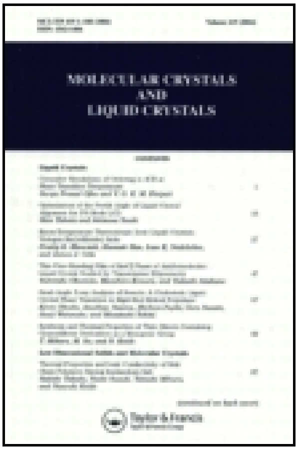

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Structure and Dynamics of the Solid States of MBBA

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Structure and Dynamics of the Solid States of MBBA

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When referring to a fast-cooled (or glassy) liquid crystal (GLC), we mean that if a mesophase of a liquid crystal is cooled sufficiently rapidly to below a certain temperature, an amorphous solid state may be produced that retains a structure similar to that of the starting phase. A selective review of the published results on MBBA is given based on the structural and dynamic concept of the GLC state.

The structure of the different modifications due to neutron diffraction and small angle scattering measurements is described. Raman scattering and inelastic incoherent neutron scattering results are presented, and intermolecular vibration spectra are analysed to show the role of relaxation and non-crystallinity of the structure in the coherence formation of phonons.

Keywords: MBBA, solid phases, structure, spectroscopy, fast-cooling

INTRODUCTION

Besides the research into the liquid crystal (LC) state, increased attention has been focused on the solid state of mesomorphic substances. Two lines of investigations are of importance: 1) the study of crystalline states of mesogenic materials, 2) the study of structures formed by fast cooling from a LC mesophase. The first field of activity is not really different from the usual problems of the physics of molecular crystals. The second direction is more directly linked with liquid crystal research since fast cooling of a LC phase may provide a solid state which virtually conserves the structure of the starting phase.

The quenched or glassy liquid crystal (GLC) state may also be related to the physics of the amorphous solids. In analogy with liquid crystals, which are intermediate—in the sense of the structure and dynamics—between liquids and crystals, fast-cooled liquid crystals may be placed between ordinary amorphous solids and crystals. This is the reason why they can be termed oriented glasses or solid mesophases.

In the last few years a considerable number of materials have been studied with respect to the fast-cooled state. A comprehensive study has been carried out on the typical nematic substance: MBBA. This work has involved structural measurements by X-ray,[1,2] neutron diffraction,[3-5] and small angle scattering of neutrons;[6] experiments on inter- and intramolecular dynamics by means of Raman scattering[7-9] and incoherent inelastic scattering of neutrons;[10,11] as well as phase transition investigations[3,5,9] by calorimetry[12-14] and other methods. In this paper we present a brief survey covering the structural and spectral investigations of MBBA.

STRUCTURAL PROPERTIES OF THE MBBA GLASSY PHASE

Figure 1 shows neutron diffraction patterns[3,4] of the liquid crystal and the fast-cooled state of MBBA (labelled N and C_0, respectively). The wide maxima correspond to intermolecular distances in the plane perpendicular to the "director." Experiments[2] in a wide momentum transfer range, in particular at small Q values ($Q = 4\pi/\lambda \sin\theta$; θ-scattering angle, λ-wavelength), have shown that small blurred peaks can be obtained corresponding to a distance of about one molecular length in the direction along the long axis of the molecules. The similarity of the diffraction curves in Figure 1 as well as the rocking curves measured on magnetic field oriented samples[2,4]—where the magnetic field determines the "nematic director"—indicates the agreement of the translational short range and the orientational long range ordering between these structures. On the other hand the diffraction patterns of the C_0 phase represent an intensity distribution characteristic of amorphous solids since no elements of translational order can be obtained. Thus in the sense of translational disorder the quenched nematic liquid crystal (C_0 phase in MBBA) is equivalent

