

Lattice Dynamics and Baric Behavior of Phonons in Hg_2Cl_2 Crystals at High Hydrostatic Pressures

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Abstract—A theoretical model based on long-range dispersion corrections of the charge density functional is proposed for model Hg_2Cl_2 calomel crystals, typical representatives of molecular inorganic compounds where the intermolecular interaction is found to play an important role. This model successfully describes the electronic state and the phonon spectrum of the above crystal, predicts the earlier unstudied phase transition at high hydrostatic pressure. Study of the baric behavior of the phonon spectrum with Raman spectroscopy observes the soft mode in the low-symmetry orthorhombic phase with the frequency softening as the pressure rises. Pressures above 9 GPa considerably transform the Raman spectra, indicating a structural phase transition.

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INTRODUCTION

So-called molecular crystals (MCs) stand out among the wide variety of crystal systems. They are formed by molecules linked with one another by long-range forces (i.e., hydrogen bonds and Van der Waals forces). Inside the molecules, the atoms are coupled by much stronger (covalent or ionic) bonds.

Among the inorganic molecular crystals that undergo structural phase transitions, the Hg_2Hal_2 univalent halide crystals (Hal = F, Cl, Br, I) stand out and are often used as model objects in studying the phase transitions general problems. These crystals are composed of Hal–Hg–Hg–Hal linear molecule chains that at room temperature form a bulk-centered tetragonal lattice (a D_{4h}^{17} space group); upon cooling to $T_c = 186$ K (Hg_2Cl_2) and $T_c = 144$ K (Hg_2Br_2), these crystals undergo $D_{4h}^{17} \rightarrow D_{2h}^{17}$ ferroelastic phase transitions from the tetragonal phase to the orthorhombic. The phase transitions are induced by the condensation of the slowest TA branch with the lowest frequency at the X-point of the boundary of the Brillouin zone (BZ) of the tetragonal paraphrase and are accompanied by the doubling of the unit cell, transfer $X \rightarrow \Gamma$ in BZ, and the emergence of spontaneous strain and ferroelastic domains [2].

NUMERICAL METHODS

Our initial calculations were made with Crystal-09 package [4, 5] in the context of the density functional theory with basis set functions represented as linear

combination of atomic orbitals (LCAO) with using the B3LYP hybride functional [3]. As the basis functions, we used the atomic functions of the Cl atom from [6] and the complete electronic valence-split basis for the Hg atom from [7] for the slightly modified pseudopotential from [8], while assuming the $5s$, $5p$, $5d$ and $6s$ states of the Hg atom in the $5s^2 5p^6 5d^{10} 6s^2$ configurations to be valence.

Latter investigations proved necessary to extend the model by adding long-range dispersion corrections to the C_6R^{-6} charge density functional [9]. Tabulated parameters for the empirical coefficients for the Cl atoms were used in our calculations, while the parameters for the Hg atoms were selected to achieve good correlation between the experimental and calculated phonon frequencies at the BZ boundary (X-point). Summation over the BZ was done using Monkhorst–Pack points (MP) of $8 \times 8 \times 8$ [10]. In order to ensure almost equal point density in the direction of each of the three reciprocal lattice vectors, a set of special MP points was reduced inversely to the translation vector of the direct lattice in the corresponding direction. For each method, we used full geometry optimization procedure with relaxation of both the lattice parameters and the atomic positions in the primitive cell. The accuracy of summation in the square lattice was assumed to be 10^{-6} for all integrals over the atomic functions, except for the exchange integrals, for which this accuracy was assumed to be 10^{-12} . Self-consistency with respect to the density matrix was brought up to 10^{-10} atomic units. for the full-energy difference per cell of two subsequent iterations.

