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Liquid Crystals

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Mössbauer spectroscopy of ferrocene in a crystal G liquid crystal

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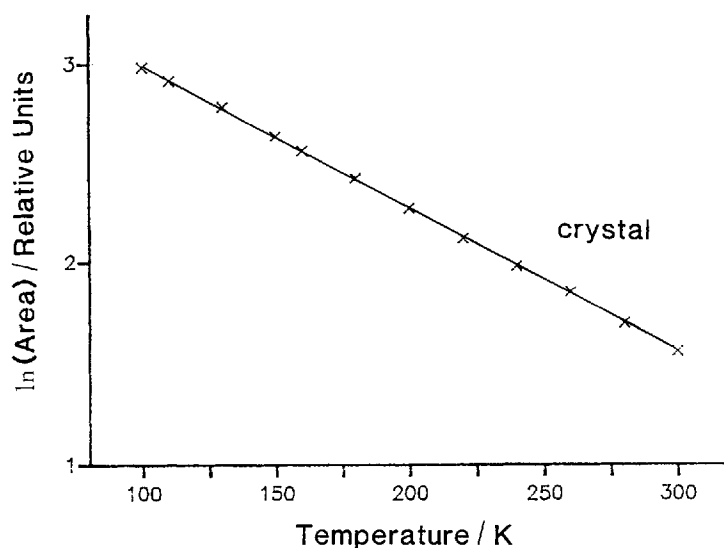


Figure 1. $\ln(\text{area})=f$ versus temperature for the crystal phase of 0.6% DAF in 5O.6.

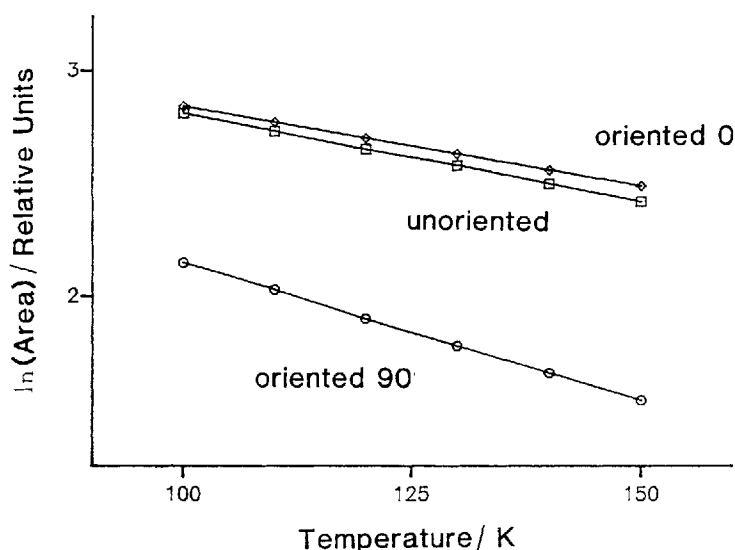


Figure 2. $\ln(\text{area})=f$ versus temperature for the unoriented, 0° and 90° orientations of the glass phase of 0.6% DAF in 5O.6.

as described by equation (1) for the temperature range of 100–150 K. This means that the glass transition for 5O.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 $\theta_{LC}=47.9 \pm 3$ 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

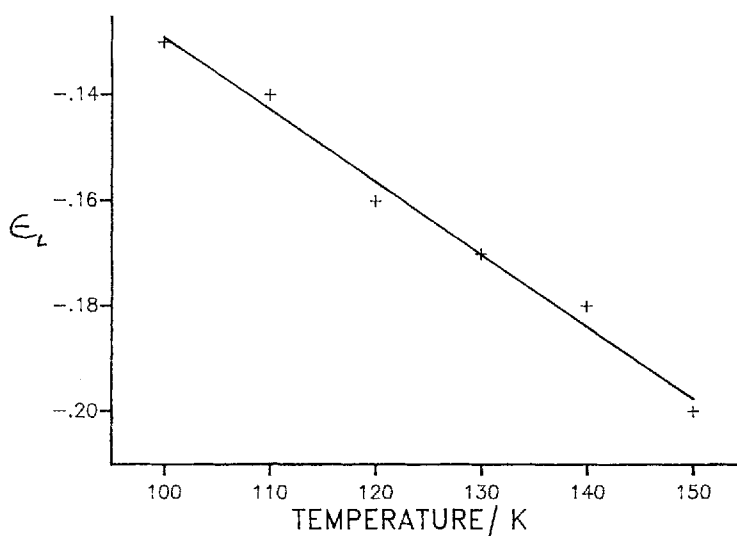


Figure 3. The intermolecular contribution to the vibrational anisotropy versus temperature for 0.6% DAF in the crystal G glass of 5O.6.

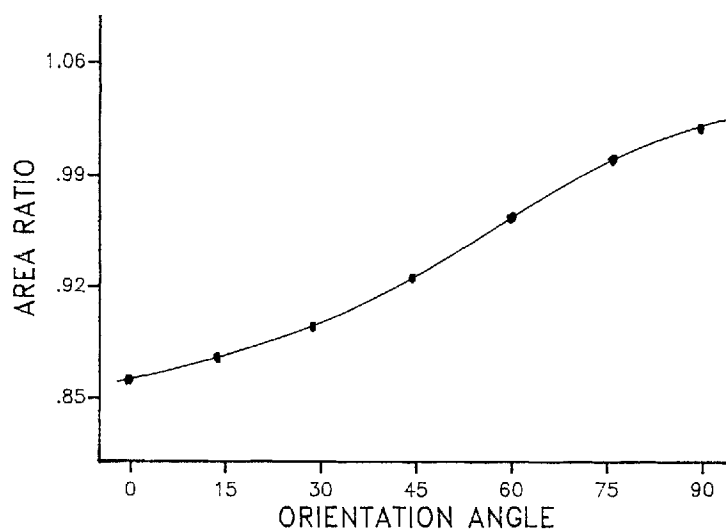


Figure 4. Plot of the area ratio versus orientation angle for 0.6% DAF in 5O.6. The data were all recorded at 100 K.

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 5O.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 5O.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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