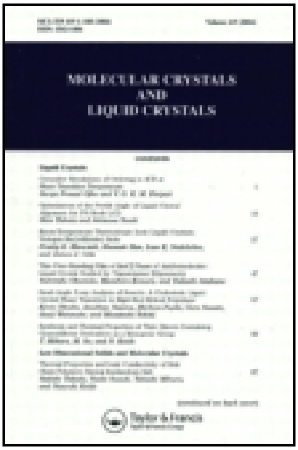

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A. V. Belushkin [a] , V. K. Dolganov [a b] , I. Natkaniec [a c] & V. G. Simkin [a]

[a] Joint Institute for Nuclear Research, Dubna, (near Moscow), USSR

[b] Institute of Solid State Physics of the Academy of Sciences of the USSR, Cher-nogolovka, USSR

[c] Instytut Fizyki Jadrowej, Radzikowskiego 152, 31-342, Krakow, Poland

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The Phonon Spectra of Ordered and Disordered Phases of MBBA

A. V. BELUSHKIN, V. K. DOLGANOV,† I. NATKANIEC,‡ and V. G. SIMKIN

Joint Institute for Nuclear Research, Dubna (near Moscow), USSR

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The spectra of inelastic incoherent neutron scattering (IINS) in the methoxy-benzilidene-butylaniline (MBBA) have been measured with the simultaneous phase control of the sample using the neutron diffraction (ND). The experiments were carried out in the nematic liquid crystal state (NLC) at T = 300 K as well as in seven solid modifications in the temperature range from 90K to 290K. The variety of polymorphous transformations in the MBBA (an amorphous state C_0, two disordered solid state mesophases C_1 and C_2, four ordered crystalline phases C_3, C_4, C_5, C_6) enabled us to trace the transformation of the vibrational spectrum at the transition from amorphous into crystalline state. For solid state modifications the weighted density of phonon states has been obtained. In the disordered phases (C_0 and C_1) as compared with the crystalline ones the Debye approximation is applicable for a narrower frequency range, and an increasing excess of the phonon density of state is observed in the low frequency range.

Keywords: liquid crystal property measurements

I. INTRODUCTION

In the last few years the disordered solid structures as well as the amorphous state have been the focus of much attention due to a number of interesting features in the dynamics of these systems and their increasing practical application. However, they remain poorly studied as compared with the crystalline state for which vast experimental data are available, and the theory in many cases permits one

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†Institute of Solid State Physics of the Academy of Sciences of the USSR, Chernogolovka, USSR.

‡Permanent Address: Instytut Fizyki Jadrowej, Radzikowskiego 152, 31–342 Krakow, Poland

to calculate the phonon spectrum which is in quantitative agreement with the experimental one. Difficulties in understanding the non-crystalline state dynamics are caused by the following reasons

i) there is no reliable information about the relative positions of atoms and molecules in the amorphous state, while the knowledge of the crystal structure is the basis for understanding and calculating the crystal dynamics,

ii) the collective motions in the amorphous state have a more complicated character as compared with the crystalline one and in some cases are incomprehensible even qualitatively at microscopic level. An example is the low frequency dynamics in an amorphous material, which is formally described either by two-level scheme or fracton theory. Another restrictive factor for the understanding of the dynamics of disordered systems is a lack of a rather complete set of experimental data. The peculiarities of the amorphous state spectrum are interpreted, as a rule, by correlating them with the spectrum of the crystalline state. It is important therewith to have as much as possible crystalline modifications of the material in order not to generalize the phonon spectra characteristics, which are peculiar only to one modification.

The present paper describes the results of the IINS measurements in solid and liquid crystal states of the MBBA. The choice of the MBBA crystal is explained by a number of advantages this compound exibits as an object for the phonon spectrum investigation:

i) MBBA has a rather large set of crystalline modifications (4phases). Three of them can be studied at low temperatures.[1]

ii) the transition from the amorphous state into the ordered crystalline one occurs step-by-step, through two intermediate phases (mesophases) with the size of coherent elastic scattering regions of about 100 Å.[1-4] These phases can be studied at low temperatures.

iii) the phonon spectrum of organic compounds has a variety of forms in contrast to that of inorganic compounds, and consists of intermolecular vibrations, which depend on the mutual position of molecules in the solid state, and intramolecular vibrations which to a minor degree depend on the packing of molecules.

