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Raman study on several smectic phases in terephtal-*bis*-butylaniline (TBBA)

D. Dvorjetski, V. Volterra, and E. Wiener-Avnear
Department of Physics, Ben-Gurion University of the Negev, Beer-Sheva, Israel

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Raman investigation on the lattice modes (8–200 cm^{-1}) of several smectic phases in terephtal-*bis*-butylaniline (TBBA) reveals significant spectral differences. Softening of the lowest lattice 19-cm^{-1} mode, observed very near to the solid–smectic-*B* phase transition, is correlated with the gradual release of the smectic inter-layer glide motion. The Raman spectra add new insight into the ordering within the layers of the metastable smectic phases and also indicate the existence of molecular dynamic rotations in the smectic-*B* phase.

I. INTRODUCTION

Many smectic mesophases have been discovered lately in liquid crystals,[1,2] corresponding to the various possibilities in the build up of layered structures and in the ordering within the smectic planes. Techniques such as x rays[2-4] and NMR[5] have been employed to study these mesophases and partial knowledge on their structures has been gained. Particularly interesting is the information collected on the ordering in the smectic *B* mesophase.[2-6] In this phase, besides the planar structure, there exists a pseudohexagonal arrangement of the molecules in each plane. In several smetic *B* materials the ordering even correlates several layers with a resulting local 3-dimensional structure. For such smectic mesophase the name smectic *H* has been proposed.[4] It is not clear if there is physically a sharp distinction between the smectic *B* with a 3-dimensional order (smectic *H*) and with only 2-dimensional order or if there is a rather continuous variation of the interlayers correlation in the various smectic *B* materials.[6] Recently, various proposals for the classification of these and other high ordered smectic phases have been made,[7-9] which contribute to a better understanding of the ordering possibilities of the layered structures.

Terephtal-bis-butylaniline (TBBA) is a liquid-crystal system with three stable smectic mesophases[2]; the one at lowest temperature being a smectic *B* (or *H*). In addition two more metastable phases have recently been discovered[3,5] on a cooling cycle below the smectic *B* melting point. A partial phase diagram through the temperature cycle, which is relevant to the present work is as follows[3]:

$$\begin{tikzcd}
\begin{pmatrix}\text{VIII}\\ \text{Cr}\end{pmatrix} \arrow[r, "113\,^{\circ}\mathrm{C}"] & \begin{pmatrix}\text{V}\\ S_B\end{pmatrix} \arrow[r, shift left, "144\,^{\circ}\mathrm{C}"] \arrow[d, shift right] & \begin{pmatrix}\text{IV}\\ S_C\end{pmatrix} \arrow[l, shift left] \\
(\text{VII}) \arrow[u, "52\,^{\circ}\mathrm{C}"] \arrow[r, shift right, "68\,^{\circ}\mathrm{C}"'] & (\text{VI}) \arrow[u, shift right, "84\,^{\circ}\mathrm{C}"'] \arrow[l, shift right] &
\end{tikzcd}$$

We present here Raman scattering measurements on the low-frequency lattice vibrations in several phases of TBBA, including the solid VIII, the S_B (smectic *B* — phase V), and also the two metastable phases VI and VII. Incorporating the Raman spectral results of the different phases with the lately reported x-ray structural data,[2,3] a new insight into the ordering of these smectic phases is gained, particularly into the controversial problem about the molecular orientations around their long axis in the smectic *B*. As the one-dimensional melting process from the solid to the S_B phase, at $T_S = 113\,^{\circ}\mathrm{C}$, is found to be associated with a softening of the lowest Raman mode near the phase transition, a possible mechanism for the breakdown of the bondings between the layers is suggested. This low-frequency lattice mode, which appears only in the solid VIII and in the phase VII, allows for further conclusions on the structural differences between the different smectic mesophases in TBBA.

II. EXPERIMENT AND RESULTS

A conventional Raman setup with Spex double monochromator and 30-mW exciting 5145-Å Argon laser source was used in order to study the capsulated TBBA samples, sealed under N_2 gas. The inert atmosphere was essential in order to diminish the sample decomposition at high temperatures. Nevertheless, long-time irradiation of the samples by the laser light, even at low intensities, did reveal some irradiation damage, which tends to smear out the Raman spectra. An ultraviolet filter in front of the sample and careful minimization of the laser power did reduce the laser-induced degradation and no effects were observed for sufficiently short measurements. Recycling the temperature without any laser irradiation on a virgin sample did reveal the same results as obtained with the shortly irradiated samples. Only the depolarized Raman scattering component was monitored, which enabled detection of the active Raman lines down to 8 cm^{-1} from the laser frequency. The purified polycrystalline sample[10] was temperature controlled to ±0.1 °C (in the temperature range 20–130°C) utilizing a copper oven.

