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Spectroscopy of the Pressure-Induced Virtual Phase Transition in Hg_2I_2 Crystals

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Abstract—Raman spectra of incipient ferroelastics, namely, Hg_2I_2 crystals, have been investigated over a wide range of hydrostatic pressures. Linear pressure dependences of phonon frequencies have been obtained at $P < P_c$). It has been found that jumps and breaks are observed in these dependences at the phase transition point $P_c = 9$ kbar. The Grüneisen parameters of the Hg_2I_2 crystals have been determined and discussed. The Raman spectra of the ferroelastic phase ($P > P_c$) in different polarizations exhibit excitation of acoustic vibrations from the X point of the Brillouin zone boundary, including transverse acoustic (TA_1 and TA_2) and longitudinal acoustic (LA) phonons. The Raman spectra of the ferroelastic phase have been interpreted based on the analysis of the experimental results, and a model of the phase transition in these crystals has been proposed.

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1. INTRODUCTION

Crystals of mercury(I) halides Hg_2Hal_2 (Hal = F, Cl, Br, I) at room temperature have a very simple structure consisting of chains of linear Hal–Hg–Hg–Hal molecules oriented parallel to the optic axis $C_4(Z)$ of the crystal, which are weakly bound to each other and form the body-centered tetragonal lattice D_{4h}^{17} with two molecules per unit cell [1]. The chain-like structure of mercury(I) halide crystals leads to a very strong anisotropy of their physical properties, including elastic, optical, and other properties. These crystals exhibit unique physical properties. For example, among the known solids, these materials possess record-low velocities of transverse acoustic (TA) phonons $V_{[110]}^{[1\bar{1}0]} = 347$ (Hg_2Cl_2) and 253 m/s (Hg_2I_2), record-high birefringences $\Delta n = +0.66$ (Hg_2Cl_2) and +1.48 (Hg_2I_2), and acousto-optical interaction constants $M_2 = 640 \times 10^{-15}$ s^3/kg for the TA wave in Hg_2Cl_2 and $M_2 = 4284 \times 10^{-15}$ s^3/kg in Hg_2I_2 [2].

Owing to the aforementioned unique properties, mercury(I) halide crystals have been successfully used as base elements of polarizers, acoustic delay lines, acousto-optical filters, modulators, deflectors, and others.

Considerable interest expressed in the family of isomorphous mercury(I) halide crystals is also associated with the fact that they have become model crystalline systems for the investigation of general problems of structural phase transitions. Upon cooling to $T_c = 186$ (Hg_2Cl_2) and 144 K (Hg_2Br_2), these crystals undergo improper ferroelastic phase transitions $D_{4h}^{17} \longrightarrow D_{2h}^{17}$ from the tetragonal phase to the orthorhombic phase, which are induced by the condensation of the "slowest" and lowest-frequency TA branch at the X point of the Brillouin zone boundary in the tetragonal paraelectric phase. At temperatures $T \le T_c$, these transitions are accompanied by the doubling of the unit cell parameter, the $X \longrightarrow \Gamma$ folding of the Brillouin zone, the generation of spontaneous strains, and the formation of ferroelastic domains [3, 4].

However, the isomorphous Hg_2I_2 crystals do not undergo a ferroelastic phase transition at atmospheric pressure even upon cooling to very low temperatures (down to 1.5 K), but the Raman spectra of these crystals exhibit a softening of one of the low-intensity low-frequency vibrations [5, 6]. By analogy with similar effects observed in isomorphous crystals of mercury halides Hg_2Cl_2 and Hg_2Br_2, it was assumed that this vibration is an overtone of the soft TA mode from the Brillouin zone boundary (the X point). At atmospheric pressure, the Hg_2I_2 crystals are incipient ferroelastics ($T_c \approx -20$ K). The ferroelastic phase transition in these crystals has been observed only at a high hydrostatic pressure of 9 kbar ($T = 300$ K) [7, 8].

