

Effects of Pressure-Induced Phase Transition in Model Hg_2Br_2 Ferroelastics

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Abstract—Raman spectra of model improper ferroelastics (Hg_2Br_2 crystals) have been analyzed in a wide range of hydrostatic pressures. The baric dependences of the phonon frequencies are obtained. The revealing and anomalous behavior of the soft mode, which is genetically related to the acoustic phonon (TA_1) at the Brillouin zone boundary (point X) of the tetragonal phase, are most interesting. The buildup of the second acoustic phonon (TA_2) from the same point has also been found in the ferroelastic-phase spectra, and its baric behavior has been investigated. The splitting of doubly degenerate phonons of the E_g symmetry has been revealed at fairly high pressures and explained.

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Crystals of halides of monovalent mercury (Hg_2Hal_2 , $\text{Hal} = \text{F}, \text{Cl}, \text{Br}, \text{or I}$) have a very simple structure at room temperature, which consists of chains (oriented parallel to the $C_4(Z)$ optical axis) of weakly bound linear molecules $\text{Hal}-\text{Hg}-\text{Hg}-\text{Hal}$, which form a body-centered tetragonal lattice D_{4h}^{17} with two molecules in a unit cell (Fig. 1) [1]. The chain structure of these crystals leads to very strong anisotropy of their physical properties (including elastic, optical, etc.). These crystals exhibit unique physical properties. For example, they are characterized by unprecedentedly low (among solids) transverse speeds of sound (TA) ($V_{[110]}^{[1\bar{1}0]} = 282$ m/s (Hg_2Br_2) and 253 m/s (Hg_2I_2)), unprecedentedly high birefringence ($\Delta n = +0.85$ (Hg_2Br_2) and $+1.48$ (Hg_2I_2)), and acousto-optic interaction for the TA wave ($M_2 = 1804 \times 10^{-18}$ CGS units (Hg_2Br_2) and 4284×10^{-18} CGS units (Hg_2I_2)) [2].

The aforementioned unique properties make it possible to successfully apply these crystals in technology as main elements of polarizers, acoustic delay lines, acoustooptical filters, modulators, deflectors, etc.

The great interest in this family of isomorphous crystals is also due to the fact that they are model crystal-line systems for analyzing general problems of structural phase transitions (PTs). Upon cooling down to $T_c = 186$ K (Hg_2Cl_2) and 144 K (Hg_2Br_2), these crys-

tals undergo improper ferroelastic PTs $D_{4h}^{17} \rightarrow D_{2h}^{17}$ from the tetragonal phase to the orthorhombic one. The PTs are induced by condensation of the slowest (with the lowest frequency) TA branch at the point X of the Brillouin zone (BZ) boundary of the tetragonal paraelectric phase and accompanied (at $T \leq T_c$) by the unit-cell doubling, $X \rightarrow \Gamma$ umklapp in the BZ, and occurrence of spontaneous deformation and ferroelastic domains [3–5].

Notably, no PT occurs in isomorphous Hg_2I_2 crystals at atmospheric pressure even upon cooling down to very low temperatures (1.5 K); however, the softening of one of weak low-frequency vibrations was observed in the Raman spectra [6]. It was suggested by the analogy with similar effects in isomorphous Hg_2Cl_2 and Hg_2Br_2 crystals that this vibration is an overtone of the soft TA mode from the BZ boundary (point X). At atmospheric pressure, Hg_2I_2 crystals are virtual ferroelastics ($T_c \approx -20$ K). The PT in these crystals was implemented only under a high hydrostatic pressure; the PT pressure at room temperature is $P_c = 9$ kbar [7]. Much attention has been paid to analysis of the baric behavior of the soft modes in both paraelectric ($P < P_c$) and ferroelastic ($P > P_c$) phases [8, 9].

Recently, we have theoretically and experimentally investigated isomorphous and model ferroelastic Hg_2Cl_2 [10], analyzed the baric behavior of phonons (including soft ones), and found a fundamental effect—new structural PT.

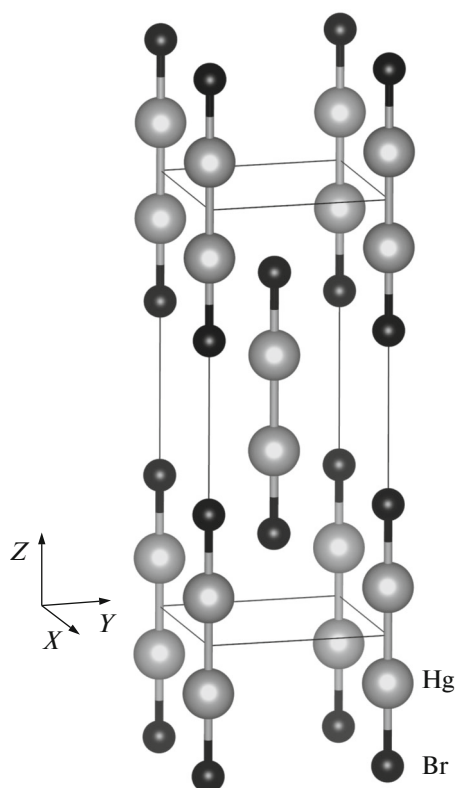


Fig. 1. Hg_2Br_2 lattice at room temperature and normal atmospheric pressure.

