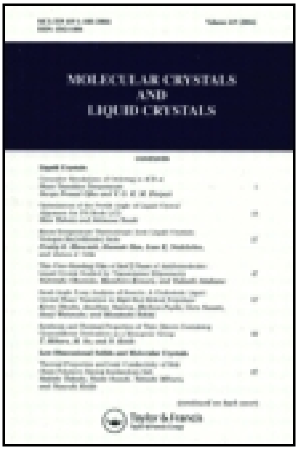

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A Mössbauer Temperature Study of Ferrocenyl-4′-Methoxyaniline and Ferrocenyl-4′-*n*-Butylaniline in a Cold Smectic B Liquid Crystal

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The Fe-57 Mössbauer effect (ME) was used to study two solutions 0.4% (by weight) of ferrocenyl-4′-methoxyaniline (FMA) in the liquid crystalline material 4-*n*-butoxybenzylidene-4′-*n*′-octylaniline (40.8) and 0.4% (by weight) of ferrocenyl-4′-*n*-butylaniline (FBA) in 40.8. The ME parameters were determined for the temperature range 110–170 K in the crystalline solid phase and 110–150 K in the cold smectic B phase of 40.8 for both samples. The ln recoil-free intensity (*f*) *vs* *T* data exhibited linear Debye behavior for the solid phase over the entire temperature range for both systems. The cold smectic ln *f* *vs* *T* data also exhibited Debye behavior, and the smectic glass gave a Mössbauer-Debye temperature (θ_{LC}) about 23 K lower than the crystalline phase for the FMA-40.8 system and about 30 K for the FBA-40.8 system. The smectic B glass yielded an order parameter of $S = 0.28$ for the FMA molecules at 110 K and $S = 0.24$ for FBA molecules at 110 K. The intermolecular contribution to the vibrational ellipsoid (ϵ_L) declined linearly with increasing temperature for both systems.

1. INTRODUCTION

The Fe-57 Mössbauer effect (ME) was used to study two different solutions 0.4% (by weight) of ferrocenyl-4′-methoxyaniline (FMA) in 4-*n*-butoxybenzylidene-4′-*n*′-octylaniline (BBOA or 40.8) and 0.4% (by weight) of ferrocenyl-4′-*n*-butylaniline (FBA) in 40.8. The measurements spanned the temperature range of 110–170 K for both the

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FMA and FBA in the crystalline solid phase of 40.8 and 110–150 K for FMA and FBA 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 temperature liquid crystalline phase of a given liquid crystalline material will supercool and form a glass.[1,2]

For 40.8 the lowest temperature cold liquid crystalline phase is a smectic B.[3] The smectic B phase of 40.8 is called the crystal B where the interactions between the smectic layers are strong and this kind of B phase has three-dimensional order.[4,5] This structure is a crystal with the aliphatic chains at the ends of the molecules in a molten state, whereas in a regular solid phase the chains are strongly aligned. The 40.8 liquid crystalline material has the following transitions:

$$\text{crystal} \xleftrightarrow{303\text{K}} \text{smectic B} \xleftrightarrow{316\text{K}} \text{smectic A}$$

$$\xleftrightarrow{336\text{K}} \text{nematic} \xleftrightarrow{352\text{K}} \text{liquid}$$

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 references 6 and 7.

The two ME samples were prepared by dissolving 0.4% (by weight) FMA and FBA independently into the liquid crystalline material (40.8). For a complete discussion of the sample preparation and the aligned glass, consult the experimental section of reference 7.

The collection of data for these two samples (FMA and FBA in 40.8) was particularly difficult. The reason for the difficulty was the poor signal to noise ratio for temperatures greater than 150 K. A solution to this problem would be to enrich the solute molecules with Fe-57. However, samples of FMA and FBA enriched with Fe-57 were not available for these experiments.

The ME spectra were fit with Lorentzian line-shapes using a Burroughs 6800 computer. The area ratio (A_π/A_σ), f, the quadrupole splitting (ΔE_Q), the linewidth (Γ), and the chemical shift (δ) were all obtained from the computer fits to the data.