The Stokes side of the Raman spectra at room temperature in the frequency range up to 2000 cm^{-1} reveals about fifty strong resolvable lines. The strongest among them have characteristic benzene frequencies, representing the modes of the three benzene rings in TBBA. The higher frequency modes above 200 cm^{-1} reveal only slight changes on the solid-smectic *B* phase transition; the lines usually become smaller and broader, thus less resolvable. The upper frequency range contains mostly internal modes of the constituting chemical groups, which build up the TBBA molecule. These internal modes are probably less sensitive to the changes in the molecular lattice arrangements. However, at the low-frequency range below 200 cm^{-1}, which usually characterizes the lattice modes, significant changes are observed on the phase transitions (Fig. 1). This range consists of four broad Raman features at about 19 cm^{-1}, 100 cm^{-1}, 150 cm^{-1}, and 170 cm^{-1}. Sometimes a richer internal structure could be observed in the broad Raman features of the solid phase, which was attributed mostly to a certain damage in the particular sample.

On increasing the temperature of the solid phase there is no change in the three higher-frequency features of the Stokes spectrum as long as the transition temperature to the smectic *B* phase, $T_S = 113$ °C, is not reached. However, the lowest mode softens at temperatures very near to the melting point (Fig. 2). This line broadens and shifts to lower frequencies drastically at a few tenths of a degree below T_S, while the Rayleigh background increases. The line disappears completely in the smectic *B*. To distinguish between the real shift of the line and the apparent one due to the change in the background, the low-frequency Stokes spectra were computer fitted to a sum of two Lorentzians, namely, a zero-frequency Lorentzian for the Rayleigh contribution and a Lorentzian corrected for the population factor for the Stokes Raman peak. The resulting temperature dependence of the low-mode frequency is plotted in Fig. 3. In Figs. 2 and 3 the quoted temperatures are referred to the apparent transition temperature—T_S, which was determined during the experimental runs when the line first disappears. In fact due to laser heating there is a systematic error in the temperature of the sample and the relative temperatures are more accurately determined than the absolute ones.

In the smectic *B* phase the three higher-frequency Raman peaks are still apparent but they become very broad and are barely seen. They disappear completely only in the smectic *C* phase. On cooling back to the metastable phase VI these features

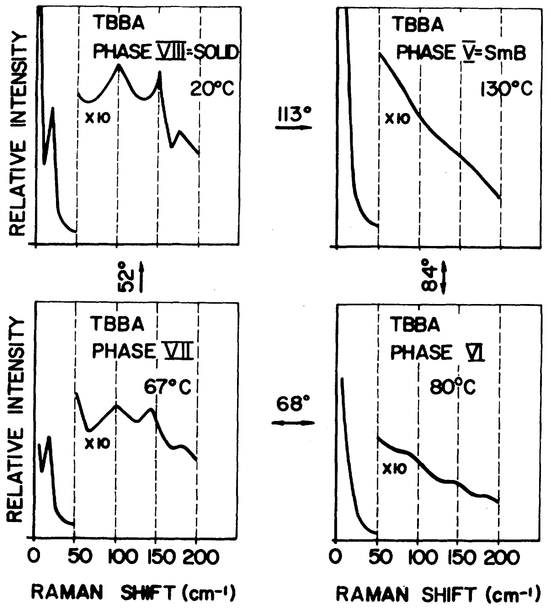

FIG. 1. The low-frequency Raman scattering spectra of the different phases of TBBA.