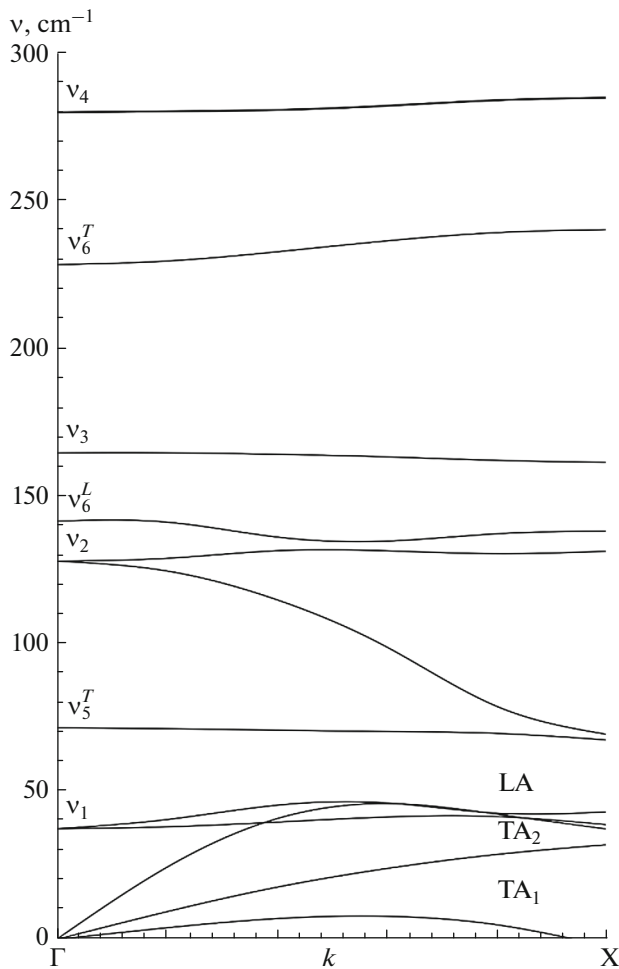


Fig. 1. Phonon dispersion in tetragonal Hg_2Cl_2 crystals for the high-symmetry $\Gamma \rightarrow X$ direction in the Brillouin zone, calculated using dispersion LRDC corrections.

EXPERIMENTAL

Our experiments under high hydrostatic pressure (up to 11.5 GPa) were made on a setup with diamond anvils at temperature of 295 K. The diameter of the chamber with the sample was 0.25 mm at a height of 0.1 mm. The pressure-transfer medium was a carefully dehydrated ethylene–methylene alcohol mixture. The Raman spectra were excited with polarized radiation of 514.5 nm from an Ar laser (Spectra-Physics Stablite 2017) with a power of 5 mW on the sample. The spectra in 180° geometry were obtained using a Horiba Jobin Yvon T64000 spectrometer over the frequency range of 8 (15) to 600 cm^{-1} .

RESULTS AND DISCUSSION

Theoretical modeling of the lattice dynamics in calomel crystals (Hg_2Cl_2) has been attempted many times. Early ab initio studies using a generalized Gordon–Kim model were unsuccessful, resulting in an

attempt to describe the main structural properties and calculate the phonon spectrum using the semi-empirical dynamic lattice model [11]. This model was then expanded and improved, allowing us to study the influence of hydrostatic pressure on acoustic and optical phonons at different high-symmetry BZ points. The development of nonempirical calculations led to successful calculation of the phonon spectrum of Hg_2Cl_2 crystals, and to estimates of the Raman tensor components in the context of the density functional theory.

Good agreement between the theory and experiment was achieved. The maximum deviation of the calculated phonon frequency from the experimental values at the center of the BZ in particular was less than 10%. The calculated Raman spectrum matches the experimental profile, and the calculated lattice parameters coincided with those determined experimentally. However, no softening of the slowest acoustic TA_1 phonon was observed at the BZ boundary. To address this shortcoming, the electronic structure and vibrational spectrum of calomel crystals were calculated in the context of the density functional theory using long-range dispersion corrections (LRDC) [9].

A theoretical model based on long-range dispersion corrections to the charge density functional was thus proposed using the model calomel crystals as typical representatives of molecular inorganic compounds in which intermolecular interaction is found to play an important role. This method demonstrated successful description of the electronic state and the phonon spectrum of the above crystal, and the detection of instability of a TA_1 acoustic branch (soft mode) at the BZ boundary (the X-point) (Fig. 1).

