the planar normal for 4O.8 and the 90° orientation corresponds to the gamma ray being directed within the layers. This anisotropy accounts for the anisotropic Debye temperatures.

A possible explanation for the different Debye temperatures is as follows: it is known from previous work [4, 5, 7] that the probes will reside in the tail region of 4O.8 and it is reasonable to expect that both FMA and DNF will reside in the tail region also. DNF being more massive than FMA can account for a small increase in the θ_{LC} s for DNF [1]. Further, DNF has a more polar tail region than FMA and it is expected that this will lead to a stronger dipolar interaction between DNF and 4O.8 than FMA and 4O.8. Thus, an increase in the force constant between DNF and 4O.8 leading to the larger θ_{LC} s for the DNF–4O.8 system.

3.1.2. Glass transition temperature (T_g)

The glass transition temperature is taken to be the temperature where the $\ln f$ versus T plot starts to deviate

Table 2. Glass transition temperature for FMA and DNF in 4O.8.

Liquid crystal system	Orientation	T_g
FMA in 4O.8	Unoriented	172
	0°	175
	90°	176
DNF in 4O.8 (outer)	Unoriented	170
	0°	174
	90°	174
DNF in 4O.8 (inner)	Unoriented	
	0°	
	90°	

from Debye-like behaviour. This non-Debye behaviour can be associated with an increase in the number of relaxations experienced by the DNF or FMA molecules. These relaxations occur because of the increase in free volume and configurational entropy which occur at this temperature.

Table 2 lists the values of T_g obtained for the oriented and unoriented smectic B glass for both the FMA and DNF systems. T_g for 4O.8 is essentially independent of orientation for each system.

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

$$\ln f = AT + B(T - T_g)^2 + C \quad (4)$$

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 [8, 9]. 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 . The ME technique in determining T_g is very sensitive to changes in the molecular vibrational motion via equation (1). Also the ME T_g was determined using FMA and DNF (which are of different sizes) whose presence must distort the local liquid crystal packing. These distortions could give rise to secondary relaxations [10, 12] which in turn would account for the different T_g s of the FMA and DNF systems.

3.1.3. Vibrational anisotropy (ϵ_L)

From figures 1 to 4 it can be seen that 4O.8 does exhibit an anisotropic f . For the case when the intramolecular contributions to the vibrational anisotropy is small and the orientational order parameter is small, the angular dependence of f is given by [13]

$$\frac{f(\theta)}{f(\theta=0)} = \exp(\epsilon_L \sin^2 \theta) \quad (5)$$

$\epsilon_L = k^2(\langle x_{\perp}^2 \rangle_L - \langle x_{\parallel}^2 \rangle_L)$ is the intermolecular contribution to the nuclear vibrational ellipsoidal where \parallel and \perp mean parallel and perpendicular to the planar normal of the smectic B planes. The intramolecular contributions to the nuclear vibrational anisotropy, ϵ_m , is similarly defined. For FMA $\epsilon_m = 0.20$ [13], and for DNF $\epsilon_m = 0.21$. Figures 5 and 6 show the temperature dependence of ϵ_L for FMA and DNF in 4O.8 from equations (2) and (5) it is easily shown that figures 5 and 6 exhibit behaviour of ϵ_L for materials which are described by an anisotropic Debye temperature.

