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OPTICAL PROPERTIES

Phonon Spectrum of a Naphthalene Crystal at a High Pressure: Influence of Shortened Distances on the Lattice and Intramolecular Vibrations

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Abstract—The Raman spectra of a naphthalene crystal have been measured at room temperature in the pressure range up to 20 GPa. The pressure shift and Grüneisen parameters for intermolecular and intramolecular phonons have been determined. The maximum rate of the pressure shift for intermolecular phonons is 44 cm^{-1}/GPa, and the rate of the pressure shift for intramolecular phonons lies in the range from 1 to 11 cm^{-1}/GPa for different modes. The pressure dependence of the phonon frequencies for direct and inverse pressure variations has a hysteresis in the pressure range from 2.5 to 16.5 GPa. It has been shown that the linear dependence of the intermolecular phonon frequency on the crystal density has a peculiarity, which indicates a possible phase transition at a pressure of 3.5 GPa. The pressure dependence of intramolecular phonons related to the stretching vibrations of hydrogen atoms exhibits features that are characteristic of intermolecular phonons, which is associated with the influence of shortened distances between the hydrogen atoms of the neighboring molecules on the intermolecular interaction potential.

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1. INTRODUCTION

Investigations of molecular crystals under high pressure have revealed that these crystals exhibit characteristic features associated with van der Waals intermolecular and covalent intramolecular interactions [1]. A high compressibility observed in the initial pressure range, which rapidly decreases with an increase in the pressure, is determined by the van der Waals interaction and is typical of organic crystals. Measurements of the relative volume of crystals of aromatic hydrocarbons at a high pressure have demonstrated that the compressibility is adequately described by the Murnaghan equation of state with the bulk modulus of compressibility in the range from 5 to 10 GPa [2]. For comparison, the bulk modulus of compressibility of an allotropic form of carbon, namely, fullerite, which also forms molecular crystals, is equal to 16 GPa, whereas the bulk modulus of compressibility of the hardest natural mineral, i.e., diamond (another allotropic form of carbon), reaches 600 GPa.

The crystal structure and the phonon spectrum of naphthalene at a high pressure had been investigated using the methods of elastic and inelastic neutron scattering and optical Raman spectroscopy [2–7]. The investigations had been focused on the search for polymorphic phase transformations [3], determination of the bulk compressibility and elastic constants [2, 4], and analysis of the phonon spectrum and its evolution at a high pressure [5–7]. The polymorphism in crystals of benzene, naphthalene, and anthracene was investigated using optical microscopy in the pressure range up to 5 GPa and at temperatures up to 550°C [3]; however, this study did not confirm the early results obtained by Bridgman regarding the phase transition in a naphthalene crystal at 3 GPa [8]. Experiments with crystals of benzene-II (monoclinic phase of the parent orthorhombic benzene-I at a pressure $P \geq$ 1.2 GPa), naphthalene, and anthracene did not reveal structural phase transitions at a high pressure, which is explained by the initial low symmetry of the crystals belonging to the monoclinic system. The irreversible transformations observed in [3] at high pressures and temperatures are associated with the breaking of the covalent C–H bonds and correlate with the data on the stability of these materials at normal pressure and high temperatures.

In addition to the experimental investigations, numerical calculations of the crystal structure and the phonon spectrum of the crystals were carried out in the approximations of rigid and flexible molecules with the pair interaction potential between pairs of atoms of the neighboring molecules, i.e., the so-called Buckingham potential (exp–6) [9]. These calculations give good agreement with the experimental results at normal pressure with the use of sets of the Kitaigorodskii and Williams parameters; however, calculations of the structure and the phonon spectrum of the crystals at a high pressure were not performed [7]. The shortest

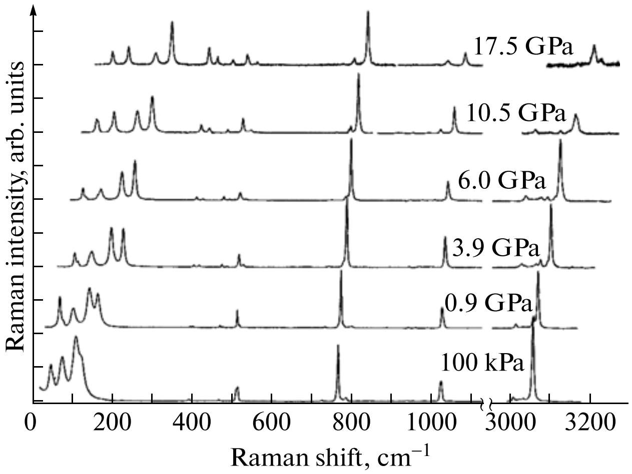

Fig. 1. Raman spectra of the naphthalene crystal at room temperature and pressures up to 17.5 GPa.