The purpose of this Letter was to continue these baric studies for different model and isomorphic crystals (Hg_2Br_2).

The experiments were carried out under a high hydrostatic pressure (up to 13 GPa) on a system with diamond anvils at a temperature of 295 K. The chamber with the sample was 0.25 mm in diameter and 0.1 mm high. Different oils (at pressures up to 4–5 GPa) and thoroughly dehydrated mixture of ethyl and methyl alcohols (at higher pressures) were used as the pressure-transfer medium. The pressure in the diamond chamber was determined based on the shift of the luminescence band of a ruby microcrystal placed near the sample under study [11]. The error in measuring the pressure did not exceed 0.05 GPa.

To obtain Raman spectra, the polarized 514.5-nm radiation of an Ar laser (Spectra-Physics Stabilite 2017) with a power of 100 mW (20 mW on the sample) was used for excitation. The spectra in the 180° geometry were recorded by a Horiba Jobin Yvon T64000 spectrometer in the frequency range of 20–400 cm^{-1} .

Prior to the experiments, the Hg_2Br_2 crystals were split over the $\{110\}$ cleavage plane and cut over the $\{001\}$ planes; then the samples for measurements were fitted to the necessary size. The samples no larger than $\sim 0.25 \times 0.1$ mm in size were placed in the chamber

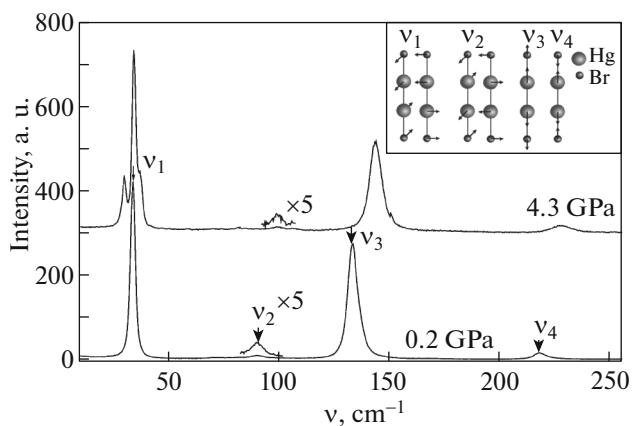


Fig. 2. Raman spectra of Hg_2Br_2 crystals at low (0.2 GPa) and high (4.3 GPa) hydrostatic pressures. The normal phonon coordinates are shown in the inset.

with diamond anvils, which allows one to carry out optical analyses (including polarization ones) at pressures from 0.2 to 13 GPa.

Figure 2 shows the Raman spectra (RSs) of the Hg_2Br_2 single crystals under study recorded at room temperature and a pressure of 0.2 GPa in the diamond chamber. Two lines resolved in the XZ (YZ) polarization (E_g symmetry), ν_1 and ν_2 , and two lines resolved in the ZZ polarization (A_{1g} symmetry), ν_3 and ν_4 , can be observed in the spectra, which is in agreement with the results of the group-theoretical consideration. According to this approach, the first-order RSs of these crystals, which have a tetragonal lattice with the D_{4h}^{17} symmetry and one formula unit (four-atom linear molecule $\text{Br}-\text{Hg}-\text{Hg}-\text{Br}$) in a primitive cell at room temperature, have four resolved vibrations: two doubly degenerate vibrations with the E_g (XZ , YZ) symmetry and two totally symmetric vibrations A_{1g} ($XX + YY$, ZZ) (the polarizability components that are active in the RSs are given in the parentheses). The eigenvectors (normal coordinates) of these vibrations are also shown in Fig. 2 (see the inset). Note that the first doubly degenerate vibration with the E_g symmetry is libration (rocking of a linear molecule as a whole with respect to the horizontal X (or Y) axis) and denoted as ν_1 . The second vibration with the E_g symmetry is deformation zigzag vibration (ν_2). The totally symmetric stretching vibrations A_{1g} correspond mainly to the $\text{Hg}-\text{Hg}$ (ν_3) and $\text{Br}-\text{Hg}$ (ν_4) displacements.

Figure 2 also shows the spectrum of the Hg_2Br_2 crystal under high (4.3 GPa) hydrostatic pressure, which mainly correlates with the spectrum for 0.2 GPa; however, it exhibits significant and comparable shifts of the frequencies ν_2 , ν_3 , and ν_4 ; in the vicinity of librational vibration ν_1 , both small shifts of phonon frequencies and their anomalous behavior

(including splitting of degenerate vibrations $\nu_1(E_g)$) are pronounced (see also Fig. 3).