II. EXPERIMENTAL CONDITIONS AND PHASE TRANSFORMATIONS IN MBBA

The MBBA was mounted into a thin aluminium container 160 × 180 × 1 mm^3 at room temperature when the sample is in liquid crystalline state. The container was placed in the neutron cryostat equipped with the system of temperature control.

The measurements were carried out on the KDSOG-M spectrometer[5] of the IBR-2 reactor[6] using the time-of-flight technique. The IINS spectra were recorded at four scattering angles : 80°, 100°, 120° and 140° simultaneously with the neutron diffraction spectrum for the scattering angle of ~29°. The procedure of the phase production as well as the temperature intervals of their existence are described in detail in Refs. 1, 3. The amorphous state (C_0) was obtained by cooling the MBBA from liquid crystal state down to 80 K (~50 deg/min). Phases C_1, C_2, C_3, C_4 were obtained successively on heating the amorphous state to 208 K, 220 K, 250 K and 270 K, respectively. The C_0—C_4 phase transitions are irreversible and all the above phases once they have been produced can be cooled to low temperatures. The ND spectra used for phase identification are shown in Figure 1. The results of ND are in agreement with the X-ray[1] and neutron[3] measurements performed earlier. The structure of the main peak in C_4-phase has not been observed in Ref. 3 because of a poorer resolution. The ND spectra of NLC and C_0-phases differ from those obtained in Refs. 1, 3 due to the filtering of the incident neutron beam by aluminium of the neutron guide and by the cryostat walls. The C_6 phase is formed during slow cooling of MBBA (~1 deg/min) and near 205 K it reversibly transforms into the C_5 phase. The corresponding ND spectra are shown in Figure 2.

The previous spectral and diffraction studies[1-3] have revealed two branches of transformations in the solid state of MBBA: the first one—an irreversible branch of phase transitions C_0–C_1–C_2–C_3–C_4 is related to the heating of amorphous phase; the second one—reversible structure transformations NLC–C_6–C_5—is realized on slow cooling of MBBA from liquid crystal phase. The transition between the states that belong to different branches of phase transformations was not studied. We revealed the transformation of the ND spectrum of phase C_6 into phase C_4 at a prolonged exposure of the sample of a nearly melting temperature. Figure 3 illustrates the results of the diffraction measurements at 290 K at 10 to 20 hrs intervals. The final state corresponds to the phase C_4 which is a stable crystalline modification. Probably this phase transition have been observed earlier when studying phase transitions in MBBA using the methods of adiabatic calorimetry and IR spectroscopy.[7] For the phase C_4 the intensity distribution in main diffraction peaks in Figure 3 differs slightly from that in the diffraction pattern in Figure 1, which seems to be due to the difference in the dimensions of blocks and in their ori-