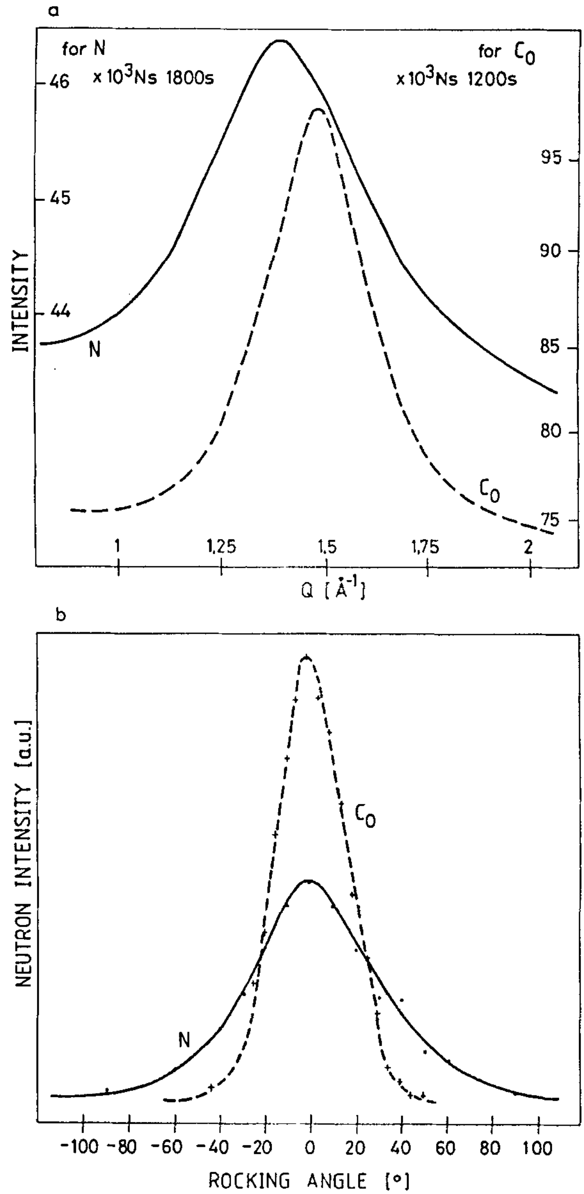

FIGURE 1 Neutron diffraction patterns of the nematic (N) and fast-cooled (C_0) phases of MBBA (curves *a*) and rocking curves for magnetic field aligned sample in the same phases (curves *b*).[5]

to the usual amorphous state with the additional feature of the orientational ordering characterized by the nematic director.

INTERMOLECULAR VIBRATIONS IN FAST-COOLED MBBA AND EBBA

Translational disorder of the GLC state leads to a considerable transformation of the optical vibrational spectra in relation to crystalline phases[4,8,9] (Figure 2). In a crystal, single peaks correspond to transitions of phonon zones at zero momentum transfer according to the selection rules. In the C_0 phase of MBBA there is no coherence of intermolecular vibrations thus all the phonon states take part in forming the optical spectra (without selections). This allows one to determine from the optical data the density of phonon states $g(\nu)$ normalized to the photon-vibration interaction function $C(\nu)$[9]:

$$C(\nu)g(\nu) \sim \nu I(\nu)\,[n(\nu) + 1]^{-1}$$

where $I(\nu)$–experimental spectrum, ν–frequency, $n(\nu)$–number of modes (see Figure 3).

The density of the phonon state has been determined independently by inelastic incoherent scattering of neutrons.[10,11] The neutron spectra are shown in Figure 4. From a comparison of the curves in Figure 2 and 3 one can conclude, a part from the loss of the spatial correlation of vibrations, that in the C_0 phase there is also a redistribution in energy. This means that no singularities are presented in the $\nu < 160$ cm^{-1} range (Figure 4) which would be connected with single phonon zones. Optical (Figure 3) and neutron scattering (Figure 4) data also show that the light-interaction with phonons, resulting in the Raman scattering spectra, increases considerably (~10 times) in the $10 < \nu < 120$ cm^{-1} range.