3. RESULTS AND DISCUSSION

3.1.1. Mössbauer-Debye Temperature (θ_L) The plots of ln f *vs* T data for 40.8 are presented in Figures 1 to 4 (Figures 1 and 2 for FMA in 40.8 and Figures 3 and 4 for FBA in 40.8). 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 (110–170 K) for both samples, and it is in accord with the expectations of the Debye model of a solid.[8]

The expression for f is:

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

In the high temperature limit, the result of the Debye model is[6,7,9]:

$$\ln \mathrm{f} = \frac{-3\, E_r^2 T}{Mc^2 k_B \theta_L^2} \quad T \geq \left(\frac{\theta_L}{2}\right), \tag{2}$$

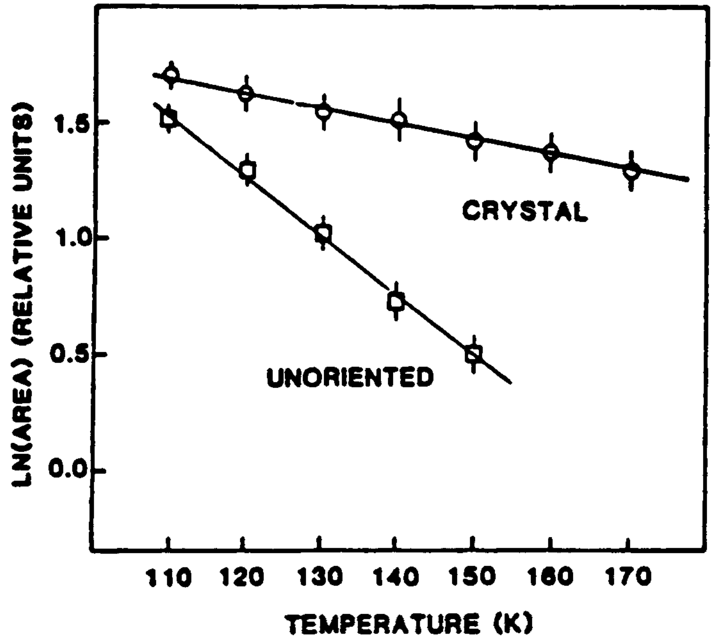

FIGURE 1 In (area) versus temperature for the crystal and unoriented glass phases of 0.4% FMA in 40.8. The solid line is a fit of Equation (2) to the data.

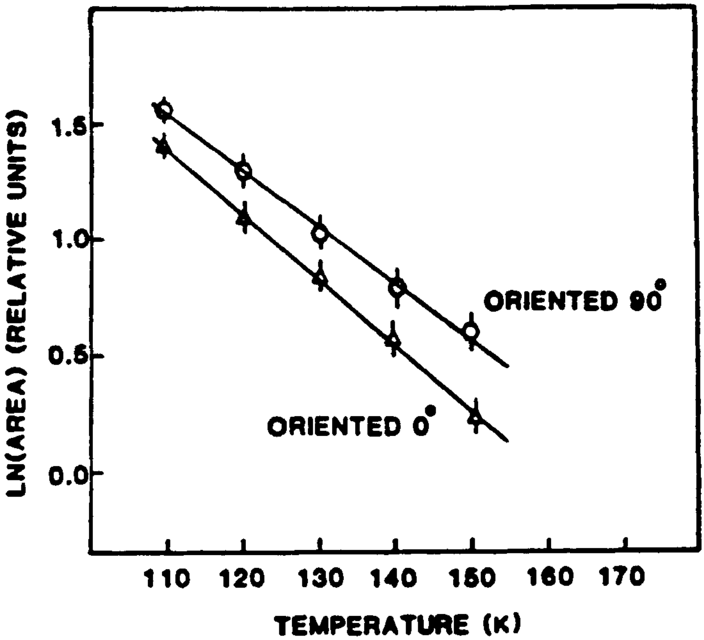

FIGURE 2 In (area) versus temperature for the 0° and 90° orientations of the glass phase of 0.4% FMA in 40.8. The solid line is a fit of Equation (2) to the data.

