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RAMAN SCATTERING STUDY OF FLUIDLIKE MOLECULAR DYNAMICS IN A SMECTIC-B LIQUID CRYSTAL

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ABSTRACT - A Raman scattering study has been made in N-(p-butoxybenzylidene)-p-n-octylaniline. Sharp changes in the intensity ratios near frequency shifts of 1200 and 1600 cm^{-1} occur at the solid to smectic-B transition, with no further changes upon heating to the isotropic liquid. The results suggest the smectic-B phase already exhibits completely fluidlike dynamics of the central molecular core.

The nature of the highly ordered smectic-B liquid crystal has been a subject of considerable speculation (1-4). Additional interest has been generated recently by its possible relevance to the theory of two-dimensional melting (5). Most experimental studies have been focussed on the solidlike features of the smectic-B phase and its distinction from the higher temperature liquid crystal and liquid phases (6,7). In order to provide adequate information to construct a realistic model for the smectic-B phase, it is also important to elucidate all its fluidlike molecular properties, namely, those properties which undergo a major change at the solid to smectic-B (SB) transition and which remain essentially unchanged upon further heating to the isotropic liquid. The only studies in this direction have been spin label (8) and volumetric (9) experiments which show a melting of the aliphatic chains at the SB transition. We report here the results of a Raman scattering study near the SB transition which has revealed additional fluidlike molecular properties of the smectic-B phase.

Raman scattering has been shown to be a useful probe of liquid crystal phase transitions (10). Most work has been done on nematics and relatively little on the smectic phases (11-14). Difficulty sometimes arises in the interpretation of low frequency intermolecular modes. Raman experiments on the highly ordered smectic phases have been performed almost exclusively on terephthal-bis-butylaniline (TBBA), with emphasis on the low temperature phases and on the low frequency spectra (15-18). The complicated phase diagram of TBBA, while interesting, introduces additional experimental complexity. Furthermore, its high transition temperature makes it extremely susceptible to sample degradation, thus affecting the consistency of the results. We have chosen to study the intramolecular modes of known assignment in N-(p-butoxybenzylidene)-p-n-octylaniline (40.8), a simpler compound which has a direct SB transition at 36°C.

Our supply of 40.8 was obtained from CPAC, Inc. Raman spectra were taken with a Spex 14018 double monochromator at 3 cm^{-1} resolution. The light source was an argon ion laser operating with a power of 20 mW at a wavelength of 514.5 nm. Samples were contained in sealed capillary tubes. The sample temperature was controlled thermoelectrically to a stability of 0.1°C. Consistent spectra were obtained even after repeated thermal cycling, showing no evidence of sample degradation. All spectra reported here were taken with increasing temperature starting with the solid phase. Upon cooling, the smectic-B phase supercools. The solid obtained at low temperatures gave spectra identical to those of the original solid. We will concentrate our discussion on changes in the relative peak intensity of several prominent adjacent bands. This simple approach is adequate since our main objective is to examine whether the spectral features in the smectic-B phase are solidlike or fluidlike.

The relative intensities of the adjacent bands at 1173 and 1200 cm^{-1} undergo a drastic change at the SB transition. The ratio of the 1173 cm^{-1} peak intensity to the 1200 cm^{-1} peak intensity drops from almost 4 to 2. The detailed temperature dependence of this ratio is shown in Figure 1. It can be seen that the major change occurs at the SB transition and the ratio remains essentially the same through the higher temperature phases all the way to the isotropic liquid. The smectic-B phase thus has the completely fluidlike molecular conformation characterized by these vibrational bands.

Similarly, the peak intensities of the adjacent bands at 1574, 1600 and 1627 cm^{-1} show interesting relative changes. In the solid, the first two bands have almost identical peak intensity. Upon entering the smectic-B phase, the 1574 cm^{-1} intensity decreases by a factor of 2

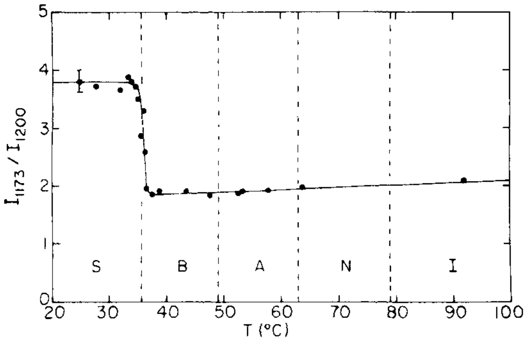

FIGURE 1. Ratio of peak intensity of the 1173 cm^{-1} to the 1200 cm^{-1} band in the solid (S), smectic-B (B), smectic-A (A), nematic (N) and isotropic (I) phases of 40.8.

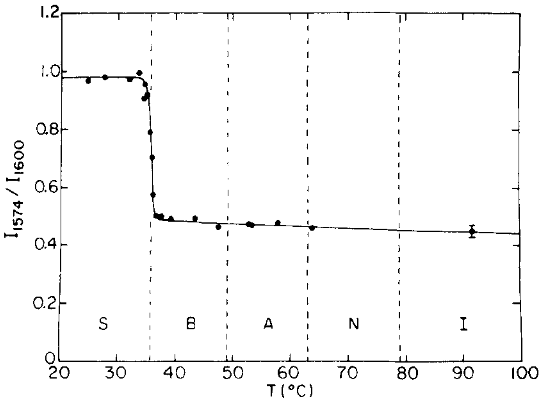

FIGURE 2. Ratio of peak intensity of the 1574 cm^{-1} to the 1600 cm^{-1} band from the solid to the isotropic liquid in 40.8.

relative to the 1600 cm^{-1} intensity. Figure 2 shows the temperature dependence of the peak intensity ratio of these two bands. Again the major change takes place at the SB transition, and the smectic-B phase exhibits the spectral feature that characterizes the isotropic liquid.