distances between the atoms of the neighboring molecules, which lie in the range from 2.40 to 2.66 Å for the H–H contacts and amount to 2.82 Å for the C–H contacts at normal pressure, significantly decrease at a high pressure [10]. This can lead to a correction of the intermolecular interaction potential and a change in the structure and the phonon spectrum of the crystal. In particular, it was found that, in the Raman and infrared absorption spectra of the HBr molecular crystal at a high pressure, the frequency of phonons generated by stretching vibrations of the hydrogen atom decreases abruptly. The softening of the vibrations is caused by the elongation of the covalent H–Br bond at a high pressure due to the displacement of the hydrogen atom toward the bromine atom of the neighboring molecule [11].

Therefore, the role of shortened distances between the atoms of the neighboring molecules in molecular crystals at a high pressure requires a more detailed investigation. In this respect, we have measured the Raman spectra of a naphthalene crystal at a high pressure and room temperature for the purpose of investigating the behavior of the intermolecular and intramolecular phonon modes at pressures up to 20 GPa. We have determined the rate of the pressure shift $\partial\Omega_i/\partial P$ and Grüneisen parameters $\gamma_i = (\partial\Omega_i/\Omega_i)/(\partial V/V)$ for all the phonon modes. The pressure shift has a maximum value for the intermolecular phonons and a minimum value for the intramolecular phonons associated with the C–C vibrations of the molecular skeleton. It has been established that the pressure shift of the intramolecular phonons generated by stretching vibrations of the hydrogen atoms along the C–H bond is comparable with the pressure shift of the intermolecular phonons. The pressure dependences of the phonon frequencies for the direct and inverse pressure variations differ in the pressure range 2.5–16.5 GPa, and the hysteresis is maximum for the intermolecular phonons. The dependences of the relative frequency of intermolecular phonons (Ω/Ω_0) on the relative density of the crystal (ρ/ρ_0), where Ω_0 and ρ_0 are the phonon frequency and the crystal density at normal pressure, respectively, have a specific feature at $\rho/\rho_0 \approx 1.25$, which can be associated with a phase transition at a pressure of 3.5 GPa.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Crystals of the naphthalene $C_{10}H_8$ belong to the monoclinic system (space group $P2_1/a$), contain two molecules in the unit cell, and have the following unit cell parameters: $a = 8.235$ Å, $b = 6.003$ Å, $c = 8.658$ Å, and $\beta = 122°55'$. The naphthalene single crystals were grown from the gas phase using the analytical-grade naphthalene (with a purity of 99%) preliminarily purified by floating zone melting. For measurements of Raman spectra at a high pressure, the samples were prepared in the form of thin plates with a transverse dimension of 150 μm and a thickness of 10–30 μm.

The Raman spectra were measured in the backscattering geometry with a DILOR XY-500 triple monochromator equipped with a CCD liquid-nitrogen cooled detector system. The focusing on the sample and the collection of the scattered light were performed with an OLYMPUS microscope and an objective with magnification 20× and a working distance of 18 mm. The spatial resolution of the optical system was ~2.5 μm, and the spectral resolution was ~3 cm^{-1}. Raman scattering was excited with the use of the 5145 Å line of an argon laser and the 6471 Å line of a krypton laser. The intensity of the laser beam directly in front of the sample was in the range from 0.5 to 2.5 mW. The Raman spectra at a high pressure were measured with a high-pressure Mao–Bell-type diamond-anvil cell [12]. An ethanol–methanol–glycerol (4 : 1 : 5) mixture was used as the pressure-transmitting medium. The pressure was calibrated using the R_1 luminescence line of ruby microcrystals in accordance with the ruby pressure scale with an accuracy of 0.1 GPa [13]. The phonon frequencies were determined by the approximation of the experimental contour of the bands by the Voigt curve (50% Gaussian + 50% Lorentzian). The accuracy in the determination of the phonon frequencies with inclusion of the preliminary calibration of the spectrometer using the emission lines of a neon lamp was no less than 0.5 cm^{-1}.