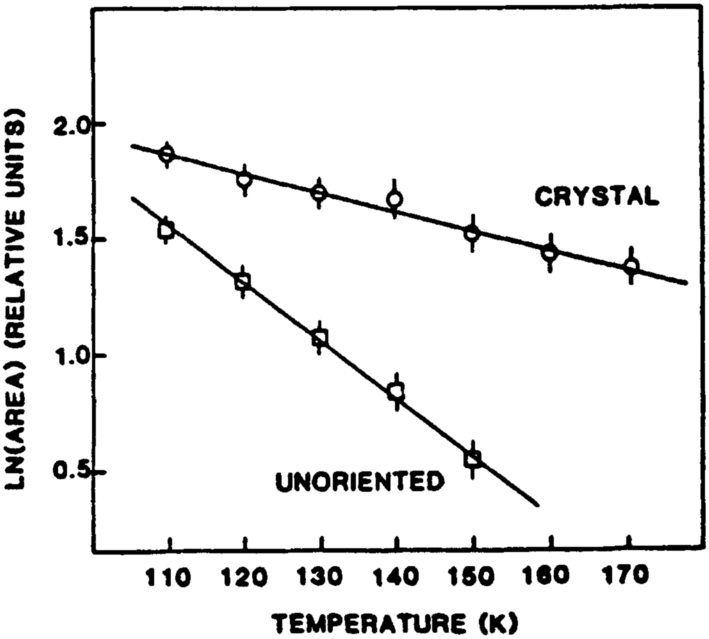

FIGURE 3 In (area) versus temperature for the crystal and unoriented glass phases of 0.4% FBA in 40.8. The solid line is a fit of Equation (2) to the data.

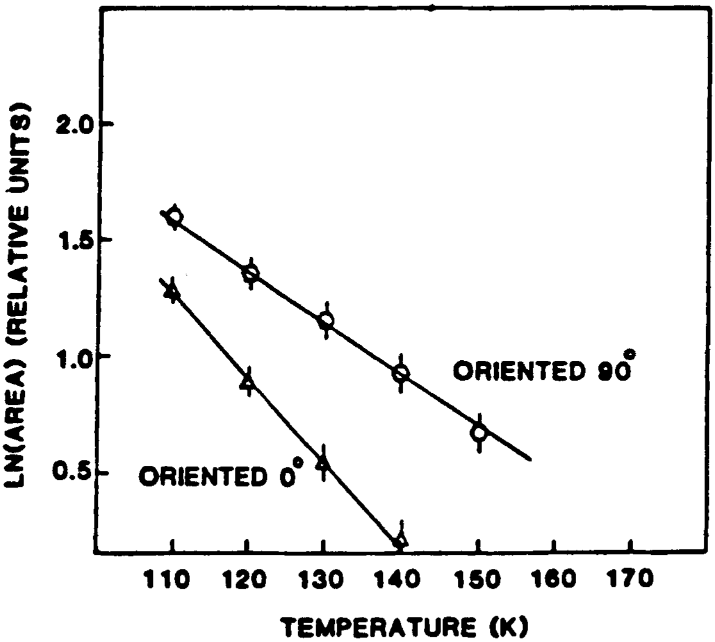

FIGURE 4 In (area) versus temperature for the 0° and 90° orientations of the glass phase of 0.4% FBA in 40.8. The solid line is a fit of Equation (2) to the data.

here M is the mass of the vibrating unit (thus for FMA $Mc^2 = 2.99 \times 10^8$ kev and for FBA $Mc^2 = 3.24 \times 10^8$ kev) 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 B glass) the following expression must be used[8]:

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

here M_{probe}/M_{LC} is the ratio of mass of the probe molecule to the mass of the host molecule.

The cold smectic B data for either sample (FBA or FMA) show a linear temperature dependence for the temperature range (110–150 K). Therefore, no glass transition temperature (T_g) was measured for the above systems. The glass transition temperature (T_g) is the temperature at which deviation from linear behavior begins. Previous Mössbauer studies of 1,1′-diacetylferrocene (DAF) in 40.8 determined the glass transition temperature range was 175–185 K.[3]

Table I lists the Debye temperatures observed from the plots 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.

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 40.8 and the 90° orientation corresponds to the gamma ray being directed within the layers. This anisotropy accounts for the anisotropic Debye temperatures.

Of interest is the comparison of the θ_{LC}'s for FMA, FBA in 40.8 to previous experiments of DAF in 40.8, which were performed by W. J. LaPrice.[3] Table I compares θ_{LC} values for (FMA and FBA) in 40.8 to corrected[6] values of θ_{LC} for DAF in 40.8. It is interesting to note that the θ_{LC}'s for DAF in 40.8 are considerably greater than θ_{LC}'s for FMA or FBA in 40.8 indicating a larger force constant between the DAF and 40.8 than between FMA or FBA and 40.8.