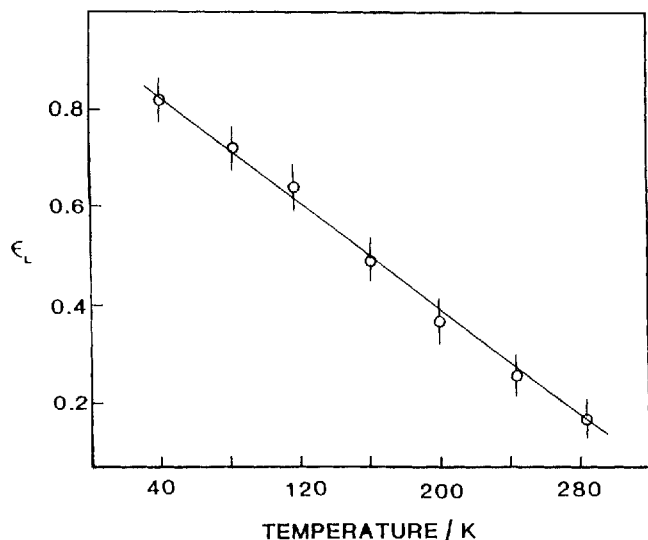


Figure 5. The intermolecular contribution to the vibrational anisotropy versus temperature for 0.4 wt% FMA in the smectic B glass of 4O.8.

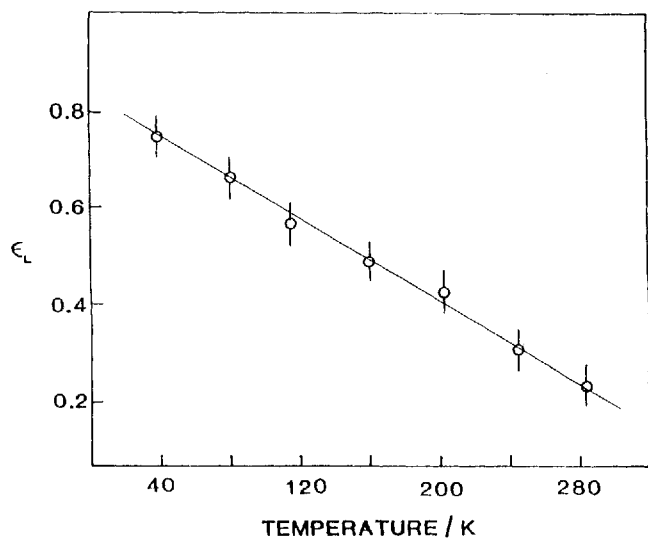


Figure 6. The intermolecular contribution to the vibrational anisotropy versus temperature for 0.4 wt% DNF in the smectic B glass of 4O.8.

3.2. Intensity ratio of the quadrupole split lines

To obtain the glass phase, the FMA and DNF-liquid crystal systems were cooled at a rate of $\sim 20 \text{ k min}^{-1}$. At this cooling rate crystallization was avoided and any ordering of the FMA or DNF molecules by the 4O.8 host molecules were 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 FMA and DNF in 4O.8 is independent of temperature and exhibits an angular dependence as shown in figures 7 and 8. The theoretical expression for the θ -dependence of $A\pi/A\sigma$ for FMA and DNF for small ϵ_m is as follows:

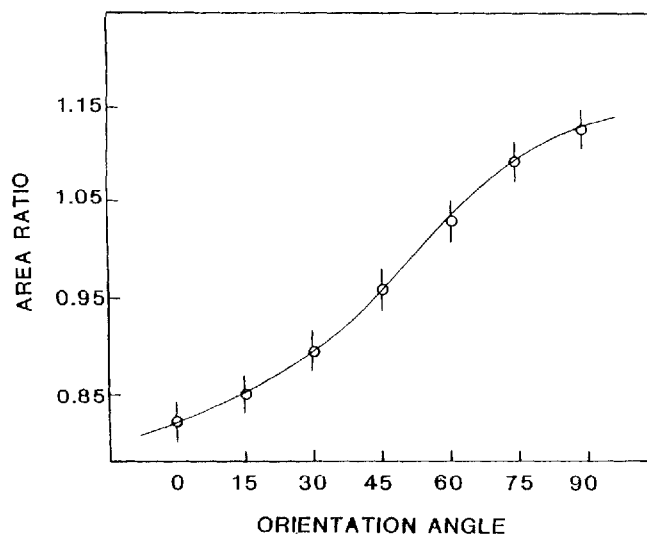


Figure 7. Plot of the area ratio versus orientation angle for 0.4 wt% FMA in 4O.8. The data were all recorded at 40 K.