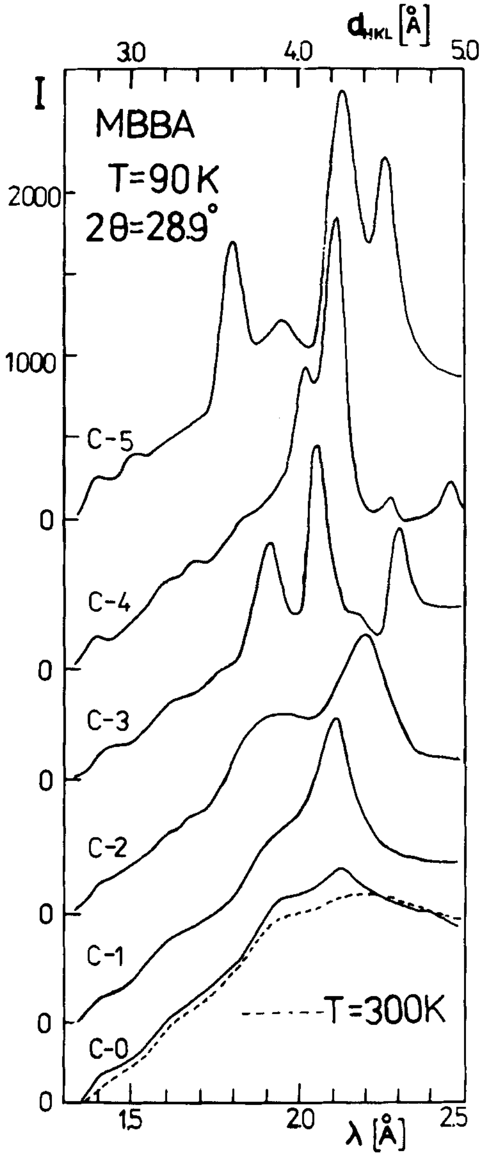

FIGURE 1 ND spectra for different solid phases of MBBA. The dashed line stands for the ND spectrum of nematic phase at 300 K. The lower horizontal axis is for neutron wavelength; the upper one for $d = \lambda/2\sin\theta$.

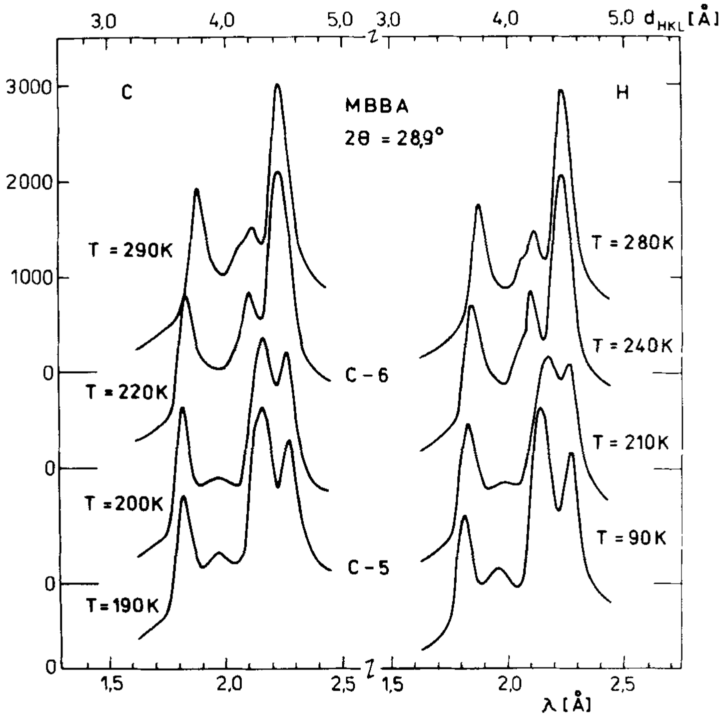

FIGURE 2 Changes in the ND spectra of MBBA at $C_6 \leftrightarrow C_5$ phase transition. C—means the sample cooling, H—means the heating.

entations when C_4 is obtained from amorphous state at rather fast C_0–C_4 phase transformations and a slow transformation C_6–C_4. X-ray measurements[1] performed for oriented and nonoriented samples have also shown the difference between the relative intensities of diffraction peaks. The C_6–C_4 phase transition confirmed by the present investigations have locked up the two branches of phase transformations in MBBA as it is shown in Figure 4.

III. RESULTS OF IINS MEASUREMENTS AND THEIR DISCUSSION

The results of IINS measurements are represented in Figures 5, 6. The background produced by the cryostat and container was subtracted, then, in order to improve the statistics, the spectra measured at different scattering angles were summed up. The mean time of spectrum measurements was about 10 hours. The function of spectral