To explain the above, it is worth recalling that Raman spectra of paraphase Hg_2Cl_2 crystals contain two lines, ν_1 and ν_2 , in $\text{XZ}(\text{YZ})$ polarization (E_g symmetry). Line ν_1 is attributed to librational (i.e., the molecule vibrating as a whole relative to the X or Y axis), while ν_2 reflects the zigzag deformational vibrations. The ZZ and $\text{XX} + \text{YY}$ (A_{1g} symmetry) spectra also exhibit lines ν_3 and ν_4 of the fully symmetric stretching vibrations corresponding to $\text{Hg}-\text{Hg}$ (ν_3) and $\text{Cl}-\text{Hg}$ (ν_4) displacements along the Z axis. Our experimental results are in agreement with the theory group if we assume there is one linear molecule in the primitive cell of the tetragonal lattice. E_u (ν_5) and A_{2u} (ν_6) vibrations (odd with respect to symmetry vibration inversion) are allowed and emerge in the paraphase IR spectra of these crystals. They correlate with the displacement of the chlorine atom sublattice relative to the mercury atom sublattice in the basis plane and along the Z axis, respectively.

Cooling in the ferroelastic phase at $T < T_c$ (i.e., below the phase transition temperature) produces new lines in the Raman spectra of Hg_2Cl_2 single crystals from the X-point at the BZ boundary. The lines are

similar to those of the soft mode, the slowest transverse acoustic (TA_1) branch; the transverse acoustic (TA_2) IR-active branch (E_u at the BZ center); and other less intense lines in the spectrum. The phase transition is expected to induce six lines in the Raman spectra in definite polarizations, five of which were clearly observed in the experiment [2].

The instability at the BZ boundary (the X-point) (see Fig. 1) confirms the instability of tetragonal phase at absolute zero. It is worth noting that the calculations do not consider the temperature factor, and the results correspond to the crystal's state at absolute zero. In order to study the symmetry of Hg_2Cl_2 crystals, we must distort the tetragonal phase geometry, i.e., displace the atoms along the normal vector of the soft-mode vibration at the X-point of the BZ boundary. This allows us to distinguish the rhombic phase, which was found to be stable in studying the phonon spectra at different high-symmetry BZ points. The PT model in the context of the above theory coincides with the experimental results and the model proposed earlier. The estimated frequency values are shown in the table. The experiment and theory are clearly in good agreement.

Our calculations initiated our further studies of calomel crystals at high hydrostatic pressures. The above model allowed us to predict the softening of phonons at the BZ center, which is genetically related to the acoustic branch at the BZ boundary (X-point) in the paraphrase. The acoustic mode at the BZ boundary of the ferrophase (Z-point) was softened as well. The second phase transition was therefore expected at high hydrostatic pressures. Our experimental studies revealed that the rhombic phase is stable at 0.3 to 9 GPa, while the higher pressures result in structural distortion because of the second phase transition.

Figure 2 displays the Raman spectra of calomel crystals over a wide range of pressures above $P_c = 0.25$ GPa. It is important to recall that the Raman spectra of the orthorhombic phase are composed of odd-symmetry phonons (B_{1u} , B_{2u} , and B_{3u}) at the BZ boundary, since the phase transition is induced by the condensation of the odd-symmetry B_{3u} soft mode at the X-point of the BZ boundary. The phonon symmetry in these spectra is determined by multiplying the irreducible soft-mode representations and the odd phonons considered in this work. The new lines are allowed in the polarizations related to the irreducible representations in the D_{2h}^{17} orthorhombic lattice.

Our interpretation of the experimental spectra was corroborated by nonempirical calculations of the electronic structure in the context of the density functional theory using LRDCs at various pressures. The baric behavior of the lattice parameters, along with the influence of external hydrostatic pressure on the Raman spectrum of this compound was studied (Fig. 3).