3. RESULTS AND DISCUSSION

The Raman spectra of the naphthalene crystal at room temperature in the pressure range up to 17.5 GPa are shown in Fig. 1. The lower Raman spectrum was measured under normal conditions, and the upper spectra were obtained at pressures of 0.9, 3.9, 6.0, 10.5, and 17.5 GPa. The spectra are normalized so that the relative intensity of the band at 790 cm^{-1} is identical for all pressures. The bands in the frequency range up to 200 cm^{-1} in the spectrum under normal conditions correspond to intermolecular phonons, whereas the peaks located at higher energies correspond to intramolecular phonons. The bands in the frequency range above 3000 cm^{-1} are assigned to the intramolecular phonons generated by stretching vibrations of the hydrogen atoms. With an increase in the pressure, all the bands in the Raman spectrum are shifted toward higher energies. In this case, the maximum increase in the frequency is observed for the intermolecular phonons, whereas the increase in the frequency of the intramolecular phonons is considerably less pronounced and depends on the character of atomic vibrations. In particular, the frequencies of intramolecular phonons generated by stretching vibrations of the hydrogen atoms are increased to a considerably larger extent as compared with the frequencies of phonons associated with vibrations of the carbon atoms in the skeleton of the molecule. It should also be noted that the bandwidth of intermolecular phonons in the spectrum at a pressure of 0.9 GPa is substantially smaller than that in the spectrum measured under normal conditions and decreases with an increase in the pressure to 6 GPa, whereas the bandwidth of intramolecular phonons remains almost unchanged. However, with a further increase in the pressure above 6 GPa, all the spectral bands undergo a gradual broadening due to the solidification of the pressure-transmitting medium. The narrowing of the bands of intermolecular phonons makes it possible to resolve in the spectrum two more peaks in the form of satellites of two phonon modes at 45.3 and 74.0 cm^{-1} under normal pressure. It should be mentioned that a similar narrowing of the peaks attributed to the intermolecular phonon is also observed at normal pressure with a decrease in the temperature from room temperature to 30 K [5]. The intensity of the bands slightly varies with an increase in the pressure because of the change in the conditions of resonant excitation of Raman scattering due to the shift of the electronic levels [14]. A more noticeable decrease in the intensity of phonon peaks of the C–H vibrations in the spectra at pressures of 10.5 and 17.5 GPa is associated with the use of a krypton laser for the excitation of Raman scattering. In this case, the bands of C–H vibrations fall in the low-sensitivity region of the CCD detector near the upper boundary of its spectral range. With an increase in the pressure, the luminescence background also increases as a result of the formation of defects due to the compression of the crystal under quasi-hydrostatic conditions. The luminescence background significantly increases at pressures above ~6 GPa, when the pressure-transmitting medium becomes solid (in Fig. 1, the spectra are shown after the subtraction of the background). With a decrease in the pressure, the behavior of the bands in the Raman spectrum is reversible: the phonon frequency decreases, but the luminescence background decreases only slightly.

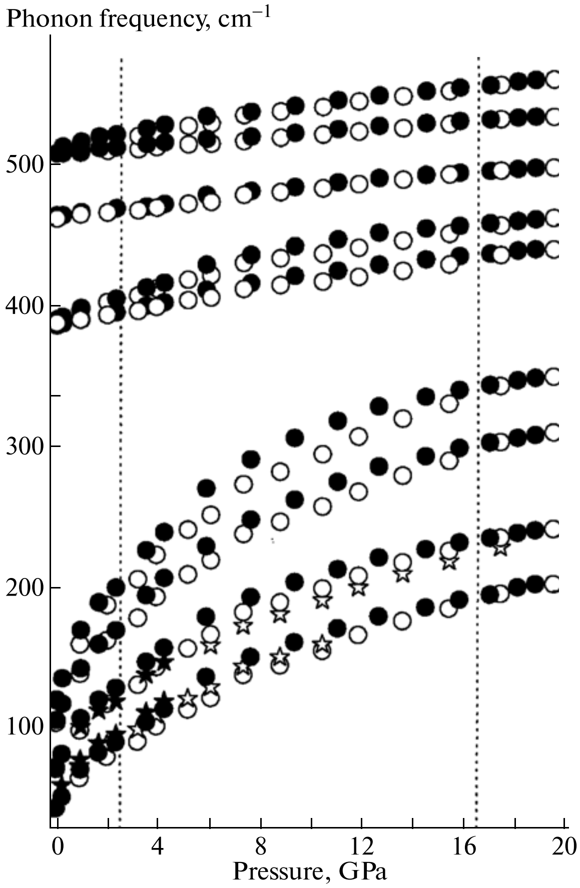

Fig. 2. Pressure dependence of the phonon frequency with an energy up to 500 cm^{-1} in the naphthalene crystal at pressures up to 20 GPa. Open and closed symbols correspond to the direct and inverse pressure variations, respectively. Asterisks indicate the frequencies of phonons that appear in the spectrum after the narrowing of the bands of intermolecular phonons at a high pressure.