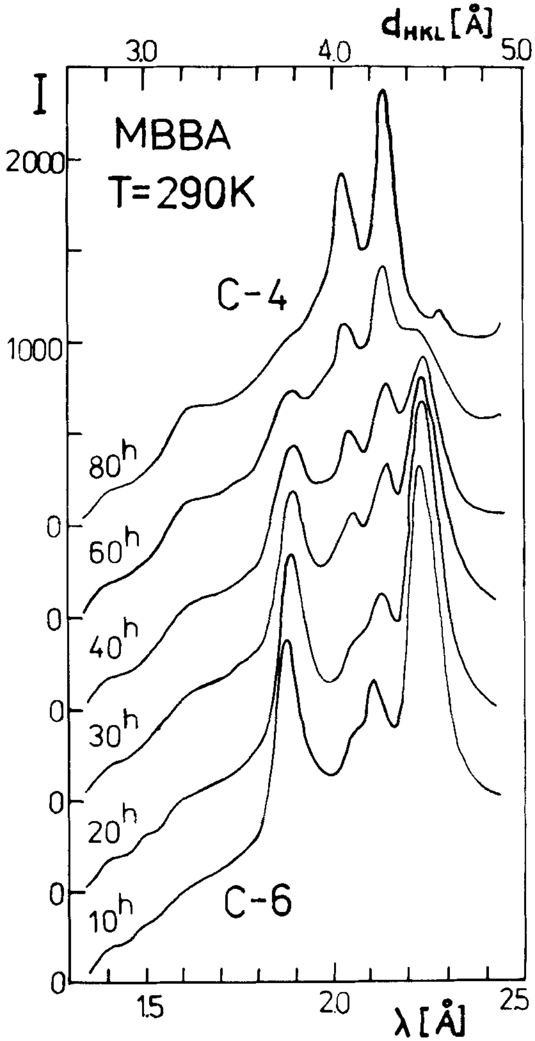

FIGURE 3 Diffraction patterns of MBBA measured during phase transition $C_6 \rightarrow C_4$.

resolution of KDSOG-M changes for the IINS from 1 cm^{-1} at the energy transfer of 20 cm^{-1} to 15 cm^{-1} at 300 cm^{-1}. At 90 K (Figure 5) the crystal phases exhibit differences within the whole range of frequencies. At high temperatures (Figure 6) in the range $\nu > 80$ cm^{-1} the spectra are structureless and similar. In the low frequency range the discrepancies in the dynamics are seen as well at high

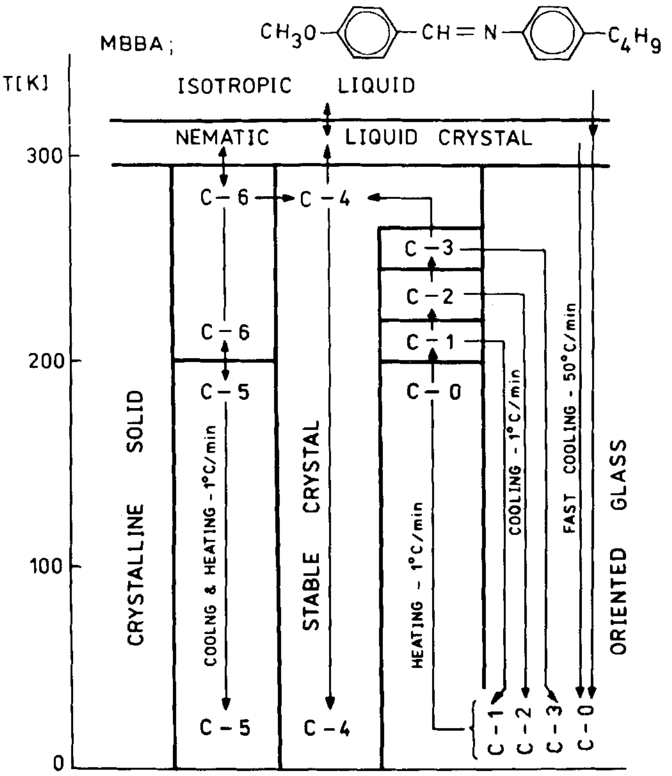

FIGURE 4 Sketch of polymorphous transformations of MBBA.

temperatures. The spectrum peculiarity of the C_4 phase at 90 K in the range ~ 25 cm^{-1} is preserved with the shift to 20 cm^{-1} even at 290 K. In the nematics within the whole range of frequencies $\nu < 40$ cm^{-1} an excess scattering is observed as compared with phases C_4 and C_6 (50% for $\nu < 10$ cm^{-1}). Since the temperature of measurements for crystalline and nematic phases are very close (290 K and 300 K), the excess scattering is not the result of the difference in population of vibrational states and should be related to the softening of the vibration spectrum in the disordered phases (the analogous effect also is observed in C_0[8,9] at lower temperatures). The considerable elastic peak broadening is connected with the quasielastic scattering in the nematic phase of MBBA (Figure 6). The quasielastic scattering in the nematic phase of MBBA is connected with the rotational diffusion of molecular groups.[10] A wing of analogous broadening is observed, but to a less extent, in the phase C_6 (Figure 6).