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Optical measurements of the Hg_2I_2 crystals were performed on a DILOR-Z24 triple-monochromator Raman spectrometer with a helium–neon laser at a low power (from several units to several tens of milliwatts). The crystals were cleaved along the {110} cleavage planes and cut along the {001} planes. Then, the

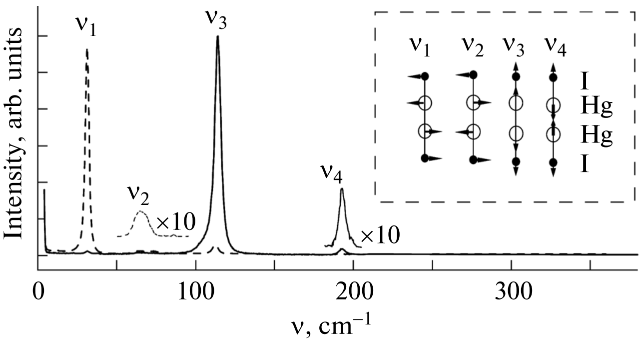

Fig. 1. Raman spectra of Hg_2I_2 crystals in different polarizations: *XZ* (*YZ*) (dashed lines) and *ZZ* (solid lines). The inset shows the normal phonon coordinates.

samples for measurements were ground and polished. The samples with sizes of ~5 × 5 × 5 mm were placed in a stand-alone optical chamber of high hydrostatic pressure, in which polarization optical investigations could be carried out at pressures ranging from zero to 15 kbar [9]. The pressure in the chamber was measured using a manganin sensor with an accuracy of better than 0.03 kbar.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the Raman spectra of the Hg_2I_2 single crystals at room temperature and normal atmospheric pressure. The spectra contain two lines (ν_1 and ν_2) in the polarization *XZ* (*YZ*) (E_g symmetry) and two lines (ν_3 and ν_4) in the polarization *ZZ* (A_{1g} symmetry). This pattern is consistent with the results of the group-theoretical analysis, according to which the first-order Raman spectra of the studied crystals with the tetragonal lattice D_{4h}^{17} and one formula unit (four-atomic linear Hal–Hg–Hg–Hal molecule) in the primitive cell at room temperature have four allowed vibrations, namely, two doubly degenerate vibrations of the symmetry E_g (*XZ*, *YZ*) and two totally symmetric vibrations of the symmetry A_{1g} (*XX* + *YY*, *ZZ*) (given in parentheses are the Raman-active components of the polarizability). The eigenvectors of these vibrations are shown in the inset to Fig. 1. It should be noted that the first vibration of the symmetry E_g (designated as ν_1) represents a libration, i.e., the oscillating motion of the linear molecule as a whole with respect to the horizontal axis *X* (or *Y*). The second vibration of the symmetry E_g is a bending zigzag vibration (ν_2). The totally symmetric stretching vibrations of the symmetry A_{1g} correspond mainly to the Hg–Hg (ν_3) and Hal–Hg (ν_4) bond displacements.