Figure 2 shows the pressure dependence of the frequencies of intermolecular phonons and close-in-energy intramolecular phonons in the energy range up to 500 cm^{-1}. The open and closed circles correspond to the direct and inverse pressure variations, respectively. Asterisks in Fig. 2 indicate the frequencies of phonons that appear in the spectrum after the narrowing of the bands of intermolecular phonons at a high pressure. In the initial pressure region, the intermolecular phonon frequency increases very rapidly, but, then it slows down, so that the dependence of the frequency on the pressure is sublinear. The intramolecular phonon frequency increases with increasing pressure considerably more slowly, and the pressure dependence of the frequency is almost linear for the majority of the vibrations. The exception is the low-frequency intramolecular phonons associated with the torsional vibrations of the skeleton of the naphthalene

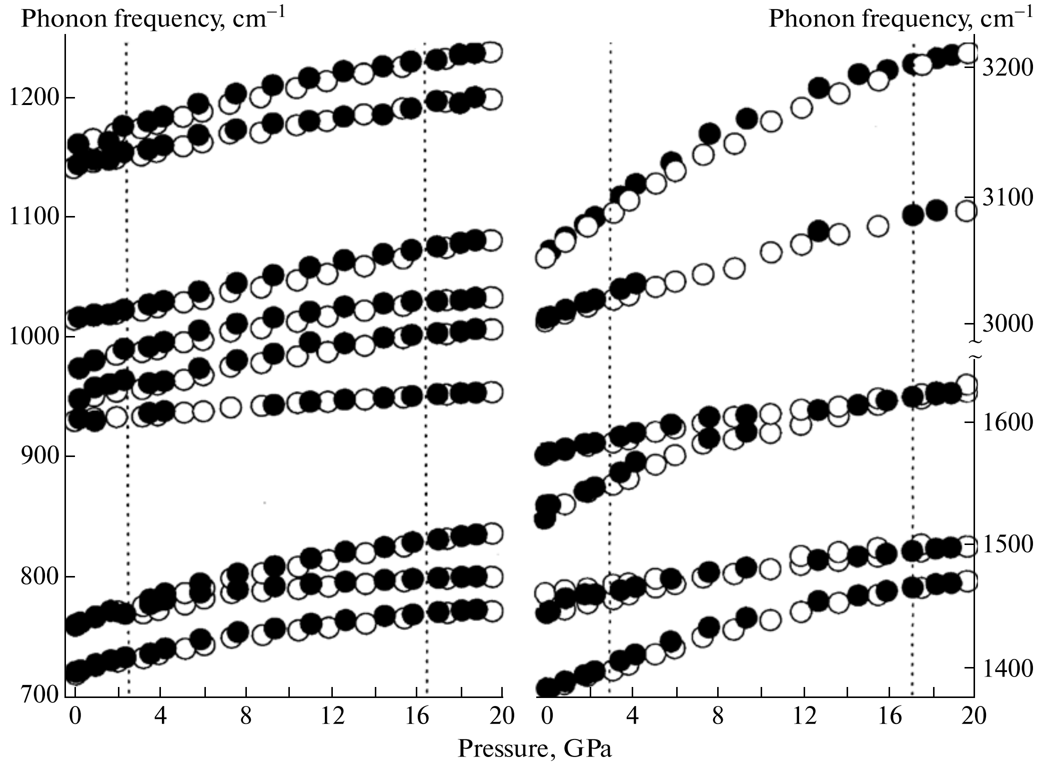

Fig. 3. Pressure dependence of the phonon frequency with an energy ranging from 700 to 3200 cm^{-1} in the naphthalene crystal at pressures up to 20 GPa. Open and closed symbols correspond to the direct and inverse pressure variations, respectively.

molecule. The rates of the pressure shifts of the phonon frequencies for the intermolecular and intramolecular phonons differ by almost an order of magnitude. The pressure dependence of the phonon frequencies at first glance does not exhibit specific features: it has neither discontinuities nor sharp changes in the slope or splitting of the bands, which are considered to be indications of phase transitions [15, 16]. At the same time, the pressure dependence of the phonon frequencies for the inverse pressure variation is slightly shifted upward in energy and differs insignificantly from that for the direct pressure variation. The difference in the frequencies for the direct and inverse pressure variations has a maximum value for intermolecular phonons. The pressure range where the pressure dependence of the phonon frequencies has a hysteresis is approximately the same for all the phonon modes and is indicated in Fig. 2 by vertical dotted lines.