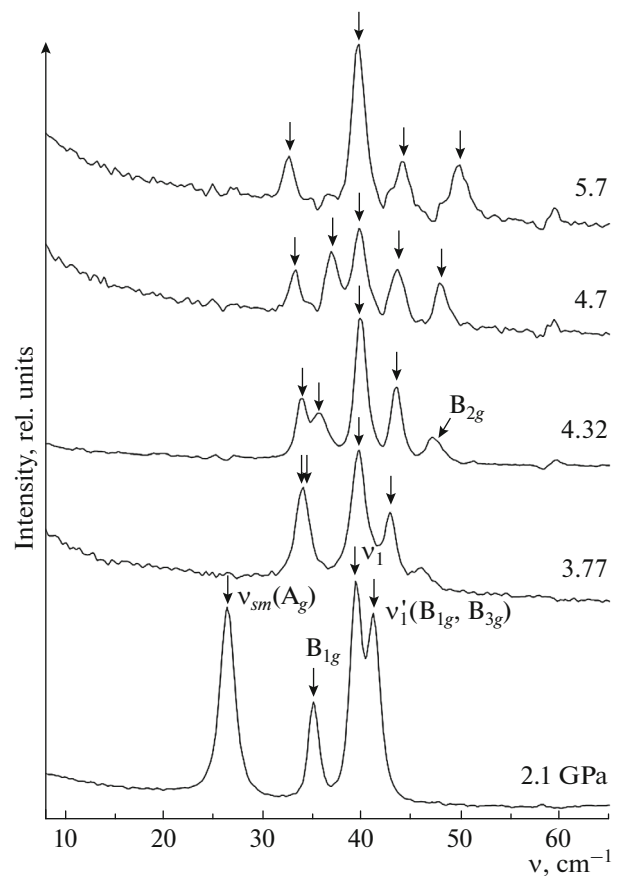


Fig. 2. Low-frequency Raman spectra of Hg_2Cl_2 crystals in the orthorhombic phase at different hydrostatic pressures ($v_{sm}(A_g)$ is the soft mode; B_{1g} is a appeared phonon genetically related to the longitudinal acoustic branch from the X-point of BZ; and v_1 and v'_1 are the librational vibration components (E_g) that emerge as degeneration vanishes in the orthorhombic phase).

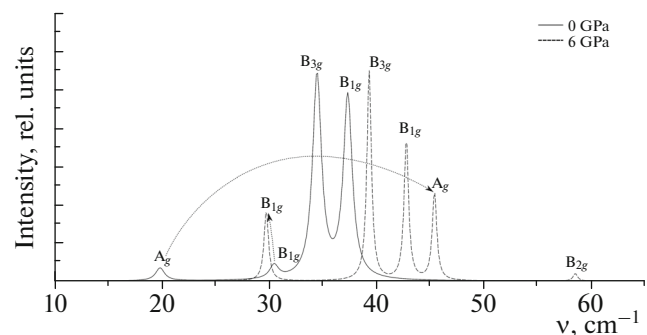


Fig. 3. Raman spectra of calomel crystals in the orthorhombic phase under ambient conditions (solid lines) and at a high hydrostatic pressure of 6 GPa (dashed lines), calculated in the context of density functional theory using LRDC.

Experimental and calculated phonon frequencies at the center and boundary of the BZ in Hg_2Cl_2 crystals

	Mode	Symmetry	Γ -point				X-point		
			Experiment [1]	DFT PBE GGA [12]	DFT B3LYP	DFT B3LYP + LRDC	Experiment*	DFT B3LYP	DFT B3LYP + LRDC
Raman, cm^{-1}	ν_1	E_g	40	35.7	40.4	37.5	45.5	43.7	38.8
	ν_2	E_g	137	134.2	127.4	128.1	148	132.4	131.49
	ν_3	A_{1g}	167	157.8	160.6	164.7	163	156.4	161.5
	ν_4	A_{1g}	275	258.8	272.6	280.0	288	277	285.0
IR, cm^{-1}	ν_5^T	E_u	67	58.13	71.8	71.7	72	67.8	67.5
	ν_5^L	E_u	135	96.5	138.9	141.6	144	139.4	138.2
	ν_6^T	A_{2u}	254	235.5	228.6	228.5	265	238.9	240.3
	ν_6^L	A_{2u}	299	280	281.1	281.8			
Acoustic, 10^3 m s^{-1}	$\nu_{[110]}^{\perp}$	E_u	0.347				6.8	21.2	-2.5
	$\nu_{[110]}^{\parallel}$	A_{2u}	1.084				39	36.2	32.1
	$\nu_{[110]}^{\parallel}$	E_u	2.054					42.4	37.3

*Experimental frequencies at X point were determined in a low-temperature phase from the frequencies of new lines emerging in the Raman spectra.