A possible explanation for the different Debye temperatures for FMA, FBA, and DAF in 40.8 is as follows. The recoil-free fraction has the dependence as given by equation (2). However, V. I. Goldanskii and E. F. Makarov[8] have shown that

$$f \propto \mathrm{EXP}\left\{\frac{-1}{M^{1/2}\epsilon}\right\} \tag{4}$$

where M is the mass of the entire vibrating unit and ϵ is the constant of the elastic bond between the liquid crystal molecules and the probe molecules (DAF, FMA, and FBA). It is easy to see that an increase in either the mass M or the elastic constant ϵ leads to an increase in

TABLE I

Comparison of θ_{LC} values for FBA, FMA, and DAF in 40.8

Cold Liquid Crystalline Glass	θ_{LC}, K Orientation			
	0°	90°	Unoriented	Crystal
Corrected Values of 0.2% DAF in 40.8	40	48	51	75
0.4% FMA in 40.8	28.8	33.9	30.5	54.0
0.4% FBA in 40.8	27.2	34.7	32.0	62.5

f. The masses of FMA and FBA are 118.6 and 128.6%, respectively, greater than that of DAF, therefore, based on mass alone, one would expect f to be larger for the FMA, FBA system. However, Table II shows that the normalized recoil-free fraction (i.e., the total integrated area per Fe-57 atom) for both the FMA and FBA systems is smaller than for the DAF system. This result indicates that ϵ for FMA and FBA in the 40.8 glass must be smaller than for the DAF system. It is known that the DAF resides in the tail region of 40.8[3,9] and thus it is reasonable to expect that both FMA and FBA will reside in the tail region also. The larger FMA and FBA molecules may cause a greater distortion of the neighboring liquid crystal molecules than the DAF or even be expelled further into the tail region of the liquid crystal. Either case would result in a smaller elastic bond constant, and a lower value for f because the probe molecule would be in a less rigid environment.

3.1.2. Vibrational Anisotropy (ϵ_L) From Figures 1 thru 4 it can be seen that 40.8 does exhibit a very small 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[10]

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

$\epsilon_L = k^2 (\langle x_\parallel^2 \rangle - \langle x_\perp^2 \rangle)$ is the intermolecular contribution to the nuclear vibrational ellipsoid, where $\parallel$ and $\perp$ mean parallel and perpendicular to the planar normal of the smectic B planes. The intramolecular contribution to the nuclear vibrational anisotropy, ϵ_m, is similarly defined. For FMA and FBA $\epsilon_m = 0.20$[10], respectively. Figures 5 and

TABLE II

Comparison of the normalized recoil-free fraction for FMA, FBA, and DAF in 40.8 at 100 K

System	Percent Effect/Fe-57 Atom		
	Orientation		
	0°	90°	Unoriented
0.2% DAF in 40.8	8.1×10^{-19}	1.1×10^{-18}	1.0×10^{-18}
0.4% FMA in 40.8	7.2×10^{-19}	9.1×10^{-19}	9.6×10^{-19}
0.4% FBA in 40.8	6.4×10^{-19}	9.3×10^{-19}	9.8×10^{-19}

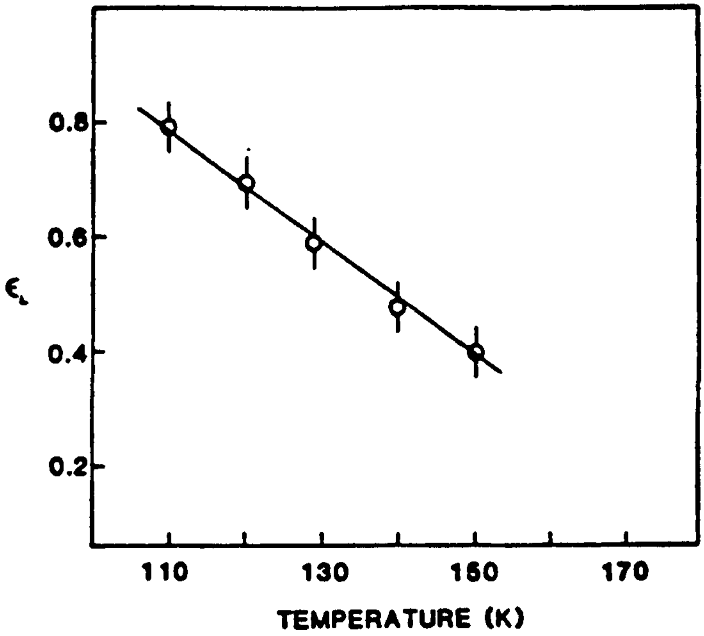

FIGURE 5 The intermolecular contribution to the vibrational anisotropy versus temperature for 0.4% FMA in the smectic B glass of 40.8.