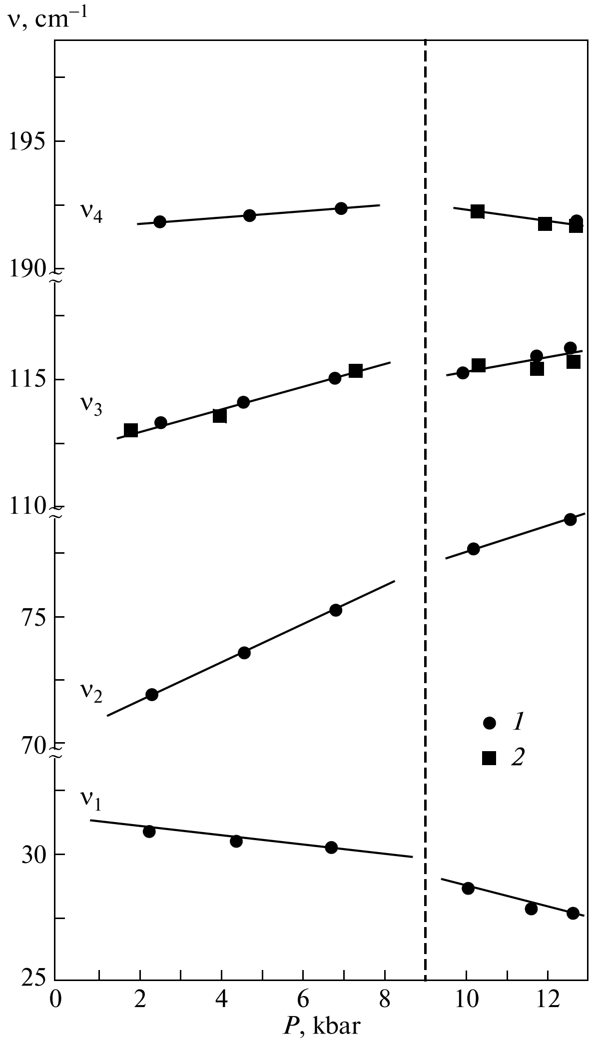

Fig. 2. Pressure dependences of the phonon frequencies for Hg_2I_2 crystals in different polarizations: (*1*) *XZ* and (*2*) *XX*. The solid lines are drawn to visualize the experimental data.

The experimental dependences of the fundamental vibrations ν_1, ν_2, ν_3, and ν_4 on the hydrostatic pressure at room temperature are shown in Fig. 2. It can be seen from this figure that the pressure dependences of these phonons can be extrapolated by straight lines in the pressure range up to the critical value $P_c = 9$ kbar (the vertical dashed line corresponds to the phase transition pressure). At a pressure $P \geq P_c$, the slopes of these dependences change; moreover, in the case of the vibrations ν_1 and ν_3, the phonon frequencies exhibit small jumps. The observed effects clearly demonstrate that these crystals undergo a phase transition with a weak first-order character. This interpretation is also confirmed by the repeatedly observed fracture of high-quality Hg_2I_2 single crystals when the pressure passes through the phase transition point P_c, which usually takes place in the case of first-order phase transitions.

The pressure dependences of the frequencies ν_2, ν_3, and ν_4 demonstrate positive values of the Grüneisen parameters (see also the table), which is usually the

Pressure coefficients of phonon frequencies

Phonon frequencies, cm^{-1} (at normal atmospheric pressure)	Symmetry of vibrations ($P < P_c$)	Pressure coefficient of the phonon frequency $\Delta\nu_i/\nu_i P \times 10^3$, kbar^{-1}	
$\nu_1 = 31$	E_g	−4.8	−12
$\nu_2 = 73$	E_g	10.0	6.4
$\nu_3 = 113$	A_{1g}	3.8	2.4
$\nu_4 = 192$	A_{1g}	0.6	−1.2

case in the majority of crystals. The intramolecular Hg—Hg stretching vibrations (ν_3) and I—Hg vibrations (ν_4) with displacements of atoms (ions) along the optic axis Z of the crystal indicate very small deformations of the bond lengths parallel to the Z axis under an applied hydrostatic pressure. This conclusion is confirmed by the minimum value of the elastic compliance modulus $S_{33} = 1.564 \times 10^{-12}$ cm^2/dyn and, accordingly, the anomalously large value of the elastic modulus $C_{33} = 104.11 \times 10^{10}$ dyn/cm^2 [10].

In the case of the bending vibration ν_2, when the displacements of the vibrating atoms (ions) occur predominantly in the basal plane (Fig. 1), the effect of hydrostatic pressure on the phonon frequencies depends, to a large extent, on the corresponding elastic moduli in the basal plane, namely, the compliance modulus (for example, $S_{11} = 54.06 \times 10^{-12}$ cm^2/dyn) and the elastic modulus ($C_{11} = 14.26 \times 10^{10}$ dyn/cm^2), and the compliance moduli in the basal plane are significantly higher than the corresponding values along the Z axis [10]. As a result, in this case (vibration ν_2), a higher strain leads to a more substantial increase in the force constants than that in the case of the vibrations ν_3 and ν_4, as well as to a stronger pressure dependence of the frequency ν_2.

