

# Soft mode at the boundary of the Brillouin zone and nature of the phase transition in monovalent mercury-halide crystals

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With  $\text{Hg}_2\text{Cl}_2$  and  $\text{Hg}_2\text{Br}_2$  as examples, we observed for the first time a soft mode in pure ferroelastics. The soft mode was observed in the Raman scattering spectra (RSS) at temperatures below the point of the  $D_{4h}-D_{2h}$  structure phase transition. A model of the phase transition is proposed on the basis of an investigation of the singularities of the RSS.

A new interesting group of artificial single crystals was recently synthesized, namely  $\text{Hg}_2\text{Hal}_2$  (Hal—Cl, Br, I).<sup>[1]</sup> They are made up of parallel linear molecules  $\text{Hg}_2\text{Hal}_2$ , forming a tetragonal lattice  $D_{4h}^{17}(I4/mmm)$ .<sup>[2]</sup> Such a structure leads, in the case of crystals, to an unprecedented (for crystals) anisotropy of the optical<sup>[3]</sup> and acoustic<sup>[4]</sup> properties of  $\text{Hg}_2\text{Hal}_2$ , and this has attracted great attention on the part of the researchers.

In<sup>[5-7]</sup> there was observed in  $\text{Hg}_2\text{Cl}_2$  ( $T_c = 185^\circ\text{K}$ ) and  $\text{Hg}_2\text{Br}_2$  ( $T_c = 143^\circ\text{K}$ ) a structural phase transition with a decrease of the crystal symmetry to rhombic  $D_{2h}(mmm)$  and with formation of ferroelastic domains at  $T < T_c$ . The transition leads to the appearance of new low-intensity lines in the Raman-scattering spectrum (RSS) below  $T_c$ .<sup>[6]</sup> We have observed in the RSS of  $\text{Hg}_2\text{Cl}_2$  and  $\text{Hg}_2\text{Br}_2$  an extremely clearly pronounced soft mode that

has enabled us to determine the nature of the transition.

The soft mode was observed at  $T < T_c$  in the form of a narrow line in the low-frequency region of the RSS of  $\text{Hg}_2\text{Cl}_2$  and  $\text{Hg}_2\text{Br}_2$  single crystals. Figure 1 shows the section of the RSS of  $\text{Hg}_2\text{Cl}_2$  near the exciting line of an He-Ne laser at various temperatures  $T < T_c$ ; a strong dependence of the position of the line maximum on  $T_c - T$  is observed. Figure 2 shows the experimental depen-

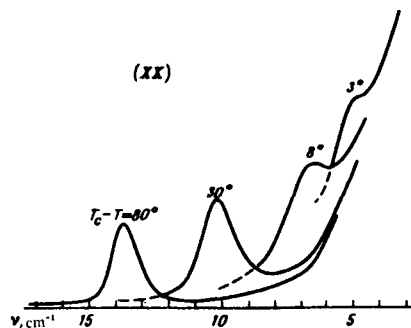


FIG. 1.

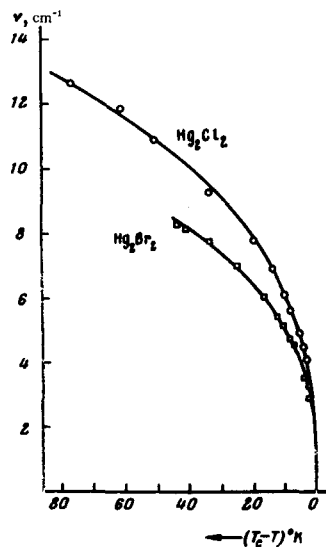


FIG. 2.

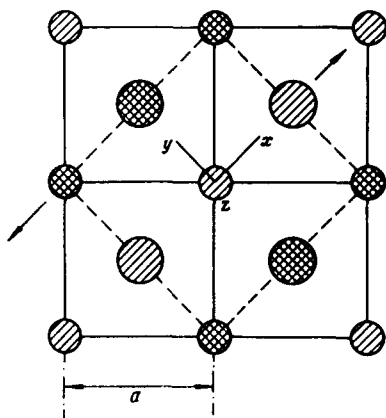


FIG. 3.

dences of the soft-mode frequency  $\omega$  on  $T_c - T$ . The points are well approximated by the curve  $\omega = \text{const}(T_c - T)^{0.35 \pm 0.02}$  (solid lines). No low-frequency line is observed in the RSS above  $T_c$ .