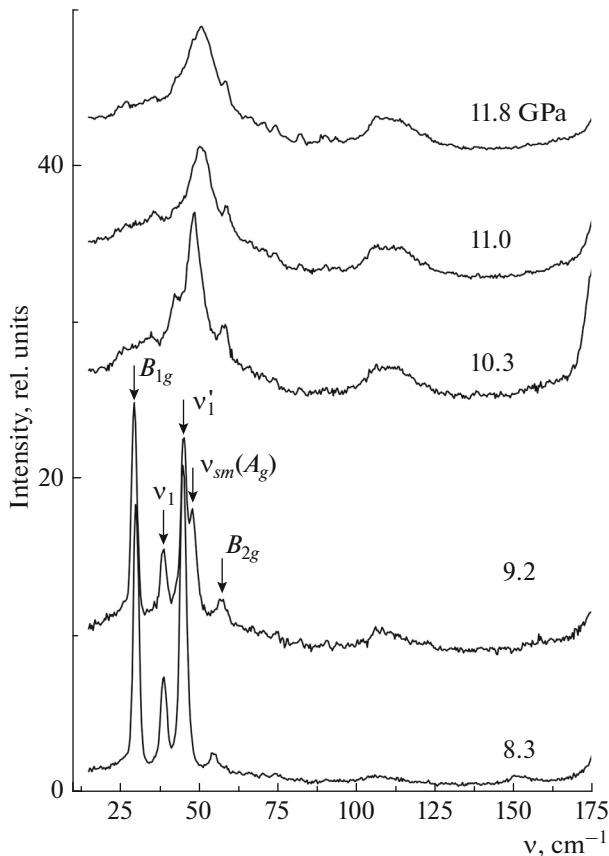


Fig. 4. Low-frequency Raman spectra of Hg_2Cl_2 crystals in the orthorhombic phase in the vicinity of the second phase transition.

A pronounced increase in the A_g soft mode frequency is evident from the figure as the pressure rises from 20 cm^{-1} ($P = 0 \text{ GPa}$) to 46 cm^{-1} ($P = 5.88 \text{ GPa}$), accompanied by a slight softening of the B_{1g} mode and a considerable increase in its intensity, along with the B_{2g} mode at 59 cm^{-1} ($P = 5.88 \text{ GPa}$) (the vibration genetically related to the IR active TO-branch with ν_5 at the X-point of the BZ in the paraphrase). The same situation was observed in our experiment (Fig. 2). As is evident from the figure, only the B_{1g} mode is softened, while the other lines are shifted upward. At a pressure of 3.77 GPa , the hardening A_g mode overlaps with the B_{1g} mode softening in the rhombic phase. A further increase in the pressure results in the overlapping of the A_g mode with the peak attributed to librational vibration ν_1 , along with the gradually increasing B_{1g} and B_{3g} librational modes splitting (vibration ν_1 in the paraphrase).

Figure 4 shows the Raman spectra of Hg_2Cl_2 crystals at high hydrostatic pressures of 9–10 GPa.

CONCLUSIONS

Pressures above 9 GPa cause drastic changes in the Raman spectra of Hg_2Cl_2 crystals. The softening lowest-frequency B_{1g} mode in particular vanishes, indicating pronounced structural modifications that are probably due to the second phase transition in this compound. Calculations for the phonon spectra at various high-symmetry BZ points revealed the softening of several vibrations at the center and boundary X and Y points of the BZ. The most pronounced mode

softening was detected at the Y point of the BZ corresponding to unit cell doubling along the long axis of the Hg_2Cl_2 molecule. Its frequency becomes imaginary at 8.95 GPa. Our calculations reveal the instability of the mode at the Y point of the BZ that causes unit cell doubling and the $D_{2h}^{17} \rightarrow D_{2h}^{16}$ structural change. According to the group theory, we should observe the emergence of mode A_g in the low-symmetry spectrum, which would be active in the XY cross-polarized Raman spectra and genetically related to the soft mode at the boundary. However, this hypothesis has yet to be confirmed because of the difficulties in preparing high-pressure polarization measurements.

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