To illustrate the PT effects in these crystals, the set of RSs at different hydrostatic pressures in the low-frequency region ($0\text{--}50\text{ cm}^{-1}$) is shown in Fig. 3. The main result is manifestation (observation) of soft phonon $\nu_{\text{sm}}(\text{TA}_1)$ in the spectra (in the low-frequency region and in the vicinity of librational vibration ν_1), the frequency of which anomalously decreases with a decrease in pressure ($P \rightarrow P_c$). The baric dependence of this phonon frequency is $\nu_{\text{sm}} \sim [((P - P_c)/P_c)/P_c]^\beta$, where the PT pressure is $P_c = 0.3\text{ GPa}$ at room temperature and parameter $\beta = 0.4 \pm 0.02$. In principle, this dependence does not contradict the model of PT occurring near the tricritical point obtained previously [3–5] based on the temperature behavior of the soft mode, which is similar to that observed in this study.

Here, we should mention some other anomalous effects related to the lattice dynamics of these crystals (mainly, PT and BZ “collapse” in the $X \rightarrow \Gamma$ direction). As a result, odd vibrations (acoustic and IR-active) from the BZ boundary (point X) become allowed in the spectrum; in particular, the second transverse acoustic branch (TA_2) from the BZ boundary from point X occurs.

In principle, we could find the manifestation of the longitudinal acoustic branch from point X of the BZ and IR-active phonons from this point in the spectra (as, for example, in the case of Hg_2I_2 crystals) [7, 8]. However, this is a rather complex problem because experiments in the diamond chamber with small microcrystallites and small chamber aperture reduce the useful signal several times. In addition, one must take into account the influence of the multidomain state of the samples under study and considerable redshift of the absorption edge, which reduces the transparency of the samples under study with an increase in the chamber pressure.

We also observed in the spectrum the splitting of the doubly degenerate vibration ν_1 into two components, which is related to the presence of two non-equivalent domain types with the scattering tensor components XZ and YZ in the Hg_2Br_2 sample under study (plate).

The experimental dependences of fundamental vibrations ν_1 , ν_2 , ν_3 , and ν_4 on the hydrostatic pressure (Figs. 2, 3) were also obtained at room temperature. Note that the frequencies of phonon ν_1 barely depend on pressure (i.e., the Gruneisen constants, which characterize its baric behavior, are very small or even negative). Similar effects also occurred in the case of Hg_2I_2 crystals [9]. Radically different (anomalous) behavior was exhibited by vibrations ν_2 , ν_3 , and ν_4 , which undergo strong frequency shifts upon increas-

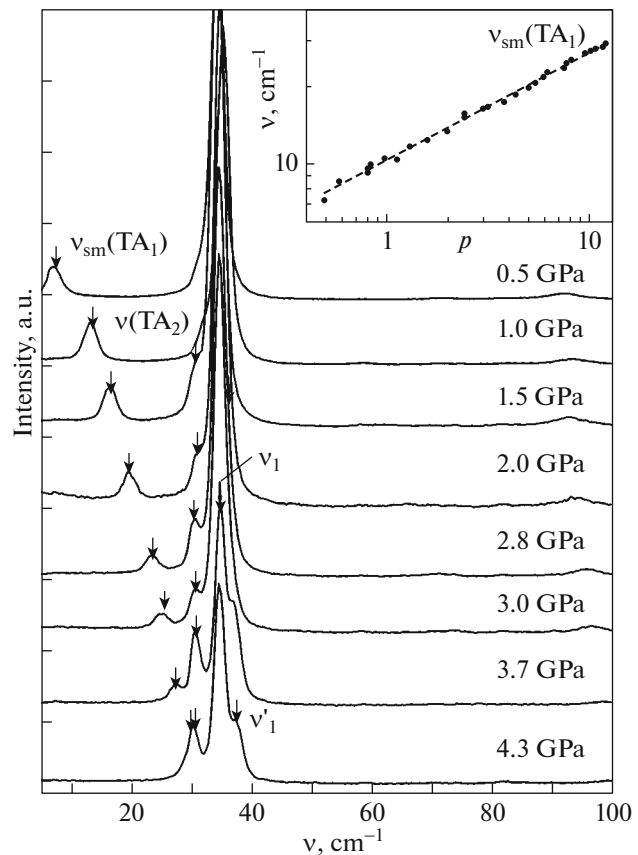


Fig. 3. Low-frequency Raman spectra of Hg_2Br_2 crystals at different hydrostatic pressures. The dependence of the soft-mode frequency $\nu_{\text{sm}}(\text{TA}_1)$ on the reduced pressure $p = P/P_c - 1$ is shown in the inset on a double logarithmic scale.

ing the hydrostatic pressure (Fig. 2) and, therefore, have large and positive Gruneisen constants.

Thus, having analyzed the RSs of Hg_2Br_2 crystals at high hydrostatic pressures, we revealed the build-up of phonons (including soft ones) in the Raman spectra, interpreted and discussed the results obtained, and confirmed the model of the $D_{4h}^{17} \rightarrow D_{2h}^{17}$ PT proposed for the PT induced by cooling Hg_2Br_2 [3–5].

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