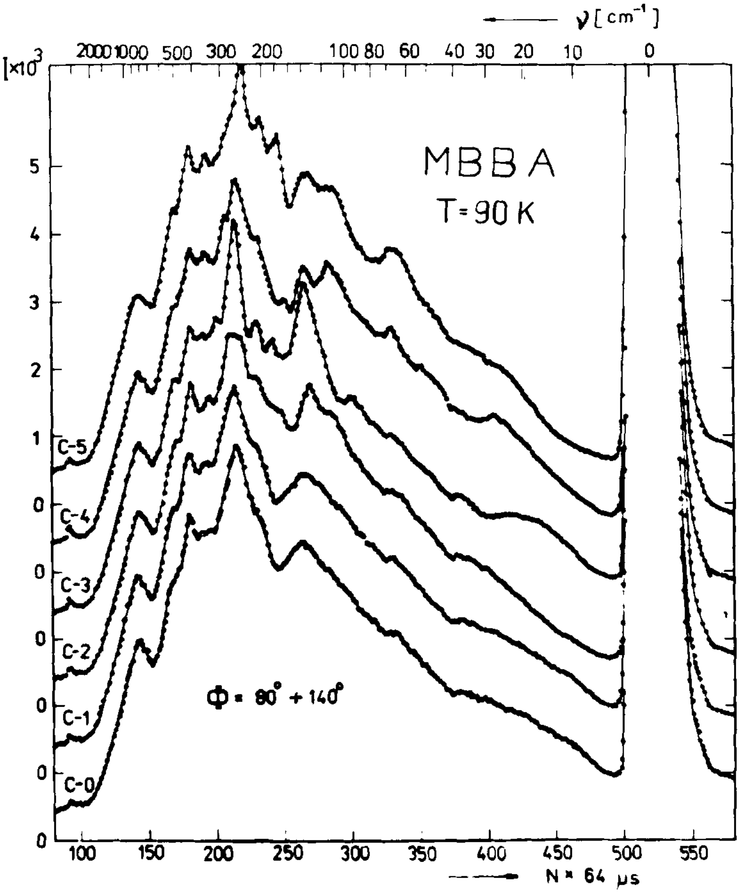

FIGURE 5 IINS spectra of solid phases (C_0 to C_5) of MBBA at 90 K.

However, it practically disappears at the phase transition C_6–C_4. The existence of a noticeable quasielastic scattering in the crystalline phase C_6 in comparison with C_4 can be explained in the following way:

i) at 290 K the C_4 phase is the stable crystalline modification, therefore, the energy minimum that corresponds to it is deeper than that for C_6. This complicates the reorientation processes which lead to quasielastic scattering.

ii) as the X-ray measurements have shown,[1] the crystalline modification C_6 is less ordered than C_4 (the halfwidth of diffraction lines in C_6 is larger), which facilitates the reorientation as well as processes of diffusion type in the C_6 phase.