The pressure dependence of the intramolecular phonon frequencies in the range from 700 to 3200 cm^{-1} at pressures up to 20 GPa is shown in Fig. 3. The open and closed circles correspond to the direct and inverse pressure variations, respectively. The pressure shift for almost all the intramolecular phonons is considerably smaller than that for the intermolecular phonons, and its dependence on the pressure is less pronounced. The exception is provided by the phonons generated by stretching vibrations of the hydrogen atoms along the C–H bond, for which the pressure shift is comparable with the shift for the intermolecular phonons and has a clearly defined sublinear dependence on the pressure. The dependence on the pressure is also sublinear for the intramolecular phonons associated with torsional vibrations of the hydrogen atoms. Thus, the phonons generated by stretching vibrations of the hydrogen atoms along the C–H bond have some indications that are characteristics of intermolecular phonons. The hysteresis for the direct and inverse pressure variations in the range from 2.5 to 16.5 GPa has a maximum value for the phonons corresponding to stretching vibrations of the hydrogen atoms along the C–H bond. The pressure dependence of the intramolecular phonon frequencies is smooth and has no specific features that can be indications of phase transitions. The phonon frequencies at normal pressure Ω_i^0, pressure shift coefficients $\partial\Omega_i/\partial P$, and Grüneisen parameters γ_i are presented in the table. The Grüneisen parameters were determined according to the formula

$$\gamma_i = (\partial\Omega_i/\Omega_i)/(\partial V/V) = (B_0/\Omega_i^0)/(\partial\Omega_i/\partial P). \quad (1)$$

The calculations were carried out using the experimental values obtained from the Raman spectra for the rates of the pressure shift $\partial\Omega_i/\partial P$ and the phonon frequencies at normal pressure Ω_i^0, as well as the bulk modulus of compressibility of the naphthalene crystal $B_0 = 6.6$ GPa. This value is the average between $B_0 = 6.727$ GPa obtained in the work by Vaidya and Kennedy [2] and $B_0 = 6.463$ GPa obtained in the classical work by Bridgman [8]. For comparison, the experimental phonon frequencies and Grüneisen parameters obtained in [6] are presented in the fourth and fifth columns of the table.

The pressure dependence of the half-width of the phonon bands in the Raman spectrum of the naphthalene crystal is shown in Fig. 4. Triangles and circles are the data obtained for two intermolecular phonons with frequencies of 107 and 123 cm^{-1}, respectively. Squares are the data for the intramolecular phonon with a frequency of 3054 cm^{-1}, which is associated with stretching vibrations of the hydrogen atoms along the C–H bond, and pentagons are the data for the phonon with a frequency of 1388 cm^{-1} due to vibrations of the carbon skeleton of the molecule. The half-width of the band of the intramolecular phonon with a frequency of 1388 cm^{-1} at normal pressure is minimal and close to the instrumental width of the spectrometer slit. The half-width of the band of the phonon with a frequency of 3054 cm^{-1} is approximately two times larger than the instrumental width of the spectrometer slit, whereas the half-width of the bands of the intermolecular phonons is approximately five times larger than the instrumental width of the spectrometer slit. With an increase in the pressure, the half-width of the bands of the intermolecular phonons decreases by a factor of approximately two and reaches a minimum value at ~6 GPa. In this pressure range, the half-width of the band of intramolecular vibrations with a frequency of 1388 cm^{-1} slightly increases, whereas the half-width of the band of intramolecular vibrations with a frequency of 3054 cm^{-1} first slightly decreases but then increases. As is known, the actual width of the bands in the Raman spectra at low temperatures is determined by the inhomogeneous broadening caused by the decrease of the phonon lifetime due to scattering by defects. The homogeneous bandwidth is determined by the phonon–phonon interaction associated with the anharmonicity of vibrations and usually is several orders of magnitude smaller than the inhomogeneous bandwidth. However, as the temperature of the crystal increases and approaches the melting point, the decrease in the phonon lifetime due to the phonon–phonon interaction becomes so great that the homogeneous bandwidth exceeds the inhomogeneous bandwidth. The very large bandwidth of intermolecular phonons under normal conditions is explained by the fact that the temperature is close to the melting point of the naphthalene crystal. After application of the pressure, the equilibrium distances between the molecules decrease, the frequency of intermolecular phonons increases, and the melting temperature of the crystal increases. The application of pressure is equivalent to a decrease in the temperature of the crystal, because in both cases the effect of anharmonicity of vibrations decreases and the homogeneous bandwidth in the Raman spectrum decreases. A similar behavior was observed in measurements of the Raman spectra of the naphthalene crystal with a decrease in the temperature to 30 K and at normal pressure [6].