It is interesting to note that the absence of spatial correlation of phonon states can be obtained not only in an amorphous sample such as the MBBA C_0 phase. Fast cooling of EBBA—a close member of MBBA in the homologous series—results in a structure which can be characterized by Raman scattering and neutron diffraction curves[16] as shown in Figures 5 and 6, respectively. Although both spectra (MBBA and EBBA fast-cooled states in Figure 5) have a broad-band nature, in the EBBA spectrum—in contrast to the MBBA one—some singularities can be observed relating to optical phonon zones. The broadband lines are due to the structure not being completely

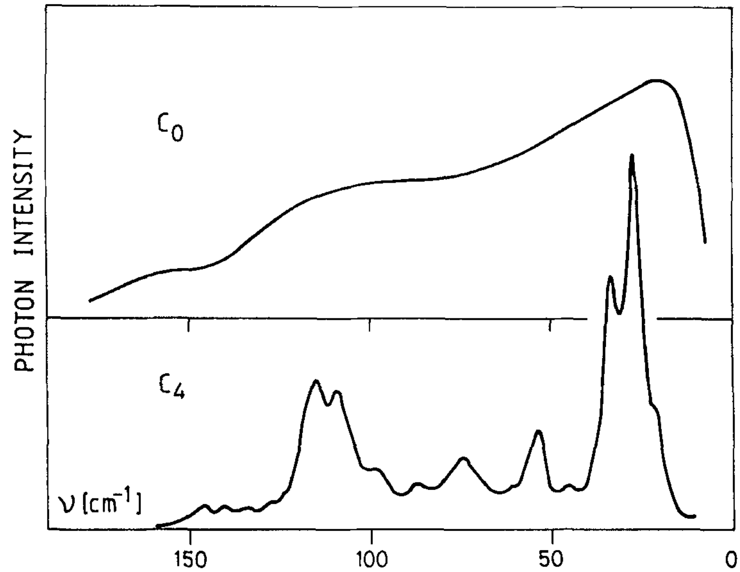

FIGURE 2 Raman scattering spectra of the fast-cooled and the C_4 crystalline phases (T = 80K).[9]

ordered, consequently the k = 0 selection rule conditions are not fulfilled for the optical modes and all phonon states appear in the spectrum. On the other hand, the presence of optical lines in the broadband spectrum is connected with ordered domains characterized by some unit cells, already formed in the C_1 phase of EBBA, and the coherence length of optical phonons is greater than in the case

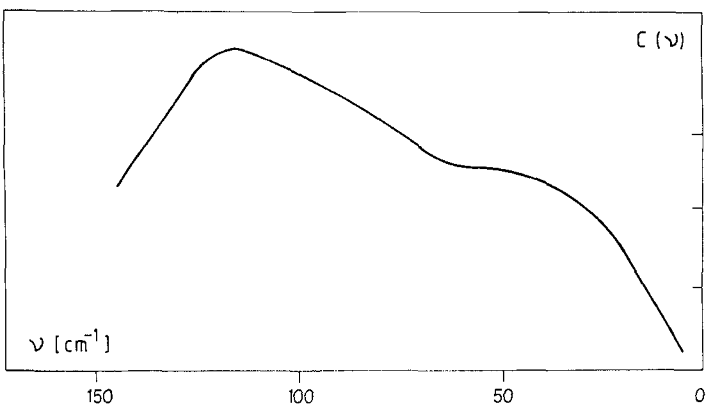

FIGURE 3 The photon-vibration interaction function for the C_0 phase of MBBA.[9]

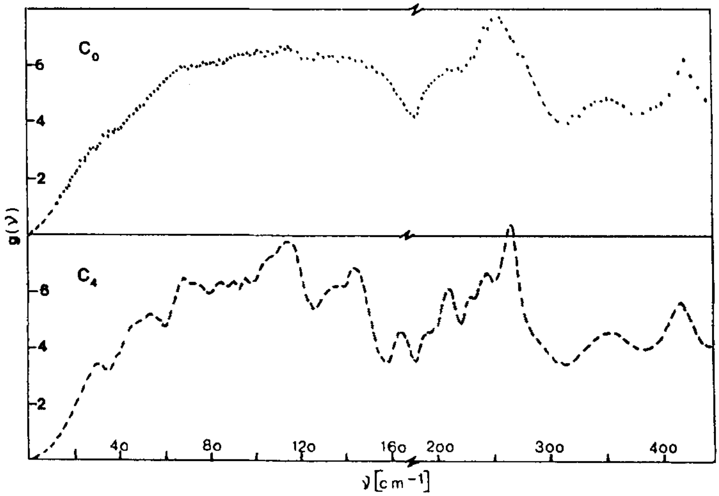

FIGURE 4 Neutron incoherent inelastic scattering spectra of the C_0 and C_4 phases, measured at 5K.[11]