A quite different pressure behavior is exhibited by the librational vibration ν_1. In this case, the Grüneisen parameter takes on negative values—a rare phenomenon in crystals. The macroscopic explanation of this effect is not obvious. However, we can attempt to relate this anomalous behavior with the competition of the force constants (attractive force constants in the case of I—Hg and repulsive force constants in the case of Hg—Hg or I—I), which are responsible for the interaction with the neighboring (along the body diagonal) molecules [11]. Our preliminary calculations, which were performed within the density functional theory with the use of empirical corrections [12] taking into account the long-range pair interaction C_6R^{-6}, also revealed that the pressure behavior of the ν_1 phonon at the center of the Brillouin zone is similar to the pressure behavior described above.

We should remind, here, the pressure behavior of the phonon frequencies in the ferroelastic phase ($P > P_c$). As was noted previously, the frequencies ν_1 and ν_3 at the phase transition point ($P = P_c$) exhibit small jumps, and the slopes of the corresponding dependences are slightly changed. Therefore, the phase transition leads to small changes in the Grüneisen parameters (see table). This is quite natural, because the symmetry of the Hg_2I_2 single crystals is reduced, the force constants change, the intermolecular distances change significantly, and the intramolecular distances change only slightly.

It is assumed that, as in the case of the Hg_2Cl_2 and Hg_2Br_2 crystals, the linear I—Hg—Hg—I molecules undergo a small "trapezoidal" bending due to the phase transition, which, in principle, can switch the sign of the Grüneisen parameter (for example, in the case of the vibration ν_4) from positive to negative. The bending of the molecules deforms mainly the I—Hg bond, which is responsible for the vibration ν_4. As a result, the observed asymmetry of the molecules at a pressure $P > P_c$ causes significant changes in the force constants themselves and in the ratio of these force constants, which can lead to another (negative) pressure dependence in the case of vibrations ν_4.

Previously, based on the known frequencies of the phonons both at the center of the Brillouin zone (see, for example, [11]) and at the Brillouin zone boundary (the X point) of the Hg_2I_2 crystals, we calculated the dispersion curves of the frequencies of acoustic and optical phonons as a function of the wave vector and investigated the effect of pressure on the frequency and dispersion of these phonons, including the soft modes.

In order to solve this problem, we developed and used the so-called hybrid model, which is a combination of the valence force field (VFF) models and the rigid ion model (RIM). In the framework of the hybrid model, the VFF model is used within the I—Hg—Hg—I molecule, where the bonds are ionic covalent, and the superposition of potentials from the VFF and RIM models is used between the molecules, where the interaction is mixed.

In the framework of this model with the LADY software [13], we calculated and plotted dispersion curves in two high-symmetry directions and obtained the parameters of the potential. As a result, we obtained a good agreement between the results of model calculations and the experimental values of the phonon frequencies both at the center of the Brillouin zone (the Γ point) and at the Brillouin zone boundary (the X point), including the LO—TO splitting of odd optical phonons. The "slowest" acoustic phonon (TA_1) is the lowest-frequency phonon at the Brillouin zone boundary (the X point) and, as will be shown below, exhibits a soft mode behavior.

