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Mössbauer spectroscopy of ferrocene in a crystal G liquid crystal

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The Fe-57 Mössbauer Effect (ME) was used to study a 0.6 per cent (by weight) solution of 1,1'-diacetylferrocene in the liquid crystalline material N-(*p*-*n*-pentyloxybenzylidene)-*p*-*n*-hexylaniline (50.6). The ME parameters were determined for the crystalline solid phase and the cold crystal G phase. Characteristic Debye temperatures, order parameters, intramolecular and lattice contributions to the nuclear vibrational anisotropy were obtained for the crystalline solid, crystal G glass, and oriented crystal G glass phases.

1. Introduction

Mössbauer Effect (ME) measurements were obtained from a 0.6 per cent (by weight) solution of 1,1'diacetylferrocene (DAF) in N-(p-n-pentyloxybenzylidene)-p-n-hexylaniline (50.6). For the crystalline solid phase of 50.6, measurements were made in the temperature range of 100-300 K, and 100-150 K for the cold liquid crystal. The cold liquid crystal in this case refers to the crystal G liquid crystalline glass. Only the lowest temperature liquid crystalline phase will supercool and form a glass [1, 2]. In this case the lowest temperature cold liquid crystalline phase of 50.6 is the crystal G phase. The molecules are in a layered structure in which the molecules have a hexagonal lateral ordering within the layers, and possess long-range three-dimensional positional order. The 50.6 liquid crystalline material has the following transitions [3]:

Solid
$$\xleftarrow{306K} CrG \xleftarrow{3116K} S_B \xleftarrow{3228K} S_C \xleftarrow{3243K} S_A$$

 $\xleftarrow{3327K} N \xleftarrow{3439K} I$

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 reference [4]. The sample was prepared by dissolving into solution 0.6 per cent (by weight) DAF in 50.6. A complete discussion of the sample preparation and the aligned

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glass is given in reference [5] under the experimental section. The ME spectra were fitted with Lorentzian line shapes using an IBM 3090 computer.

3. Results and discussion

Figures 1 and 2 show the plots of the logarithm of the recoil-free intensity (f) versus temperature (T). 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 in figure 1 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

$$\ln(f) = \frac{-3E_{\lambda}^{2}T}{M_{c}^{2}K_{B}\theta_{L}^{2}}T \ge \left(\frac{\theta_{L}}{2}\right)$$
(1)

where $E_{\gamma} = 14.4 \text{ keV}$ the energy of the gamma ray, T is the temperature of the sample, M is the mass of the vibrating unit (for DAF $M_C^2 = 2.515 \times 10^8 \text{ keV}$), K_B is Boltzmann's constant and θ_L is the Mössbauer–Debye temperature for the host (θ_{LC}) (either the liquid crystalline solid or the crystal G glass) the following must be used [6]:

$$\theta_{\rm LC} = \left(\frac{M_{\rm probe}}{M_{\rm LC}}\right)^{1/2} (\theta_{\rm L}) \tag{2}$$

where $M_{\text{probe}}/M_{\text{LC}}$ is the ratio of the DAF mass to the mass of the 50.6 host molecule.

Figure 2 shows the ln(f) versus T data for the cold crystal G glass phase. Again there is a linear behaviour

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Figure 2. $\ln(\text{area}) = f$ versus temperature for the unoriented, 0° and 90° orientations of the glass phase of 0.6% DAF in 50.6.

Figure 1. $\ln(\text{area}) = f$ versus tem-

perature for the crystal phase of 0.6% DAF in 50.6.

as described by equation (1) for the temperature range of 100-150 K. This means that the glass transition for 50.6 is greater than 150 K. At the glass transition temperature there would be a deviation from the linear behaviour and would be attributed to additional relaxation experienced by the DAF molecules as the system enters the supercooled liquid state.

The θ_{LC} for the crystal phase is $\theta_{LC} = 64.8 \pm 3$ K, for the unoriented glass $\theta_{LC} = 58.7 \pm 3$ K, the oriented 0° glass $\theta_{LC} = 58.7 \pm 3$ K and the oriented 90° glass $\theta_{LC} =$ 47.9 ± 3 K. The Debye temperatures for the glass are lower than for the crystal, thus the expectation that the glass is less rigid is confirmed. The aligned crystal G phase has the molecules lining up parallel with the magnetic field and the smectic planes being tilted. For the 0° orientation, the γ -ray direction is parallel to the long molecular axis of the 5O·6 molecules and the 90° orientation has the λ -ray direction perpendicular to the long molecules. The Debye temperatures for the 0° orientation are greater than those for 90°, which implies that DAF can vibrate more easily in a direction that is perpendicular to the molecular long axis of 5O·6. Also, the Debye temperatures for the unoriented and 0° oriented phases are the same, indicating that the mylar surfaces of the sample holder have the same effect as a 0° aligning magnetic field.

In figure 3 the intermolecular contribution to the nuclear vibrational ellipsoid is plotted versus temperature and in figure 4 the area ratio versus orientation angle is plotted. From these graphs and following the





Figure 4. Plot of the area ratio versus orientation angle for 0.6% DAF in 50.6. The data were all recorded at 100 K.

analysis in reference [7] the order parameter S was determined to be S = 0.205 at a temperature of 100 K. This order parameter is small indicating that the DAF does experience some small orientation with the principal electric field gradient axis oriented perpendicular to the molecules long axis of 50.6. It is believed that the DAF resides in the disordered tail regions of the liquid crystalline molecules.

4. Conclusions

The ME data of DAF in the cold smectic solution of 50.6 provides a detailed picture of the smectic glass. The glassy phase has a lower Mössbauer–Debye temperature than the crystalline phase showing that the glassy phase is less rigid. The anisotropic Mössbauer-Debye temperature shows that the $\theta = 0^{\circ}$ orientation is more rigid than $\theta = 90^{\circ}$. Further, the low order parameter indicates that the DAF molecules remain disordered and reside in the tail regions of the liquid crystalline material.

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