of the usual amorphous materials. Indeed, in this solid phase produced by fast-cooling from the nematic state there is a considerable shift of the characteristic diffraction maximum with respect to the nematic state; moreover the width of this maximum is much smaller (Figure 7). In addition quite a number of small intensity peaks can

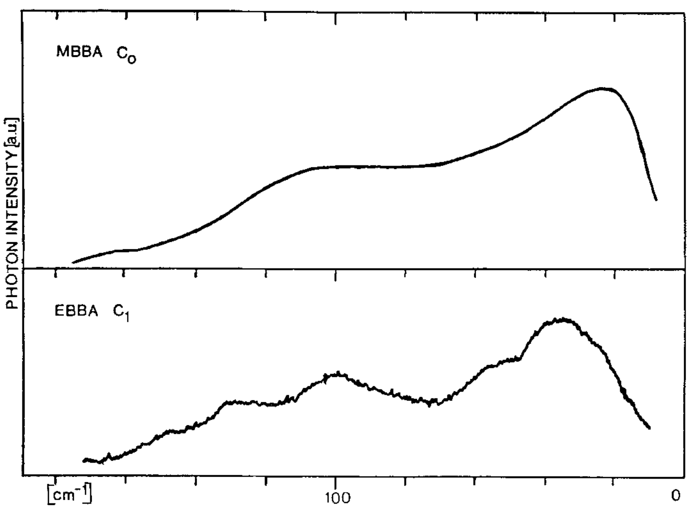

FIGURE 5 Low frequency Raman spectra of the fast-cooled phase of MBBA (C_0) and EBBA (C_1) measured at 80K.[17]

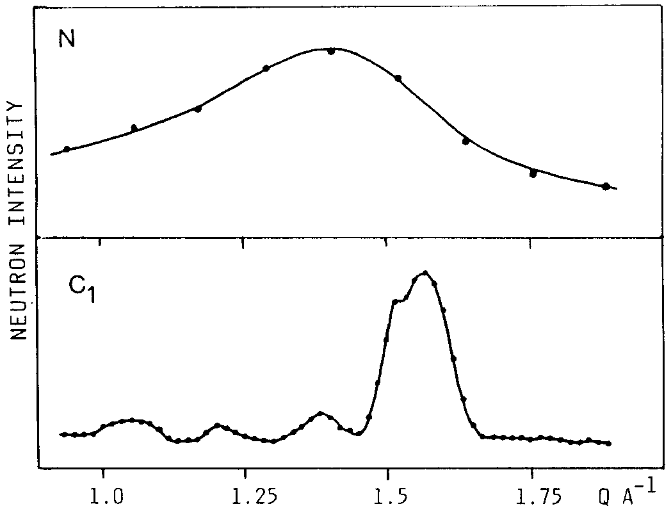

FIGURE 6 Neutron diffraction patterns of the nematic (measured at 320K) as well as the solid (80K) phases of EBBA.[17]

be seen in the given wide momentum transfer range. This indicates that the sample does not have an amorphous structure similar to that which can be produced by quenching the MBBA.

STRUCTURE OF THE SOLID MESOPHASES

The glassy phase C_0 of MBBA is stable up to ~205 K. In the temperature range 205–295 K a sequence of structural phase transitions can be observed on heating and two solid modifications can be produced by slow cooling from the nematic state. The phase diagram and the thermal conditions for producing and conserving phases, termed C_0 through C_6 are given in papers.[14,15]

The glassy state (C_0) is followed in the series of heating transitions first by two modifications (C_1 and C_2) considered as relaxed amorphous states. Their structure was studied by neutron diffraction[5] and small angle scattering of neutrons.[6] The latter experiment allowed us to conclude that C_1 and C_2 are smectic type solid mesophases. The small angle scattering pictures providing evidence of the existence of smectic layers are shown in Figure 7.[6] It was assumed that the C_1 is