6 show the temperature dependence of ϵ_L for FMA and FBA in 40.8, and from Equations (2) and (5) it is easily shown that Figures 5 and 6 exhibit 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 FMA and FBA-liquid crystal systems were cooled at a rate of 17 K/min. At this cooling rate crystallization was avoided and any ordering of the FMA or FBA molecules by the 40.8 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 FBA in 40.8 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_π/A_σ for FMA and FBA for small ϵ_m is as follows:

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

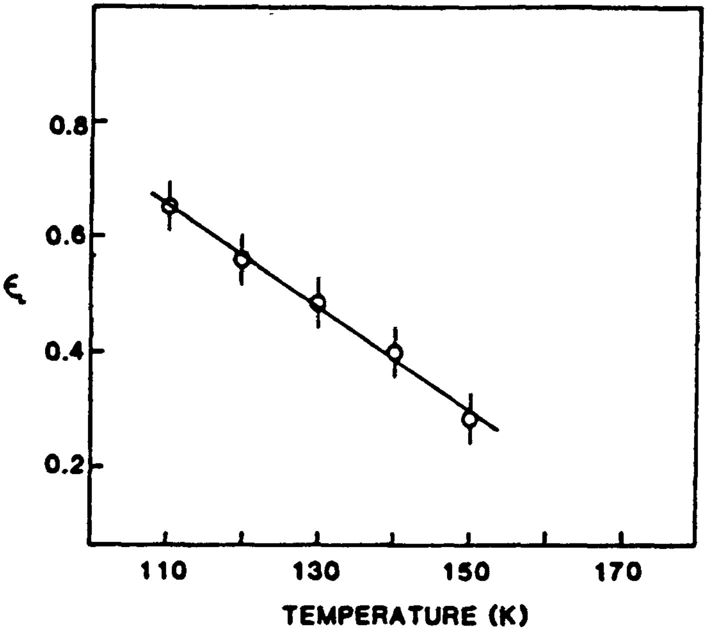

FIGURE 6 The intermolecular contribution to the vibrational anisotropy versus temperature for 0.4% FBA in the smectic B glass of 40.8.

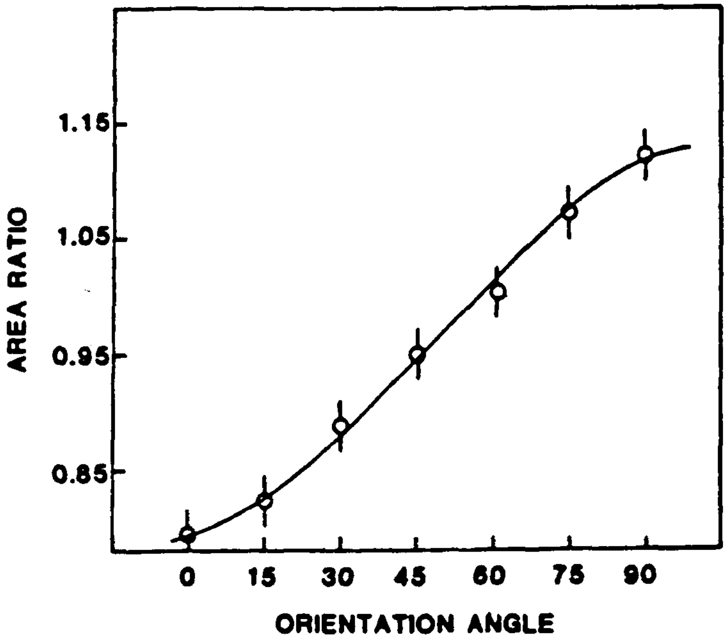

FIGURE 7 Plot of the area ratio versus orientation angle for 0.4% FMA in 40.8. The data were all recorded at 110 K.