Phonon mode frequencies of the naphthalene crystal under normal conditions (first column), pressure shift coefficients (second column), and Grüneisen parameters (third column) according to the results of the present work and the phonon mode frequencies and Grüneisen parameters according to the data obtained in [6] (the fourth and fifth columns, respectively)

Ω_i^0, cm^{-1}	$\partial\Omega_i/\partial P$, cm^{-1}/GPa	γ_i	Ω_i^0, cm^{-1} [6]	γ_i [6]
45.3	23.6	3.42	43	5.1
74	29.9	2.68	73	3.6
107	38.0	2.36	107	2.9
122.7	43.7	2.38	126	2.9
389.2	3.0	0.052	387	
392.7	5.8	0.009	391	
465.3	2.4	0.035	467	
510.2	1.0	0.013	510	
513.8	3.5	0.046	515	
724.7	4.1	0.038	722	
759.7	4.0	0.036		
763.6	5.0	0.044	762	
934.5	1.1	0.008	933	
952.5	2.7	0.019	947	
982.1	3.1	0.021	981	
1019.2	2.3	0.015	1024	
1145.3	3.1	0.018	1147	
1165.0	3.9	0.023	1172	
1381.2	6.0	0.029	1384	
1445.4	3.9	0.018	1444	
1462.1	2.2	0.01	1465	
1524.6	8.7	0.038		
1575.8	3.3	0.014	1578	
3004	5.0	0.011	3008	
3054	10.9	0.024	3058	

The dependence of the relative phonon frequency Ω/Ω_0 on the relative density of the naphthalene crystal ρ/ρ_0 is shown in Fig. 5. The relative density of the naphthalene crystal ρ/ρ_0 was determined from the Murnaghan equation of state $P = (B_0/B_0')[(\rho/\rho_0)^{B_0'} - 1]$, where P is the pressure, ρ/ρ_0 is the relative density of the crystal, B_0 is the bulk modulus of compressibility, and B_0' is the first derivative of the bulk modulus

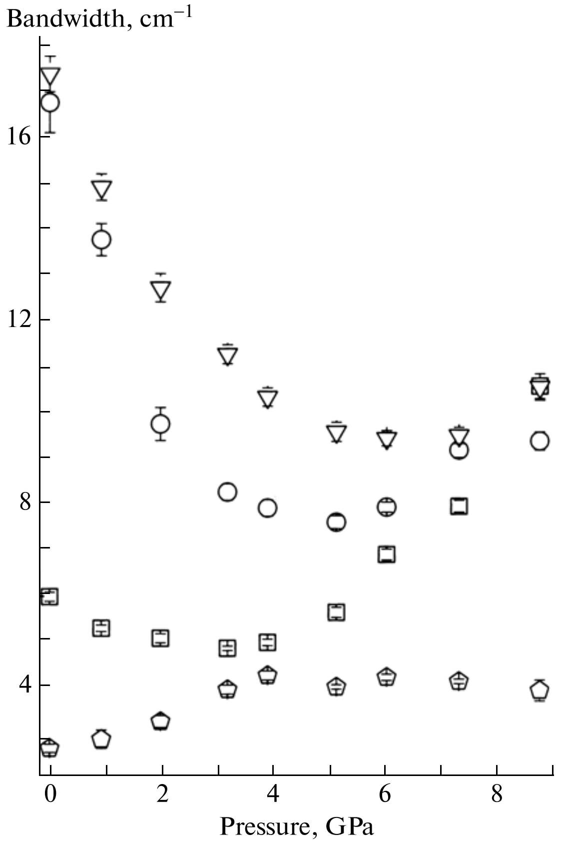

Fig. 4. Pressure dependence of the half-width of the phonon bands in the Raman spectrum of the naphthalene crystal at room temperature for phonons with frequencies of (△) 107, (○) 123, (□) 3054, and (⬠) 1388 cm^{-1}.