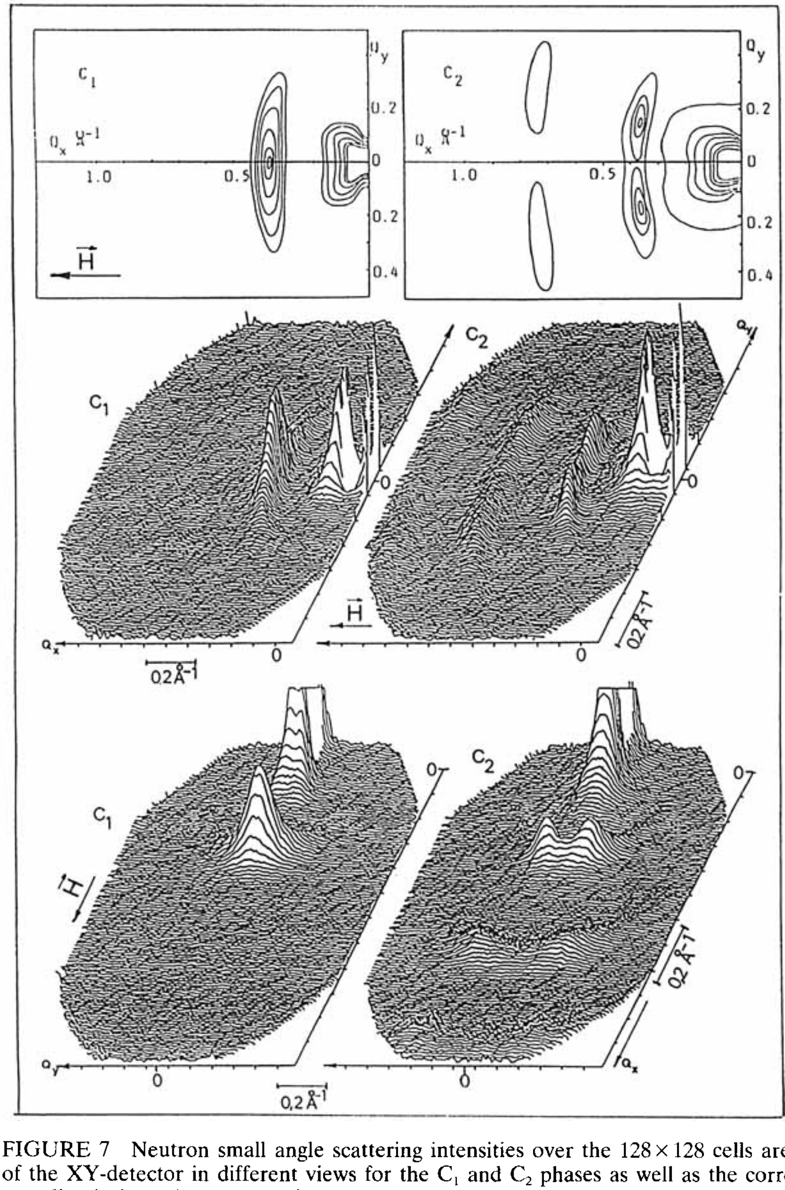

FIGURE 7 Neutron small angle scattering intensities over the 128 × 128 cells area of the XY-detector in different views for the C_1 and C_2 phases as well as the corresponding isointensity contours.[6]

an orthogonal smectic-type phase, and C_2 is a highly ordered tilt smectic-type structure.

CRYSTALLINE STRUCTURES

The structure of C_3 and C_4 (crystalline modifications of the irreversible phase sequence) as well as the C_5 and C_6 phases (produced by slow cooling from the nematic state) was studied by neutron diffraction in the $Q < 3$ Å^{-1} momentum transfer range.[15] On the basis of these experimental results and also model calculations for fitting to the experimental data a rough scheme of the crystalline structure can be given as a monoclinic lattice with two molecules in the elementary cell, and the molecules form long chains with their long axes parallel to each other. It is supposed that the monoclinic lattice is nearly conserved in each of the crystalline phases, however the atomic positions could be varied considerably due to the twisting of the benzene rings and/or the reorientations of the end-groups.