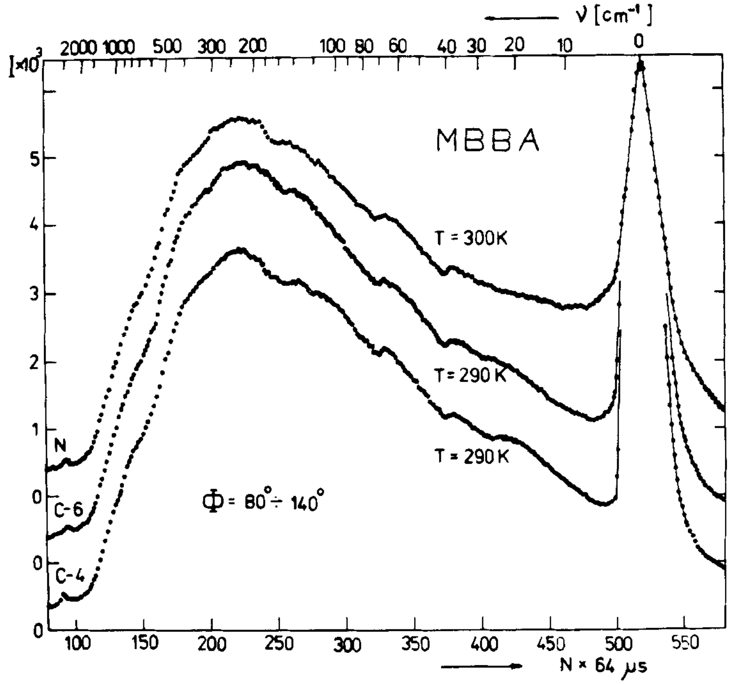

FIGURE 6 IINS spectrum of liquid crystal phase (N) at 300 K and crystal phases at 290 K (C_6—before the phase transition; . . . C_4—after the phase transition).

Figure 7 depicts the weighted density of phonon states $G_H(\nu)$ calculated from the experimental data of IINS at 90 K in the one-phonon scattering approximation.[9] In the range of intermolecular vibrations ($\nu > 180\ \mathrm{cm}^{-1}$) the differences in the spectra are caused by conformational changes of molecules. The shifts of frequencies at transitions come to 15–20 cm^{-1}. The most essential changes in the spectrum begin from the transition C_1–C_2. The C_0–C_1 transition practically does not change the spectrum of intermolecular vibrations (the analogous result also is obtained for Raman)[3,4] which is an indicative that the transition is mainly due to the long-range molecular ordering. In the next stages, when a unit cell is formed and reconstructed (Figure 1), reconstructions take place at the molecular level too.

In the range of intermolecular and low-frequency molecular vibrations ($\nu < 180\ \mathrm{cm}^{-1}$) the transition C_0–C_1 is practically not accompanied with the changes in state densities. However, the structure measurements show[1-3] a marked (~ 3 times) narrowing of diffraction lines. Since the main features of the phonon spectrum are determined

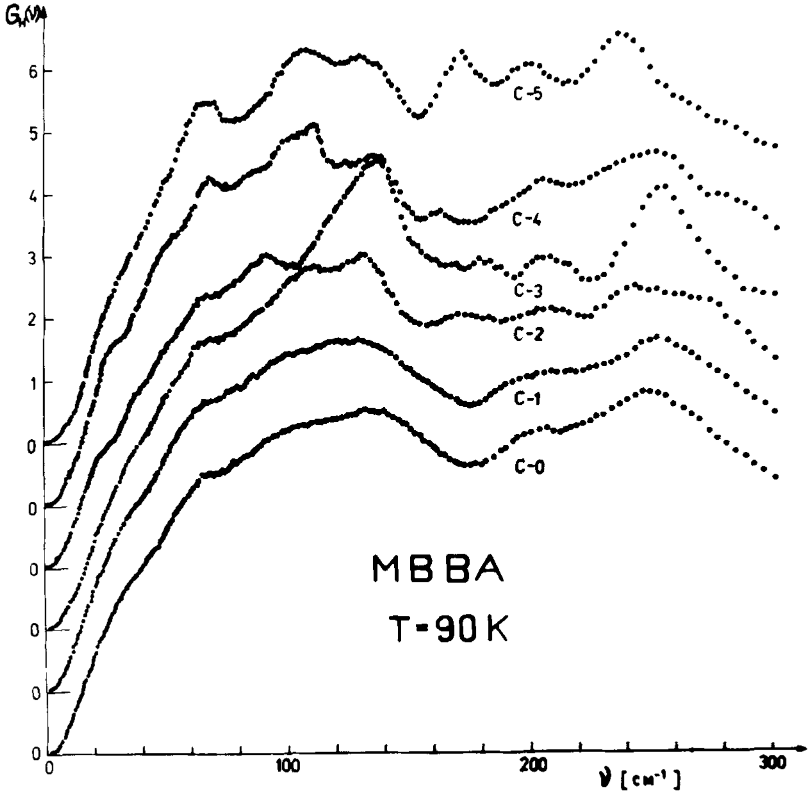

FIGURE 7 Weighted density of phonon states, $G_H(\nu)$, of MBBA.