We also carried out a theoretical analysis of the effect of hydrostatic pressure on the lattice dynamics

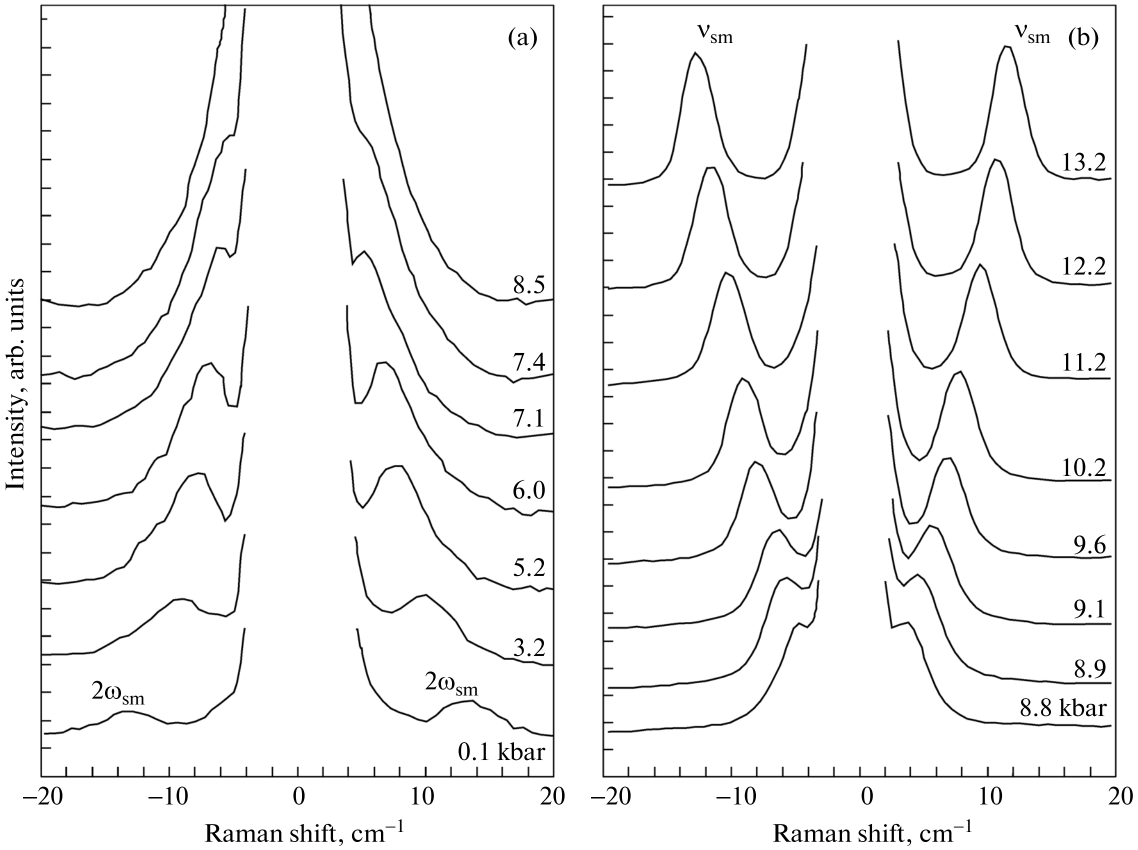

Fig. 3. Raman spectra of soft modes (the overtone $2\omega_{sm}$ and the fundamental tone ν_{sm}) at different pressures in (a) paraelectric and (b) ferroelectric crystals of mercury iodide Hg_2I_2.

of the Hg_2I_2 crystals, including the effect of hydrostatic pressure on the frequencies of the acoustic and optical phonons and on their dispersion in these crystals. It was found that an increase in the pressure leads to a significant softening of the slowest acoustic TA_1 branch (soft mode) at the X point of the Brillouin zone boundary, which correlates with the temperature dependence of the soft mode overtone [5, 6].