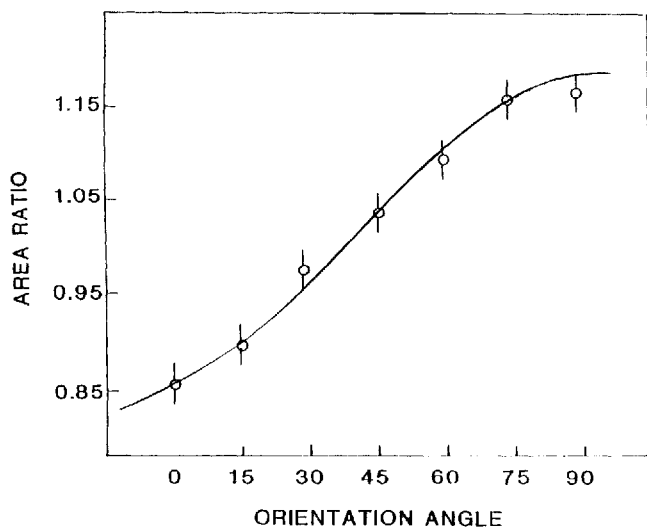


Figure 8. Plot of the area ratio versus orientation angle for 0.4 wt% DNF in 4O.8. The data were all recorded at 40 K.

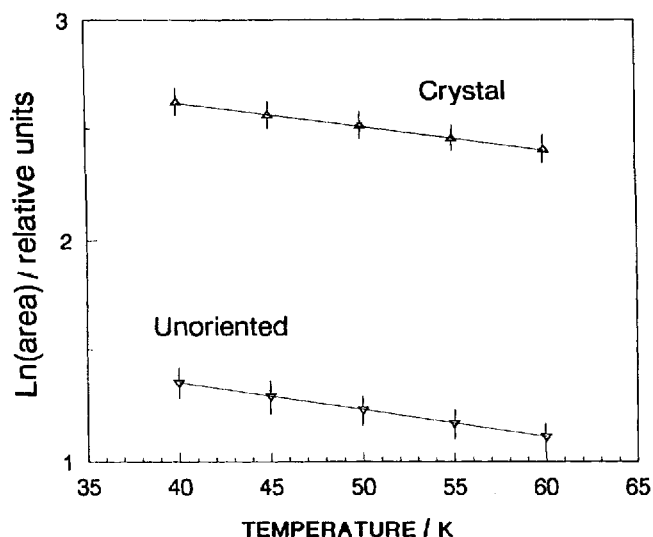


Figure 9. Plot of the $\ln f$ versus T data for the inner doublet of DNF in 4O.8 for the crystal and unoriented phases.

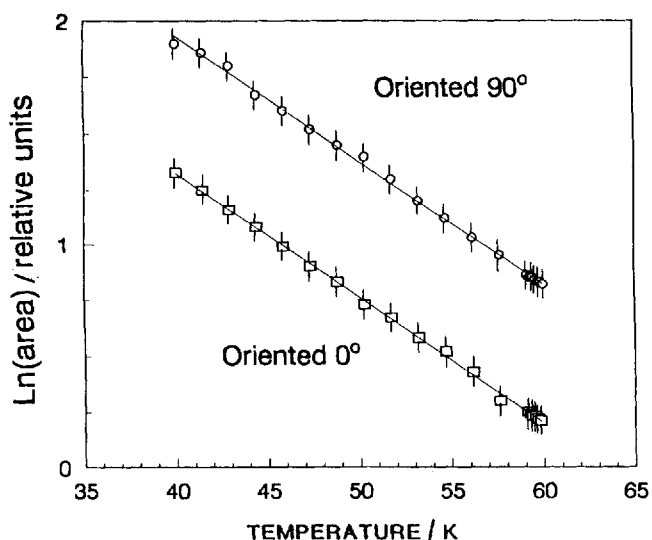


Figure 10. Plot of the $\ln f$ versus T data for the inner doublet of DNF in 4O.8 for the $\theta = 90^\circ$ orientation.