with respect to pressure. The calculation of the relative density was carried out using the values B_0 = 6.727 GPa and B_0' = 7.133 taken from [2]. The left panel of the figure presents the data for four intermolecular phonons with frequencies of 46 (hexagons), 74 (squares), 107 (triangles), and 122.6 (circles) cm^{-1}. The right panel of the figure presents the data for four intramolecular phonons with frequencies of 389 (circles), 510 (triangles), 1380 (hexagons), and 3054 (squares) cm^{-1}. As can be seen from the figure, the dependence of the relative frequency Ω/Ω_0 on the relative density ρ/ρ_0 for the intramolecular phonons is well described by a quadratic function, whereas this dependence for the intermolecular phonons is linear. It should be noted that the intramolecular vibrations with a frequency of 3054 cm^{-1}, which are generated by stretching vibrations of the hydrogen atoms along the C–H bond, fall outside of this rule; i.e., the dependence of the relative frequency Ω/Ω_0 on the relative density ρ/ρ_0 for these vibrations is linear, as in the case of the intermolecular vibrations. The quadratic dependence of Ω/Ω_0 on ρ/ρ_0 for the intramolecular phonons is an obvious consequence of the van der Waals intermolecular interaction potential. The flexible molecule approximation used in the calculation of the vibrational frequencies of naphthalene [9] suggests that the intramolecular phonon frequency in the crystal is shifted with respect to the vibrational frequency of free molecules by a certain value that is determined by the intermolecular interaction and is proportional to $(\rho/\rho_0)^2$. As regards the intermolecular phonons generated by the translational and orientational vibrations of the molecules about the equilibrium positions in the crystal, the change in their frequency at a high pressure is determined by the change in the slope of the intermolecular interaction potential with variations in the equilibrium distances and orientations of the molecules. The character of the dependence of the relative frequency of intermolecular phonons Ω/Ω_0 on the relative density ρ/ρ_0 is not so obviously related to the van der Waals intermolecular interaction potential. The linear dependence of the relative frequency Ω/Ω_0 on the relative density ρ/ρ_0 for the naphthalene crystal does not necessarily be the general rule for all molecular crystals. However, it is important to note that this dependence has a peculiarity, which is also observed for the intramolecular phonons with a frequency of 3054 cm^{-1}. The abrupt change in the slope occurs at a relative density $\rho/\rho_0 \approx 1.25$ corresponding to a pressure of ~3.5 GPa (this region is hatched in Fig. 5), which can be an indication of the phase transition. It should also be noted that, in the classical work by Bridgman, the volume jump observed at a pressure of ~3 GPa was attributed to an isomorphic phase transition in the naphthalene crystal at room temperature [8]. In later works concerned with the study of the *T*–*P* phase diagram of the naphthalene crystal at pressures up to 5 GPa and the Raman spectrum of the naphthalene crystal at pressures up to 3 GPa, this phase transition was not observed [3, 5, 6]. In the present work, we revealed a specific feature in the Raman spectra of the naphthalene crystal that takes place at a slightly higher pressure, which, possibly, can be associated with the shift in the *T*–*P* diagram due to the higher temperature of the crystal.

The obtained results indicate that the intramolecular vibrations of the naphthalene crystal have specific features due to the stretching vibrations of the hydrogen atoms along the C–H bond. Their behavior under high pressure partially resembles the behavior of the intermolecular phonons: the pressure shift of the frequency of these vibrations considerably exceeds the pressure shift of the frequency of other intramolecular phonons, and the dependences of the relative frequency Ω/Ω_0 on the relative density ρ/ρ_0 are linear and have a peculiarity at a pressure $P \sim 3.5$ GPa. In our opinion, these features are associated with the environment of the molecule in the naphthalene crystal cell and determined by the shortened distances between the hydrogen atoms of the neighboring molecules. The distances between the hydrogen atoms of