EVOLUTION OF COHERENCE OF PHONON STATES

Figure 8 shows the reduced density of vibrational states of a few MBBA phases as measured by Raman scattering.[9] The density of the phonon state functions of C_0 and C_4 phases (Figure 4) are not as different as their Raman spectra, thus the change from C_0 to C_4 (Figure 8) should essentially be connected with the formation of spatial coherence of phonon states. When transforming phase C_0 to C_1 and C_2, ranges of the molecular short distance ordering, characterized by a coherence length (L_{coh}), increase from 30–40 to 100–120 Å,[2,5] and a lattice grows by the formation of some sort of elementary cell. This leads to the evolution of the coherence of optical modes and their selections which appear as structuring of the optical spectra and sharpening of the bands (Figure 8 b, c).

In the completely ordered crystal state (C_4 phase in Figure 8d) ranges of coherent scattering are $L_{coh} > \lambda$ (λ-wavelength) thus peaks in the spectrum correspond to phonons with $\mathbf{k} = 0$, meaning the full validity of the selection rules. The above discussion illustrates the unique feature of fast-cooled liquid crystals: the evolution of the spatial coherence of phonon states follows a sequence of phase transitions from a starting non-ordered state (C_0 in the case of MBBA) to a final crystalline one, via partially ordered solid mesophases.

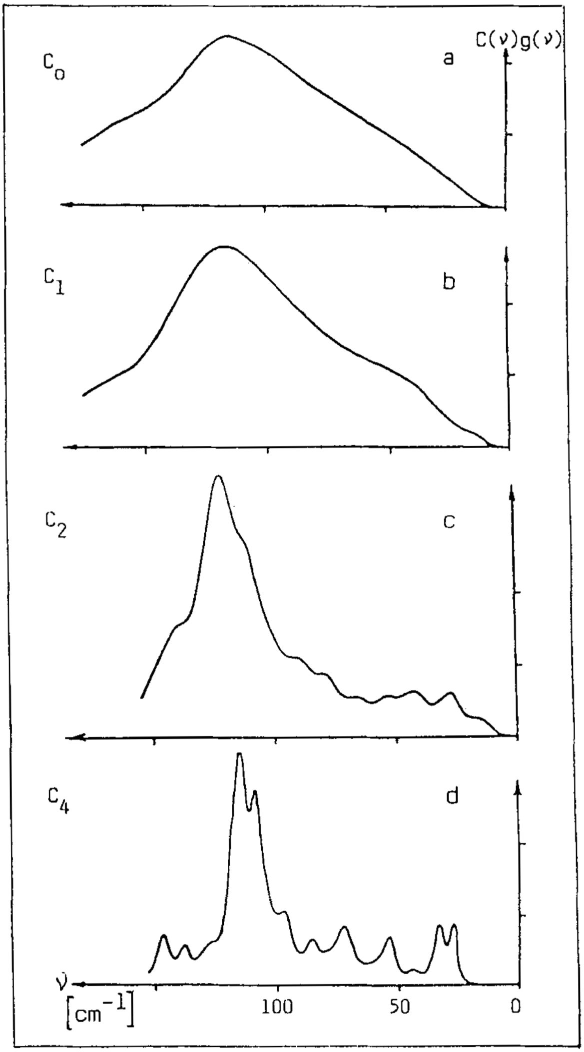

FIGURE 8 Reduced density of vibrational state curves of MBBA solid phases as obtained from Raman scattering.[9]

CONCLUDING REMARKS

Obviously, both the structure and the dynamics of fast-cooled liquid crystals—with particular regard to MBBA being relatively simple and highly polymorphic—represent a very attractive field in the research of disordered systems. It can be supposed that a considerable number of experiments will be made in the near future in order to establish the molecular packing and the arrangement of different molecular fragments relative to each other in liquid crystal structures, in order to describe the inter- and intramolecular dynamics of phonon as well as non-phonon origin.

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