Based on the results of this theoretical analysis, we can already consider the experimental data. Figure 3a shows the low-frequency Raman spectra of the Hg_2I_2 single crystals at different hydrostatic pressures $P < P_c$. The Raman spectra exhibit an overtone of the soft TA branch at the X point of the Brillouin zone, i.e., the soft mode overtone $2\omega_{sm}$, which is allowed in the polarizations XX, YY, ZZ, and XY. Since the soft TA branch has the symmetry B_{3u} at the X point Brillouin zone, the symmetry of the wave vector group at this point, i.e., D_{2h}, and, therefore, the selection rules for the overtone of the TA branch at the X point of the Brillouin zone have the following form: $B_{3u} \cdot B_{3u} = A_g (XX, YY, ZZ) + B_{2g} (XY)$. As can be seen from Fig. 1, an increase in the pressure leads to a significant shift in the maximum of the overtone $2\omega_{sm}$ toward lower frequencies from 13 to 6 cm^{-1} ($P \approx 7.5$ kbar) and to a nonmonotonic variation in the intensity (the abnormal increase in the intensity at low pressures $P \longrightarrow P_c$ is associated with an increase in the transparency of the sample) due to the short-wavelength shift of the absorption edge in the red spectral region. With a further increase in the pressure, the weak line $2\omega_{sm}$ in the spectrum approaches the strong maximum of Rayleigh scattering and "merges" with it. This is the reason why we cannot trace the behavior of the soft mode overtone up to the phase transition pressure P_c.

Figure 3b shows the first-order Raman spectra of the exciting soft mode ν_{sm} upon the phase transition, the manifestation of which is induced by the doubling of the unit cell and the $X \longrightarrow \Gamma$ folding of the Brillouin zone. The considered soft mode is already the optical vibration of the symmetry A_g (XX, YY, ZZ). This vibration corresponds to almost the same out-of-phase displacements of bent incongruent trapezoidal I—Hg—Hg—I molecules in the adjacent {110} planes as those observed in the paraelectric phase (the X point of the Brillouin zone). It can be seen from Fig. 3b that an increase in the pressure to $P > P_c$ leads to an increase in the frequency and intensity of the fundamental tone of the soft mode. The line ν_{sm} has a small half-width

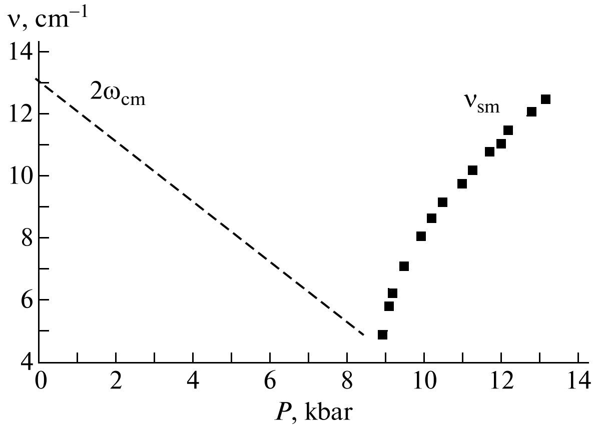

Fig. 4. Pressure dependences of the overtone $2\omega_{sm}$ and fundamental tone ν_{sm} of soft modes in Hg_2I_2 crystals.

(i.e., weak attenuation) and the highest intensity in the totally symmetric components (*XX* and *YY*), which is comparable with the intensity of fundamental vibrations in the paraelectric phase of these crystals.

The pressure (isothermal) dependences of the frequencies of soft modes both in the paraelectric phase (overtone $2\omega_{sm}$) and in the ferroelectric phase (fundamental tone ν_{sm}) were obtained by the simulation of the experimental spectra. These dependences are shown in Fig. 4. A linear pressure dependence of the frequency of the soft mode overtone $2\omega_{sm}$ is observed in the paraelectric phase over the entire pressure range under investigation.

The right dependence shown in Fig. 4 is the dependence of the frequency of the fundamental tone of the soft mode (the Γ point of the Brillouin zone in the ferroelectric phase) on the pressure ($P > P_c$), which is close to a cubic dependence and, as a first approximation, can be described by the power law $\nu_{sm} \sim (P^*)^{\beta}$ (where $P^* = (P - P_c)/P_c$ is the reduced pressure) with the exponent $\beta = 1/3$. However, in order to strictly determine the critical exponent β, the dependence $\nu_{sm}(P^*)$ was constructedt on a double logarithmic scale.