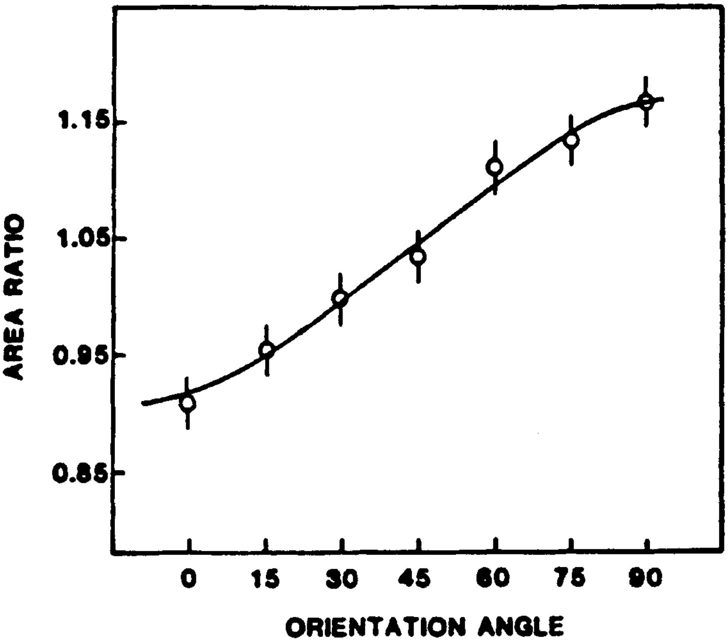

FIGURE 8 Plot of the area ratio versus orientation angle for 0.4% FBA in 40.8. The data were all recorded at 110 K.

where S is the orientational order parameter.[10] The solid lines in Figures 7 and 8 are the best fit of equation (7) to the data. The resulting order parameters for FMA and FBA in 40.8 are $S = 0.28$ and 0.24 ± 0.06, respectively, at 110 K. These order parameters are larger than the ones measured in experiments using DAF as the solute molecule.[3,6,7] This may be due to the fact that FMA and FBA have longer tails than DAF, therefore, the liquid crystal molecules may find it easier to orient them than the DAF.

4. CONCLUSIONS

The Mössbauer peaks show some anisotropy for both the FMA and FBA samples. This anisotropy is an indication that 40.8 had a small orientational effect on the FMA and FBA probe molecules. The FMA and FBA are more massive and have longer tails than the DAF. It was determined that the longer tails were responsible for the smaller elastic bond constants in the FMA-40.8 and FBA-40.8 systems compared to the DAF-40.8 system. No glass transition temperature (T_g)

was measured because the intensity of the spectral lines were very low for temperatures greater than 150 K. However, previous Mössbauer studies of DAF in 40.8[3] determined that the glass transition temperature range is 175–187 K.

Finally, the smectic B glass of 40.8 has a lower Mössbauer-Debye temperature than the crystalline phase (for both FMA and FBA) showing that the glassy phase is less rigid. Further, the smectic B glass exhibits a small anisotropic Mössbauer-Debye temperature showing that the $\theta = 90°$ orientation is the most rigid for both systems.

References

1. M. Sorai, T. Nakamura and S. Seki, *Proceedings of the International Conference on Liquid Crystals*, (Bangalore, India, 1973).
2. S. E. B. Petrie, H. K. Bucher, B. J. Klingbiel and P. J. Rose, *Eastman Org. Chem. Bull.*, **45** (1973).
3. W. J. LaPrice and D. L. Uhrich, *J. Chem. Phys.*, **71**, 1498 (1979).
4. R. Pindak, D. E. Moncton, S. C. Davey and J. W. Goodby, *Phys. Rev. Lett.*, **46**, 1135 (1981).
5. S. Chandrasekhar, *Liquid Crystals*, (Cambridge University Press, Cambridge).
6. D. L. Uhrich and R. P. Marande, *Mol. Cryst. Liq. Cryst.*, Vol. III, pp. 171–187, 1984.
7. R. P. Marande and D. L. Uhrich, "A Mössbauer Temp. Study of 1,1′-Diacetylferrocene in a Cold Smectic A Liquid Crystal," *Mol. Cryst. Liq. Cryst.*, Vol. 133, pp. 97–109 (1986).
8. V. I. Goldanskii and E. F. Makarov, *Chemical Applications of Mössbauer Spectroscopy*, edited by V. I. Goldanskii and R. H. Herber (Academic Press, New York, 1966).
9. W. J. LaPrice and D. L. Uhrich, *J. Chem. Phys.*, **72**, 678 (1980).
10. V. O. Aimiuwu and D. L. Uhrich, *Mol. Cryst. Liq. Cryst.*, **43**, 295 (1977).