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A Mössbauer Temperature Study of 1,1′-diacetylferrocene in the Liquid Crystal, N-(P-hexyloxybenzylidene) - P- toluidine

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The Fe-57 Mössbauer Effect was used to study a solution (0.2% by Weight) of 1,1′-diacetylferrocene (DAF) in the liquid crystalline material *p-n*-hexyloxy-benzylidene-*p*-toluidine (HBT). The DAF contained enriched Fe-57. The Mössbauer Effect parameters were determined for the temperature range 100–300 K in the crystalline solid phase and 100–200 K in the cold smectic *B* phase of HBT. Here "cold" means the smectic glass and the supercoded 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 ($T < 190$) portion of the cold smectic lnf *vs* T data also exhibited Debye behavior, and the smectic glass gave a Mössbauer-Debye temperature (θ_{lc}) about 30 K lower than the crystalline phase. The smectic glass-super cooled smectic transition was determined to be $T_g = 190$ K from the deviation of the Inf *vs* T data from linear behavior. Above T_g, the deviation from linear Debye behavior followed a $(T-T_g)^2$ dependence. The smectic *B* glass yielded an order parameter of $S = 0.06$ for DAF molecules at 100 K. Rotational and transitional diffusion were not observed for the cold smectic *B* phase.

Keywords: Mössbauer Effect; liquid crystal; diacetylferrocene

1. INTRODUCTION

Mössbauer studies were performed on a 0.2% (by weight) solution of 1,1′-diacetylferrocene (DAF) in N-(P-hexyloxybenzylidene) -P- toluidine (HBT).

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The DAF contained enriched Fe-57. The measurements spanned the temperature range of 100–300 K for the crystalline solid phase of HBT and 100–190 K for the cold liquid crystal. The cold liquid crystal in this case refers to the crystal B_1 liquid crystalline glass. The lowest temperature cold liquid crystalline phase of HBT is the crystal smectic *B* phase. The molecules are in a layered structure in which the molecules are perpendicular to the smectic layers and have hexagonal packing. The HBT liquid crystalline material has the following transitions [1, 2]:

$$\begin{array}{ccccc} \textit{Solid I} & \overset{327\,\text{K}}{\longrightarrow} & \textit{Nematic} & \overset{346.7\,\text{K}}{\longleftrightarrow} & \textit{Isotropic} \\ \uparrow & & \updownarrow & & \\ \textit{Solid II} & \overset{323.1\,\text{K}}{\longleftrightarrow} & \textit{Smectic B} & & \end{array}$$

The Mössbauer Effect 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 reference [3]. Starting from ^{57}Fe enriched elemental iron 1, 1′-diacetylferrocene was prepared following the procedure in reference [4]. The DAF in HBT was enriched with Fe-57. A complete discussion of the sample preparation and the aligned glass is given in reference [5] under the experimental section. The Mössbauer Effect spectra were fitted with Lorentzian line shapes using an IBM 3090 computer.

3. RESULTS AND DISCUSSION

Figures 1 and 2 show the plots of logarithm of the recoil-free intensity (f) versus temperature (T). The three experimental situations presented are as follows: The crystalline solid, and the cold liquid crystal oriented at 0° and 90°. The crystal data are shown in Figure 1 and show a linear temperature dependence for the entire temperature range (100–300 K) and is in accord with the expectations of the Debye model of a solid [6]. In the high temperature limit, the result of the Debye model is:

$$\text{Inf} = \frac{-3E_\gamma^2 T}{Mc^2 k_b \theta_t^2}, \quad T \geq \left(\frac{\theta_t}{2}\right) \tag{1}$$

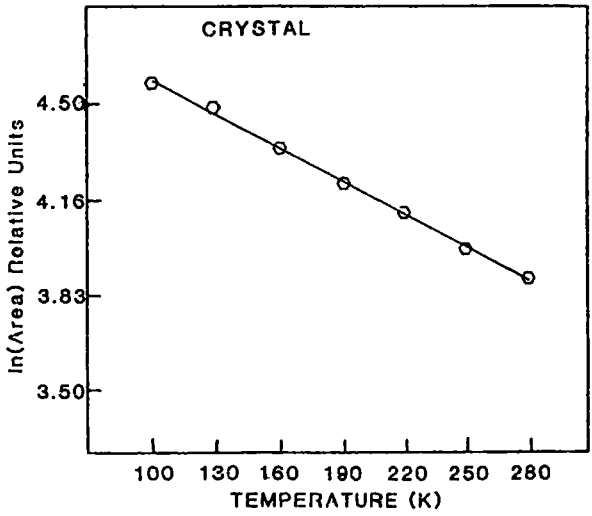

FIGURE 1 In (area) versus temperature for the crystal phase of 0.2% DAF in HBT.