Altogether, three new lines appear in the Raman-scattering spectrum of  $\text{Hg}_2\text{Hal}_2$  cooled to  $T < T_c$ : 1) the already-described low-frequency soft mode; 2) the line near the librational  $E_g$  vibration ( $38 \text{ cm}^{-1}$  for  $\text{Hg}_2\text{Cl}_2$  and  $35 \text{ cm}^{-1}$  for  $\text{Hg}_2\text{Br}_2$  at  $T = 90^\circ\text{K}$ ); 3) line in the region of the transverse  $E_u$  vibration which is active in the IR absorption ( $72$  and  $52 \text{ cm}^{-1}$  for  $\text{Hg}_2\text{Cl}_2$  and  $\text{Hg}_2\text{Br}_2$  respectively at  $T = 90^\circ\text{K}$ ).

The observed phenomena in the Raman-scattering spectrum and the other known properties of the phase transitions<sup>[7]</sup> in  $\text{Hg}_2\text{Hal}_2$  can be interpreted within the framework of the following model,<sup>1)</sup> which is illustrated in Fig. 3, which shows the  $\text{Hg}_2\text{Hal}_2$  lattice projected on the (001) basal plane. The different dimensions of the circles (the traces of the linear molecules) correspond to sites shifted by  $c/2$  along the principal  $z$  axis;  $a$  and

$c$  are the parameters of the body-centered tetragonal lattice with two molecules per unit cell, which exists at  $T > T_c$  ( $D_{4h}^{17}$ ).

When cooled to  $T = T_c$ , the molecules in the neighboring (110) planes shift in opposite directions,  $[\bar{1}10]$  and  $[\bar{1}\bar{1}0]$  (arrows in Fig. 3), and becomes noncongruent (different crosshatching of the circles). This shift corresponds to condensation of the oscillations of the transverse acoustic branch, with wave vector on the boundary of the Brillouin zone (body-centered tetragonal lattice),<sup>[9]</sup> at the point  $X(a/2, a/2, 0)$ . As a result, at  $T < T_c$  the lattice becomes base-centered rhombic (bcr) with orthogonal axes  $x$ ,  $y$ , and  $z$  (class  $D_{2h}$ ). Its unit cell contains four molecules. When the volume is doubled, the point  $X$  of the Brillouin zone of the body-centered tetragonal lattice is transformed into the  $\Gamma$  point of the Brillouin zone of the base-centered rhombic lattice and consequently the oscillations at  $X$ , which are optically inactive in the tetragonal phase, are converted into the fundamental oscillations of the lattice  $D_{2h}$  and become active in first-order optical processes. This is the cause of the appearance of the new lines in the Raman scattering spectrum at  $T < T_c$ .

The table lists the results of a group-theoretical analysis of the properties of the new lines that are resolved in the Raman-scattering spectrum at  $T < T_c$ . Owing to preservation of the inversion in the transition  $D_{4h} \rightarrow D_{2h}$  and to the alternative exclusion rules, there can appear in the Raman-scattering spectrum only  $X$ -point oscillations from tetragonal-lattice branches corresponding to odd fundamental oscillations, i. e., acoustic oscillations and oscillations that are active in IR absorption. Column 2 of the table lists the properties of these branches in the point  $\Gamma(0, 0, 0)$  of the Brillouin zone of a tetragonal crystal, in accordance with the data of<sup>[9]</sup>, namely, the symmetry (representation of the group  $D_{4h}$ ), the polarization (the  $E$  vector for IR, the displacement  $u$  for acoustics), and also the type