$$\frac{A\pi}{A\sigma}(\theta) = \frac{8 - (3\cos^2\theta - 1)S}{8 + (3\cos^2\theta - 1)S}, \quad (6)$$

where S is the orientational order parameter [13]. The solid lines in figures 7 and 8 are the best fit of equation (6) to the data. The resulting order parameters for FMA and DNF in 4O.8 are $S = 0.28$ and 0.31 ± 0.06 , respectively, at 40 K. The low order parameters are attributed to the fact that the FMA and DNF resides in the disordered tail regions of the liquid crystalline molecules. Neither line broadening nor quadrupole relaxation was observed for FMA or DNF in the cold smectic B of 4O.8. Thus rotational and transla-

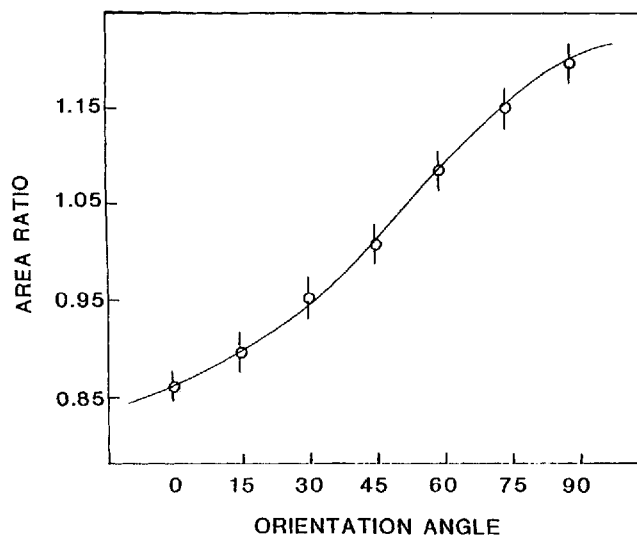


Figure 11. Plot of the area ratio versus orientation angle for 0.4 wt% DNF in 4O.8 inner doublet. The data were all recorded at 40 K.

tional diffusion were not observable for the time-scale of Fe-57 spectroscopy.

3.2.1. Results and discussion for the inner doublet of DNF in 4O.8

The data for the internal doublet are shown in figures 9 and 10. The $\ln f$ versus T plot gives a $\theta_{LC} = 46.8$ for the crystal and $\theta_{LC} = 41.1$ for the glassy phase independent of orientation. Here the θ_{LC} s for the crystal and glassy phases are very close to each other. This suggests that the DNF has a chemical interaction with the liquid crystal. Since the tail region of DNF is somewhat polar and 4O.8 has a polar tail region, then these polar regions could lend themselves to the formation of charge transfer complexes. Further evidence for the formation of a complex is that the area ratio was angle dependent giving an order parameter of $S = 0.41$, figure 11.

4. Conclusions

The ME data for FMA and DNF in the cold smectic solutions of 4O.8 provide a detailed picture of the smectic glass-supercooled smectic liquid crystal which is not available from calorimetric means. The $\ln f$ versus T data deviated from Debye-like behaviour via a $(T - T_g)^2$ dependence which is accounted for by relaxations which can be associated with a glass transition temperature. Further the DNF-4O.8 system has an inner doublet which is the result of a complexing between the DNF polar tails and the polar tail of 4O.8. The order parameter is larger for the inner doublet than the other indicating that the molecules involved in this complexing are more ordered than the rest.

Both system glasses have lower Mössbauer-Debye

temperatures than their respective crystalline phases showing that the glassy phases are less rigid. The anisotropic Mössbauer–Debye temperature shows that the $\theta = 0^\circ$ orientation is more rigid. Also, the low order parameters shows that the individual FMA and DNF molecules remain disordered and do not orient along the preferred direction of alignment.

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