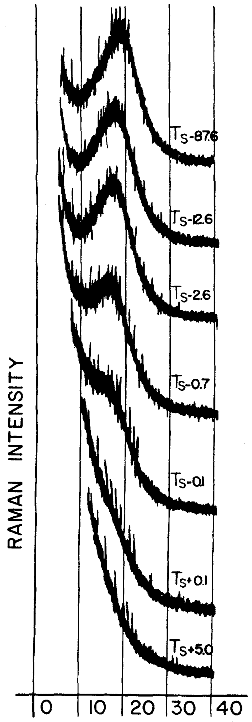

FIG. 2. The softening of the 19-cm^{-1} Raman active mode of TBBA near the solid-smectic *B* phase transition.

reappear distinctly although they are broader and somewhat shifted in comparison with the solid phase (Fig. 1). The lowest 19-cm^{-1} mode reappears only on further cooling to the VII phase, while the other three modes become sharper. Upon returning back to the solid phase at ambient temperature the previous spectrum is recorded revealing only very slight changes, thus assuring that no significant degradation of the sample has occurred through the temperature cycle.

Recently, the Raman spectra of the stable phases of TBBA (solid, smectic B, C, A, mematic and isotropic liquid) have been published by Schnur and Fontana.[11] Their spectra of the solid smectic B and C show a fine structure, which is absent in our results. Also their observation indicates very little difference between the solid and the smectic B Raman spectra of the lattice modes. The lowest 19-cm^{-1} peak, which is still seen there at 112 °C, is classified by the authors to exist also in the smectic B phase. We have no explanation for the discrepancy of the results.

III. DISCUSSION

The TBBA molecule, consisting of three benzene rings connected by conjugated double bonds, is supposed to have a planar main framework, ending on both sides with fatty C_4H_9 tails. Therefore, the molecule's orientation is determined by the direction of the longest axis and the planar orientation around it. The x-rays measurements indicate that all four phases considered here have monoclinic symmetries.[3] The c crystallographic axis is parallel to the molecular axis (or rather to its average direction) and is tilted to the ab plane. The later plane also coincides with the smectic plane. All the four phases have a distorted pseudohexagonal arrangement in the plane perpendicular to the molecular axis, whereas phase V presents a regular hexagonal arrangement (within the experimental error). The solid TBBA VIII and the metastable VII phases contain two layers per unit cell. The c-axis length of the unit cell is about two molecules (54 Å), whereas in the higher-temperature phases (smectic S_B and the metastable VI) the c-axis length is equal approximately to only one molecular length (~29 Å).

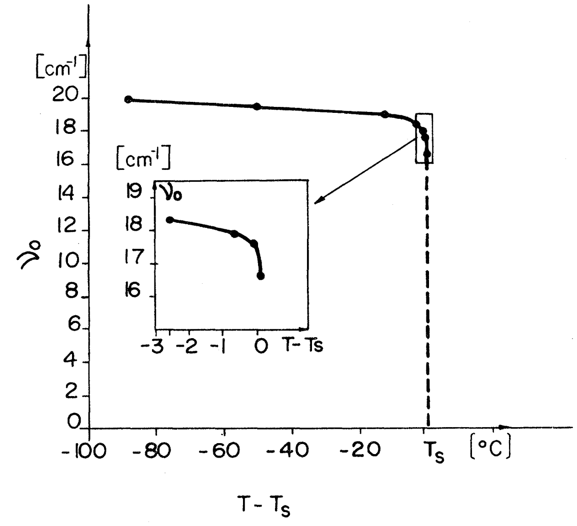

FIG. 3. The temperature dependence of the soft Raman mode of TBBA as obtained from a computer deconvolution of the low-frequency spectra.

The Raman low-frequency mode (19 cm^{-1}) appears only in the phases VIII and VII but disappears completely in the higher-temperature single-layer phases. Its disappearance is therefore connected with the loss of the degree of freedom in the shorter unit cells. As this mode softens near the S_B melting, it is suggestive to attribute this lowest Raman frequency to a mode in which molecules of two successive layers take part. The layer melting through the smectic B phase transition is probably due to the softening of this mode, thus resulting in a relaxation of the coupling between the planes and finally allowing more or less a free glide of the smectic layers, one on top of the other.

The solid phase VIII is A centered and every two successive layers are displaced by half of the b axis. The c axis in this phase is shorter by about 3 Å than twice the molecular length,[2,3] suggesting an interpenetration of successive layers. Moreover, the symmetry of its complex structure is consistent with an alternative displacement of the molecular planes (parallel to the bc planes) along the c axis. In contrast, in the higher-temperature phases (V and VI), the molecules in successive layers lie end to end and all the molecules in the smectic layer have the same c coordinate. Therefore, no systematic interpenetration of the layers do exist; although faint diffuse features in the x-ray data from phase V have been interpreted as due to movements of strings of molecules along the c axis.[3] This random displacement is supposed to help in maintaining the local three-dimensional order in this phase. The softening of the low-frequency Raman mode (Figs. 2, 3) seems therefore to be connected with the smectic melting mechanism, which loosens the bonds between the layers and finally causes the removal of the interpenetration of the molecules of successive layers. Similar low-frequency mode softening during the smectic melting process of DEAB and DEAC has been observed by Amer and Shen.[12] In the latter case too, the softening of the low-frequency mode was attributed to the loosening of the layer bonding through an increase of the distance between the layers.