$D_{4h} (T > T_c)$			$D_{2h}(T < T_c)$			
1	2	3	4	5	6	
$\text{Hg}_2\text{Cl}_2$	$\text{Hg}_2\text{Br}_2$				$\text{Hg}_2\text{Cl}_2$	$\text{Hg}_2\text{Br}_2$
IR spectra ( $\text{cm}^{-1}$ ) [9]						
$\omega_T = 254$	$\omega_T = 168$	$E \parallel c \quad ** A_{2u}$	$TO \quad B_{1u}$	$B_{2g}$	$zx$	
$\omega_L = 135$	$\omega_L = 93$	$E \perp c \quad E_u$	$LO \quad B_{2u}$	$B_{1g}$	$xy$	
$\omega_T = 67$	$\omega_T = 47$		$TO \quad B_{3u}$	$A_g$	$xx, yy, zz$	$72 \text{ cm}^{-1}$ $52 \text{ cm}^{-1}$
acoustics [4]						
$v_{\begin{smallmatrix} [001] \\ [110] \end{smallmatrix}} = 1.08 \text{ km/sec}^*$		$u \parallel c \quad A_{2u}$	$TA \quad B_{1u}$	$B_{2g}$	$xx$	$38 \text{ cm}^{-1}$ $35 \text{ cm}^{-1}$
$v_{\begin{smallmatrix} [110] \\ [110] \end{smallmatrix}} = 2.06 \text{ km/sec.}$			$LA \quad B_{2u}$	$B_{1g}$	$xy$	
$v_{\begin{smallmatrix} [110] \\ [110] \end{smallmatrix}} = 0.35 \text{ km/sec}$		$u \perp c \quad E_u$	$TA \quad B_{3u}$	$A_g$	$xx, yy, zz$	$13.5 \text{ cm}^{-1}$ $8.7 \text{ cm}^{-1}$
						soft mode

\*Upper index—polarization, lower index—wave vector of sound

\*\* $c$ —tetragonal axis

of branch,  $T$  or  $L$ , on the  $\Gamma$ - $X$  lines. In column 1 are given the experimental values IR frequencies at  $20^\circ\text{C}$ <sup>[9]</sup> and the experimental sound velocities  $v$  corresponding to the acoustic branches.<sup>[4]</sup> In column 3, the symmetries of the oscillation modes at the  $X$  point are characterized by the representations of the group  $D_{2h}$ , which is the group of the wave vector in  $X$ .

In column 4 is indicated the symmetry of these oscillations (of the representation  $D_{2h}$ ) at the  $\Gamma$  point of the Brillouin zone of a rhombic crystal after the transfer  $X$ - $\Gamma$ . In column 5 are given the nonzero components of the corresponding Raman-scattering tensors, while column 6 lists the experimental frequencies of the lines that are excited at  $90^\circ\text{K}$ . To identify the lines, we used in addition the experimental data on their symmetry, which are in good agreement with the calculated values (column 5). These data were obtained from the Raman scattering spectra in polarized light, using single-domain samples produced by uniaxial compression along  $y$ .

It is important to note that the oscillation frequencies  $\omega(X)$  that appear in the Raman-scattering spectrum at  $T < T_c$  (column 6) agree numerically with the data on the IR spectra<sup>[9]</sup> and on the acoustics of tetragonal crystals  $\text{Hg}_2\text{Hal}_2$ . Thus,  $\omega(X)$  of the optical branch is close to the IR frequency of the transverse  $E_u(\Gamma)$  oscillations of  $\text{Hg}_2\text{Cl}_2$  and  $\text{Hg}_2\text{Br}_2$ , which can be naturally expected when account is taken of the small dispersion of the intramolecular-oscillation branch. For  $\text{Hg}_2\text{Cl}_2$ , the known<sup>[4]</sup> sound velocities  $v$  make it possible to estimate in the Debye approximation the frequencies of the acoustic branches at the  $X$  point:

$$\omega(B_{3u}) = v \begin{bmatrix} 1 & \bar{1} & 0 \\ 1 & 1 & 0 \end{bmatrix} q_x c^{-1}, \quad \omega(B_{1u}) = v \begin{bmatrix} 0 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix} q_x c^{-1}.$$

The values  $\omega(B_{3u}) = 18 \text{ cm}^{-1}$  and  $\omega(B_{1u}) = 54 \text{ cm}^{-1}$  obtained at the values of  $v$  (column 1) and  $q_x (=1/\sqrt{2}a$ , where  $a \approx 4.5 \text{ \AA}$ ) agree well with the data of column 6, if account is taken of the dispersion of the branches ( $\omega$  is the frequency in  $\text{cm}^{-1}$ ,  $q_x$  is the reciprocal wavelength of the phonon in  $X$ , and  $c$  is the speed of light). The phase transition parameter in this model is the relative shift of the molecular layers (110). Thus, the crystals  $\text{Hg}_2\text{Hal}_2$  are "improper"<sup>[10]</sup> ferroelastics at  $T < T_c$ .

<sup>1)</sup>The model agrees also with the results of an x-ray diffraction investigation of the transition (M. E. Boiko and A. A. Vajpolin, private communication).

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