by the relative position of the nearest neighbour molecules, one can conclude that the transition C_0–C_1 is mainly connected with the change of the coherence length due to the long-range ordering. The optical spectrum of RS in this frequency range has a large bandwidth excluding a band of 13 cm^{-1} appearing in the C_1 phase.[3,4] As is seen from the IINS spectrum, the density of phonon states practically does not change in this frequency range, i.e. the peculiarity of optical spectrum is connected with the appearance of the phonon state coherence rather than with the frequency spectrum peculiarity. Further transitions are accompanied with a noticeable reconstruction of the state density. The spectrum peculiarities result from the formation of individual phonon bands (transition C_1–C_2) and their reconstruction (phases C_3, C_4, C_5). Among the ordered crystal phases C_3, C_4 and C_5, the state density of the C_4 modification is nearly the same as the state density of amorphous structure. The reason is apparently in the similarity of the molecules shapes in these modifications.

The low frequency region of the phonon state density is shown in Figure 8. The state density curves of ordered crystal states exibit some peculiarities in the range 15–25 cm^{-1} for the phase C_3, and in the range 22–28 cm^{-1} for the phases C_4 and C_5. These peculiarities seem to be due to the dispersion of acoustic phonons and the optical vibration contribution into the density of state including the low frequency librations of the whole molecule. In the disordered phases the analogous peculiarity in the state density either is not observed (C_2) or it shifts toward a lower frequency range (C_0 and C_1). For

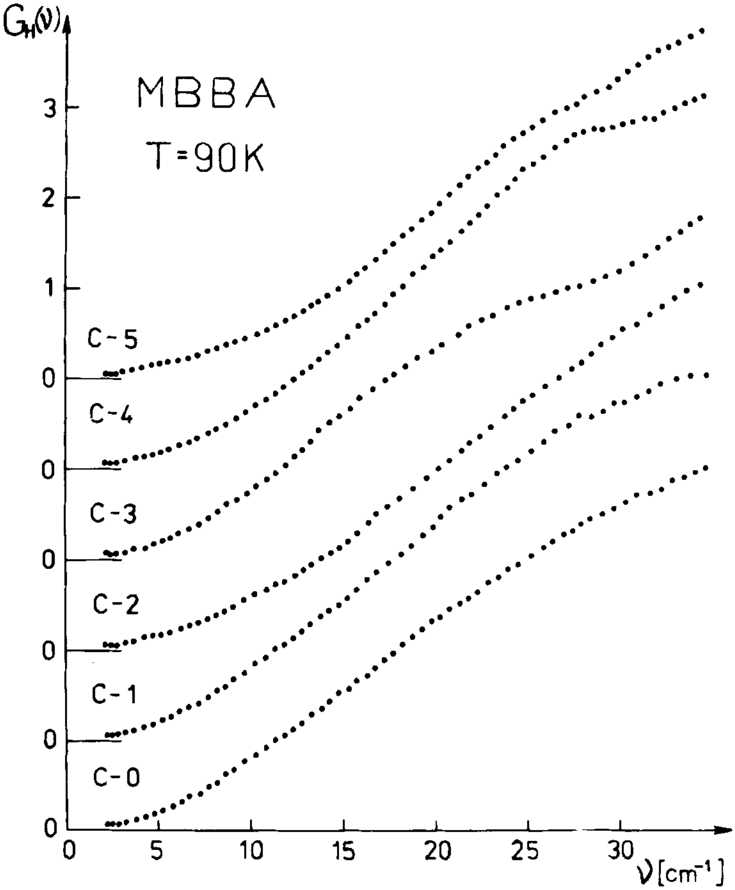

FIGURE 8 Low-frequency region of the weighted density of phonon states, $G_H(\nu)$, of MBBA.

acoustic vibrations $\rho(\nu) \sim\nu^2$. Proceeding from this, the spectrum is analysed using the function $G_H(\nu)/\nu^2$ (Figure 9). In the low frequency range the function $G_H(\nu)/\nu^2$ decreases by 27% as a result of ordering during transition from amorphous phase C_0 into C_2. In the crystal phases C_3–C_5 the value of $G_H(\nu)/\nu^2$ is determined by the sound velocity averaged over the crystallographic directions and it changes by ~25%. At the same time, the region of frequencies with linear dispersion changes. In the phase transition succession C_0–C_1–C_2–C_3–C_4 the low frequency plateau of the $G_H(\nu)/\nu^2$ function broadens. The