In all the four phases of TBBA considered here there is a regular molecular positioning in each layer. However, in the smectic *B* phase (S_B) only small remnants of the higher three Raman modes can be barely discovered at 100, 150, and 170 cm^{-1}. These modes become very broad and lose most of their Raman intensity, compared to their spectral distinction observed on cooling down to the next smectic phase (VI). It is therefore interesting to discuss the structural differences between the smectic phases V and VI, which will lead to the understanding of the observed spectral differences. Both phases are characterized by two molecules per unit cell. Whereas phase V is *C* centered, implying an equivalence of the two molecules, the same two molecules in phase VI are related only by an *A* glide plane. Accordingly, in order to account for the x-ray data it has been assumed[3] that in the metastable TBBA VI the molecules have fixed orientations around their axes with an "herring bone" orientational arrangement within the molecular planes.[4]

There are two possibilities to explain the equivalence of the two molecules in the S_B phase. One is a rather free rotation of the TBBA molecules, which results in an over-all equivalence of the molecular sites.[2,3] The second model assumes that all the molecules are parallel; the parallel arrangement was first suggested by Meyer and McMillan in their theory on the *H* phase,[13] however, the proposed orientation (30 °C to a hexagonal axis) does not seem to be consistent with the x-ray data.[14] Recently de Vries[14] has put forward strong arguments against the free rotation of the molecules and suggested a modification of the Meyer and McMillan theory. His idea that the molecules are all parallel along the *a* axis is more consistent with the x-ray data.

The broadening of the Raman features in phase V supports in our opinion the rotation hypothesis. These three high-frequency features can be assigned as modes of relative motion of molecules belonging to the same layer, as these features are not effected by the phase transition to some other planar phases (VII, VI). On the other hand, the similarity of the spectral features in the solid phase and the smectic VI of the herring bone arrangement, does show that these optical modes are not much affected by the different internal arrangements of the molecules within the layer. Thus, in order to explain the drastic smear of these modes, one has to assume a fast relaxation process to exist in the smectic *B* phase. It is therefore tempting to assume either a free or perhaps hindered rotation to be responsible for such relaxation effect, which is also consistent with the x-ray data.[6] High static distortion of the lattice due to less coherence in the smectic quasicrystal might also explain the observed smearing of the Raman features. However, for this case the sharpening of the modes observed in the smectic VI is unanswered.

IV. CONCLUSIONS

The over-all picture of the TBBA temperature loop is therefore as follows: the melting to phase S_B occurs through a loosening of the bonding between layers with corresponding disappearance of a systematic interpenetration of the layers. This process is accompanied by a one-dimensional premelting effect shown by the softening of the 19-cm^{-1} mode near the transition. The release of the hindered glide motion of the layers probably releases also a rotational motion of the molecules around their axis. The motion freezes on cooling to phase VI, but not to the same structures characterizing the solid phase. On further cooling to phase VII, the bonding between the layers is restored with doubling of the *c* axis and reappearance of the 19-cm^{-1} mode. This phase differs from the normal solid mainly in the arrangement of the molecules in each layer: It has two molecules in each layer per unit cell like in the smectic phases V and VI, while the solid contains four molecules. The Raman spectrum suggests that this hybrid smectic-solid phase, can be considered as a highly distorted solid, in which the short-range interaction inbetween the layers is strong enough to sustain the lattice mode, which are assigned to correlate molecules in different layers. The two-dimensional properties are probably due to the fact that the ordering is not a long-range one, allowing perhaps from time to time a glide of groups of layers, thus accounting for the lack of high-index reflections in the x-ray Debye Scherer patterns as observed by Douchet *et al.*[3] The length of the unit cells as predicted from the x-ray measurements, is somewhat longer than in the solid VIII, probably suggesting less interpenetration. Nevertheless, it is strongly suggested that there exist bonded groups of layers in this phase, which have almost the same characteristics as the solid phase.

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