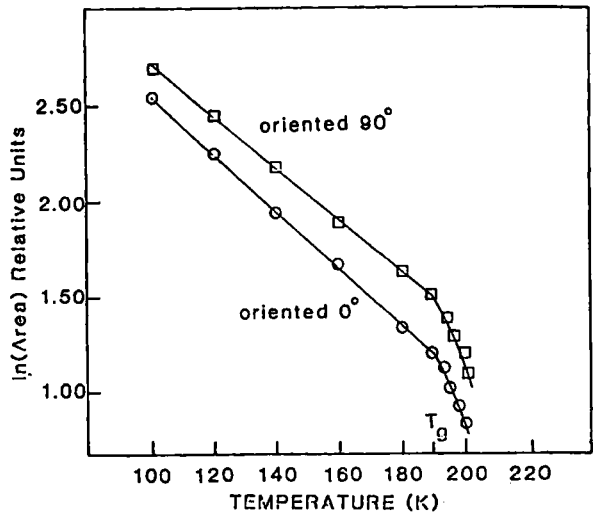

FIGURE 2 In (area) versus temperature for the 0° and 90° orientations of the glass phase of 0.2% DAF in HBT.

where $E_\gamma = 14.4\,\text{keV}$ the energy of the gamma ray, T is the temperature at which the data is collected, M is the mass of the vibrating unit (for DAF $MC^2 = 2.515\times10^8\,\text{keV}$), K_b is Boltzmann's constant and θ_l is the Mössbauer-Debye temperature. To determine the Mössbauer-Debye

temperature for the host (θ_{lc}) (either the liquid crystalline solid or the smectic B glass) the following must be used [5]:

$$\theta_{lc} = \left(\frac{M_{\text{probe}}}{M_{lc}}\right)^{1/2} \theta_l \tag{2}$$

where M_{probe}/M_{lc} is the ratio of the DAF mass to the mass of the HBT host molecule. Figure 2 Shows the Inf versus T data for the cold smectic B glass phase. Again there is linear behavior as described by Eq. (1) for the temperature range of 100–190 K. For $T > 190$ K there is a deviation from linear behavior attributed to additional relaxation experienced by DAF molecules as the system enters the supercooled liquid state.

Table I lists the Debye temperatures observed from the plot of lnf versus T data. The θ_{lc} for each glass orientation is less than the θ_{lc} obtained from the crystalline phase. The expectation that the glass phase is less rigid than the crystal is, therefore, 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 [7]. The 0° orientation has the γ ray along the planar normal for HBT and the 90° orientation corresponds to the γ ray being directed within the layers. This anisotropy accounts for the anisotropic Debye temperature. The glass transition temperature is taken to be the temperature where the lnf *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. T_g was determined by fitting the lnf *vs* T data to the following equation:

$$\text{Inf} = aT + b(T - T_g)^2 + c \tag{3}$$

where a, b and c are constants that were determined from the linear portion of the curve. Ruby, Zabransky and Flinn first proposed the $(T-T_g)^2$

TABLE I Comparison of θ_{lc} for DAF in HBT

Phase	*Debye Temperature*	
	θ_l	θ_{lc}
Crystal	69.7	71.4
Orientation 90° Glass	41	43.1
Orientation 0° Glass	38.8	39.8

dependence for isotropic glasses [10, 11]. 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. To obtain the glass phase, the DAF-liquid-crystal system was cooled at a rate of ~20 K/min. At this rate crystallization was avoided and any ordering of the DAF molecules by HBT molecules was preserved.

The π and σ transition probabilities depend on the orientation angle θ and if there is any orientational alignment, one will see an asymmetric absorption. The area ratio in this case is independent of temperature and exhibits an angular dependence as shown in Figure 3. The theoretical expression for the angular dependence of $(A\pi/A\sigma)$ for DAF and a small intramolecular contribution is:

$$\frac{A\pi}{A\sigma}(\theta) = \frac{8 - (3\cos^2\theta - 1)S}{8 + (3\cos^2\theta - 1)S} \tag{4}$$

where S is the orientational order parameter [4]. The solid line in Figure 3 is the best fit of Eq. 3 to the data. The resulting order parameter for DAF in HBT is $S = 0.06$ at 100 K. This order parameter is similar to other measurements using DAF as a solute molecule [3, 6, 7, 8, 9]. The order parameter that we have measured is independent of temperature. V. G. Bhide, M. C. Kandpal and Subkas Chandra [2] have reported an order

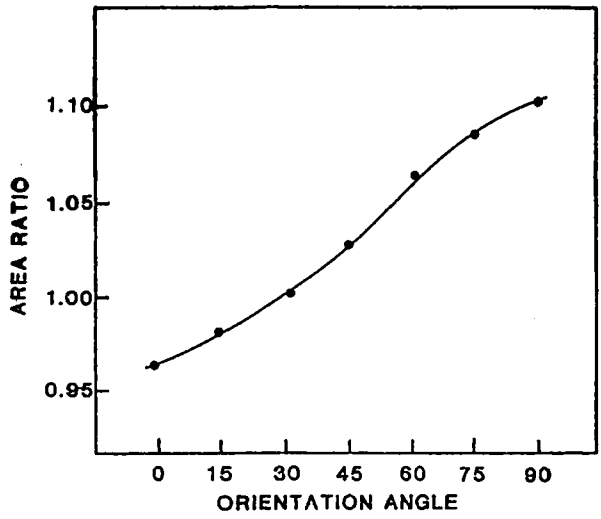

FIGURE 3 Plot of the area ratio versus Orientation angle for 0.2% DAF in HBT. The data were all recorded at 100 K.

parameter for the glassy phase that is temperature dependent for 8% by weight DAF in HBT. This could happen if the 8% sample was not a true solution but rather a suspension.

CONCLUSIONS

The Mössbauer Effect data of DAF in the cold smectic solution HBT provides a detailed picture of the smectic *B* glass. The glassy phase has a lower Mössbauer Debye temperature than the crystalline phase showing that the glassy phase is less rigid. We have found the order parameter *S* to be temperature independent and its small value indicates that the DAF molecules remain disordered and reside in the tail region of the liquid crystalline material. Further, the anistropic Mössbauer-Debye temperature shows that the 90° orientation is more rigid than the 0° orientation.

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