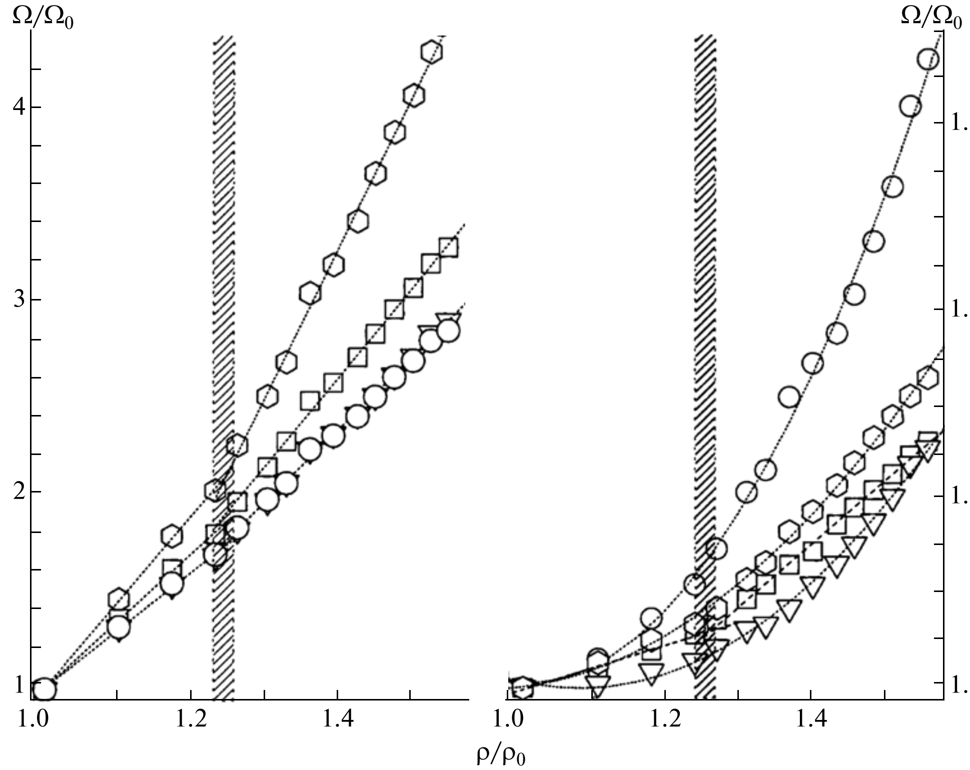

Fig. 5. Dependences of the relative phonon frequency (Ω/Ω_0) on the relative crystal density (ρ/ρ_0) for intermolecular phonons with frequencies of (⬡) 46, (□) 74, (△) 107, and (○) 122.6 cm^{-1} (left panel) and intramolecular phonons with frequencies of (○) 389, (△) 510, (⬡) 1380, and (□) 3054 cm^{-1} (right panel). Dotted lines correspond to the approximation of the experimental data by the linear and quadratic functions.

the neighboring molecules, which lie in the range from 2.40 to 2.66 Å at normal pressure, significantly decrease at a high pressure, which affects the C–H intramolecular interaction potential. A similar effect of the neighboring molecules on the stretching vibrations of the hydrogen atoms along the C–H bond was observed earlier at the Raman scattering frequencies of the molecular crystal of the hydrofullerene $C_{60}H_{36}$ at a high pressure. The interaction of hydrogen and carbon atoms in the neighboring molecules of $C_{60}H_{36}$ leads to an elongation of the C–H bond and a decrease in the frequency of stretching vibrations of the hydrogen atoms along the C–H bond at a high pressure [17]. It is also not excluded that the shortened distances between the hydrogen atoms of the neighboring molecules in the naphthalene crystal are responsible for the hysteresis of the pressure dependence for the direct and inverse pressure variations, which is especially noticeable for the intermolecular phonons and stretching C–H vibrations. Another possible cause of the hysteresis can be a slow pressure relaxation with decreasing pressure. However, the latter circumstance seems less likely, because the relaxation occurs within the first hour after the pressure release, whereas the Raman spectra were measured during several hours after the pressure release. Furthermore, the test measurements performed at a fixed pressure within five days after the next pressure release did not reveal a significant change in the phonon frequencies.

4. CONCLUSIONS

Thus, the performed measurements of the Raman spectra of a naphthalene crystal at room temperature in the pressure range up to 20 GPa have revealed some similarities in the behavior of the intermolecular phonons and the intramolecular phonons generated by stretching vibrations of the hydrogen atom along the C–H bond. In our opinion, these features are associated with the influence of short distances between the hydrogen atoms of the neighboring molecules on the intermolecular interaction potential. In addition, the linear dependence of the relative phonon frequency Ω/Ω_0 on the relative crystal density ρ/ρ_0 for intermolecular phonons has a peculiarity at $\rho/\rho_0 \approx 1.25$, which corresponds to a pressure of 3.5 GPa. These data confirm the early results obtained by Bridgman regarding the possible isomorphic phase transition in the naphthalene crystal at a pressure of 3 GPa.

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