Comparisons of the spectra from related compounds have suggested that the bands at 1173, 1200, 1574 and 1600 cm^{-1} are associated with vibrations in the central core of Schiff's base liquid crystals (19,20). This identification has been further substantiated in TBBA by studying spectral changes in molecules deuterated in the center (18). The dramatic changes we have observed in both the 1200 cm^{-1} and 1600 cm^{-1} regions imply major changes in the molecular dynamics connected with the central linkage at the SB transition. One possible motion involved is a rotation of the aromatic rings with respect to each other. Such a conformation has been suggested to exist in the smectic-H phase of TBBA on the basis of deuterium magnetic resonance (7,21,22) and Raman (18) data. There may also be a change in the vibrational relaxation processes, as evidenced by a recent Raman line shape study in 4-cyano-4'-octyoxybiphenyl (23). The onset of molecular rotations about the long axis is a third possibility. While it is not clear which is the dominant process in 40.8, our observation of sharp spectral changes at the SB transition in both the 1200 cm^{-1} and 1600 cm^{-1} regions with no further changes taking place all the way to the isotropic liquid provides evidence that the molecular dynamics of the central core in the smectic-B phase are already completely fluidlike.

It has been suggested that, in analogy to the hexatic phase appearing in the theory of dislocation-mediated melting in two dimensions (5), the bulk smectic-B phase has long-range bond orientational order but exponentially-decaying positional correlations (3). The long-range positional order found recently in X-ray studies of thick smectic-B films suggests this picture to be incorrect, at least for 40.8 (24). This raises further questions about what the principal characteristics of the smectic-B phase are that distinguish it from the solid. Our Raman scattering study has provided new insight into fluidlike molecular properties of the smectic-B liquid crystal which should be taken into account in any theoretical model.

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REFERENCES

1. P. G. de Gennes, The Physics of Liquid Crystals (Oxford U. P., London, 1974), p. 280-284.
2. B. A. Huberman, D. M. Lubin and S. Doniach, Solid State Commun. 17, 485 (1975).
3. R. J. Birgeneau and J. D. Litster, J. Phys. Lett. (Paris) 39, L-399 (1978).
4. A. de Vries, Mol. Cryst. Liq. Cryst. Lett. 49, 19 (1978).
5. D. R. Nelson and B. I. Halperin, Phys. Rev. B 19, 2457 (1979).
6. A. M. Levelut, J. Doucet and M. Lambert, J. Phys. (Paris) 35, 773 (1974).
7. A. J. Dianoux and F. Volino, J. Phys. (Paris) 36, C1-27 (1975).
8. F. Poldy, M. Dvolaitsky and C. Taupin, J. Phys. (Paris) 36, C1-27 (1975).
9. D. Guillon and A. Skoulios, J. Phys. (Paris) 37, 797 (1976).
10. B. J. Bulkin, in Advances in Liquid Crystals, Vol. 2, edited by G. H. Brown (Academic, New York, 1976), p. 199.
11. N. M. Amer, Y. R. Shen and H. Rosen, Phys. Rev. Lett. 24, 718 (1970).
12. J. M. Schnur, Phys. Rev. Lett. 29, 1141 (1972).
13. A. Sakamoto, K. Yoshino, U. Kubo and Y. Inuishi, Japan. J. Appl. Phys. 13, 1691 (1974).
14. C. Destrade and H. Gasparoux, J. Phys. Lett. (Paris) 36, L-105 (1975).
15. J. M. Schnur and M. Fontana, J. Phys. Lett. (Paris) 35, L-53 (1974).
16. D. Dvorjetski, V. Volterra and E. Wiener-Avnear, Phys. Rev. A 12, 681 (1975).
17. M. P. Fontana and S. Bini, Phys. Rev. A 14, 1555 (1976).
18. J. M. Schnur and J. P. Sheridan, in Liquid Crystals and Ordered Fluids, Vol. 3, edited by J. F. Johnson and R. S. Porter (Plenum, New York, 1978), p. 1.
19. G. Vergoten, Advan. Raman Spectrosc. 1, 219 (1972).
20. S. Jen, N. A. Clark, P. S. Pershan and E. B. Priestley, J. Chem. Phys. 66, 4635 (1977).
21. Z. Luz, R. C. Hewitt and S. Meiboom, J. Chem. Phys. 61, 1758 (1974).

22. B. Deloche, J. Charvolin, L. Liebert and L. Strzelecki, J. Phys. (Paris) 36, C1-21 (1975).

23. K. Brezinsky and B. J. Bulkin, in Liquid Crystals and Ordered Fluids, Vol. 3, edited by J. F. Johnson and R. S. Porter (Plenum, New York, 1978), p. 355.

24. D. E. Moncton and R. Pindak, Phys. Rev. Lett. 43, 701 (1979).