It was found that the critical exponent β for the ferroelectric phase changes from 0.35 to 0.28; i.e., the experimental curve cannot be adequately described by the aforementioned power-law dependence (1/3) in the entire pressure range used in this work at $P \gtrsim P_c$ (8.7–13.0 kbar). It should be recalled that, for the second-order phase transition described by the phenomenological Landau theory, the critical exponent should be equal to 1/2. For the approximation of the curve $\nu_{sm}(P)$, in the expansion of the thermodynamic potential in powers of small order parameters (see, for example, [3, 4]) it would be needed to use powers higher than the fourth ones, at least the sixth power. Then, the experimental curve $\nu_{sm}(P)$ will be described by a polynomial consisting of terms of the type $(P - P_c)^{1/2}$ and $(P - P_c)^{1/4}$. In this case, as a first approximation, we can obtain the critical exponent close to 1/3, which will depend on the pressure P. Generally speaking, this is the case of the phase transition close to the tricritical point, which was previously successfully confirmed in the case of temperature-induced phase transitions in Hg_2Cl_2 and Hg_2Br_2 crystals [3, 4].

A quite different behavior is exhibited by the frequency of the soft mode in the paraelectric phase (the *X* point of the Brillouin zone), when the Hg_2I_2 crystals demonstrate a unique linear pressure dependence. This behavior of the soft mode, taking into account the linear dependence $T_c(P_c)$ [6] (linear phase diagram), is difficult to perceive in the framework of the Landau theory of second-order phase transitions. In this case, we should observe a quadratic dependence of the frequency of the soft mode on the pressure $\omega_{sm}^2 \sim (P_c - P)$ or on the temperature $\omega_{sm}^2 \sim (T - T_c)$. The latter dependence is observed in the case of the Hg_2Cl_2 and Hg_2Br_2 crystals [3, 4]. Possibly, the phase transition in Hg_2I_2 crystals also occurs in the vicinity of the tricritical point. However, this transition is a weak first-order phase transition, even though it is sufficiently strong that the Landau theory would be inapplicable, unlike the Hg_2Cl_2 and Hg_2Br_2 crystals, where the phase transitions occur directly at the tricritical point and in its vicinity (from the side of the second-order phase transition), respectively. We also cannot ignore here that this is the case of the virtual phase transition (Hg_2I_2) induced by a high hydrostatic pressure.

The investigation of phase transitions in the isomorphous crystals Hg_2Cl_2 and Hg_2Br_2 revealed new lines (phonons) in the Raman spectra of the ferroelastic phase (at $T < T_c$ or $P > P_c$) due to the phase transition, the doubling of the unit cell, and the $X \longrightarrow \Gamma$ folding of the Brillouin zone [4]. In these experiments, the authors observed excitation of all odd phonons, primarily the acoustic vibrations TA_1, TA_2, and LA. These phonons were excited in specific regions of the spectrum and for the corresponding polarization. The irreducible representations and the corresponding polarizations of the exciting phonons were determined by multiplying the irreducible representations of the soft mode and representations of other phonons of our interest at the *X* point of the Brillouin zone boundary. Since the soft mode at the boundary of the Brillouin zone (the *X* point) has the symmetry B_{3u}, we obtain the following results: $B_{3u} \cdot B_{3u} = A_g$ (*XX*, *YY*, *ZZ*) for TA_1 (soft mode), $B_{3u} \cdot B_{1u} = B_{2g}$ (*ZX*, *XZ*) for TA_2, and $B_{3u} \cdot B_{2u} = B_{1g}$ (*XY*) for LA (given in parentheses are the polarizations in which the "former" acoustic phonons exciting in the spectrum of the ferroelastic phase are allowed). All these selection rules were realized in the Raman spectra of the Hg_2Cl_2 Hg_2Br_2 crystals at $T < T_c$.