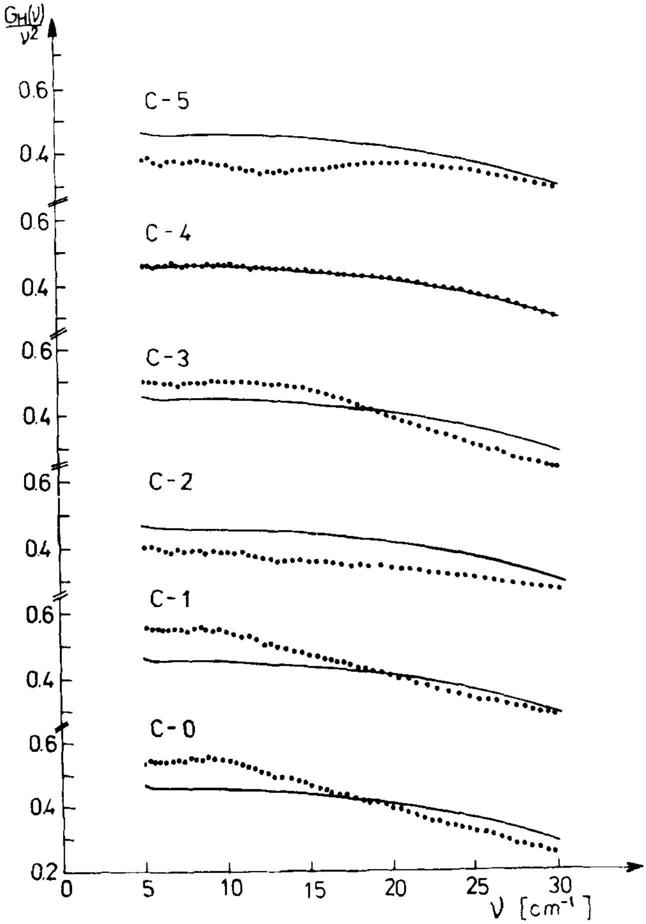

FIGURE 9 Low-frequency region of the $G_H(\nu)/\nu^2$ function for the phases C_0 to C_5.

low frequency level of function $G_H(\nu)/\nu^2$ determined from experimental points within the range 5–10 cm^{-1} deviates by 10% for the phases C_0 and C_1 at 13 cm^{-1}; for the phases C_2 and C_3 at 17 cm^{-1} and for C_4 at 20 cm^{-1}. The function reaches its maximum value in the amorphous phase C_0 and disordered phase C_1. The excess low frequency scattering in these phases as compared with the phase C_4 may be related to a smaller slope of acoustic branches. By this interpretation, the mean sound velocity in the C_0 phase is ~1.2 times less than in the crystal modification C_4. The smaller slope of dispersion branches for acoustic phonons is caused by the total decrease of the rigidity of disordered sample and the local modulation. The latter, in the case of a "soft" local bond between individual groups of atoms and molecules, may lead to the initiation of tunnel states as well as to the quasielastic scattering observed even in the crystal metastable modification C_6 at high temperatures (Figure 4) and especially explicitly in the liquid crystal phase.

IV. CONCLUSION

The main experimental results of the present study are:

—phonon spectra of different crystal phases of MBBA markedly differ from each other;

—in the low frequency spectrum range ($\nu < 15$ cm^{-1}) of disordered phases C_0 and C_1 an excess scattering is observed which disappears at transition to a more ordered phase C_2;

—the Debye approximation describes well the behaviour of the crystal phase spectra up to ~12 cm^{-1}. At high frequencies the dispersion of acoustic vibrations and the low frequency librations of the whole molecule become very important. At $T = 90$ K in the low frequency region of spectra of crystal phase C_4 a peculiarity is observed at 25 cm^{-1} which considerably broadens and softens with increasing temperature. For the crystal phase C_5 this peculiarity is much broader than in the C_4 phase, and in the C_3 phase it is broad and observed at a lower frequency (~15 cm^{-1})

—the diffraction experiment has confirmed the spontaneous transition from metastable crystal phase C_6 to the stable modification C_4 for about 100 hrs at 290 K. This transition closes the two branches of phase transformations in MBBA;

—stable crystal modification C_4 cannot be produced from nematic phase by cooling at a rate of ~1 dg/min.

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