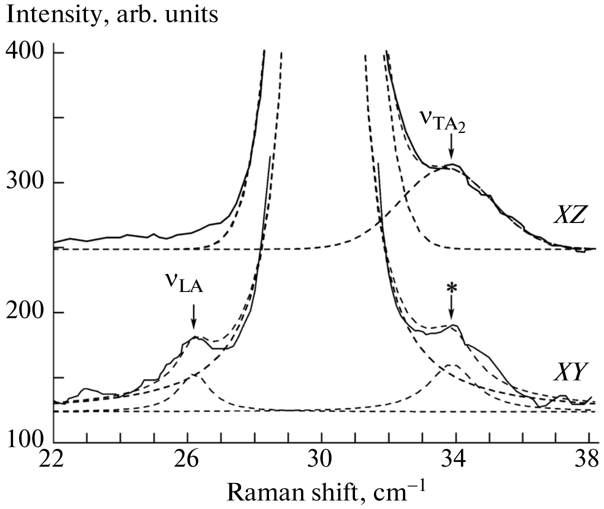

Fig. 5. Typical spectra of the exciting acoustic phonons TA_2 and LA ($P = 10$ kbar and $T = 155$ K) induced by the phase transition in Hg_2I_2. Dashed lines represent the results of the computer simulation of the experiment. The asterisk indicates the TA_2 phonon induced in the forbidden polarization due to the depolarization of light by thick sapphire windows of the pressure chamber.

Since the Hg_2I_2 crystals are isomorphous with the Hg_2Cl_2 and Hg_2Br_2 crystals, all the aforementioned group-theoretical and symmetry approaches were used in the investigation of the exciting odd predominantly acoustic vibrations from the boundary of the Brillouin zone in the paraelectric phase of the Hg_2I_2 crystals. As was shown above, at high hydrostatic pressures, these crystals exhibited excitation of the fundamental tone of the soft mode (TA_1) for the polarizations *XX*, *YY*, and *XY* in the first-order Raman spectra due to the phase transition and the $X \longrightarrow \Gamma$ folding of the Brillouin zone.

It was natural to attempt to reveal the TA_2 phonon in the allowed geometries of the experiment and in the corresponding polarizations, which was done by us. Since we previously investigated the dependence $T_c(P_c)$ [6], we could now attempt to create the best conditions for the manifestation and detection of the TA_2 phonon by analyzing the phase diagram in the region of the existence of the ferroelastic phase $P(T) > P_c(T_c)$. This phonon was revealed in the Raman spectra only in the ferroelastic phase for the polarization *ZX* (*XZ*) (Fig. 5).

The most difficult problem was to reveal, in the spectra of the ferroelastic phase, manifestations of the longitudinal acoustic phonon LA, which should be allowed in the spectrum only in the geometry *XY*. Despite the low intensity of this exciting phonon, the problem was solved but only in specific ranges of temperatures and pressures and naturally in the region of the existence of the ferroelastic phase (Fig. 5).

4. CONCLUSIONS

In this work, we measured and investigated the Raman spectra of Hg_2I_2 crystals in a wide range of hydrostatic pressures. It was demonstrated that the experimental Raman spectra are consistent with the results of the group-theoretical analysis. Linear pressure dependences of the phonon frequencies were obtained at $P < P_c$. It was found that jumps and breaks are observed in these dependences at the phase transition point $P_c = 9$ kbar. The Grüneisen parameters of the Hg_2I_2 crystals were calculated. The spectra of the ferroelastic phase ($P > P_c$) in different polarizations exhibit excitation of new lines from the *X* point of the Brillouin zone boundary, including all acoustic vibrations, i.e., two transverse acoustic (TA) and longitudinal acoustic (LA) phonons. The Raman spectra of the ferroelastic phase were interpreted based on the analysis and comparison of the experimental data and theoretical results, and a model of the phase transition induced by a hydrostatic pressure in the Hg_2I_2 crystals was proposed.

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