

Raman scattering of first and second orders by a soft acoustic mode from the Brillouin-zone boundary in $\text{Hg}_2(\text{Cl}_x\text{Br}_{1-x})_2$ crystals

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First-order Raman scattering of light by a soft acoustic mode from the boundary of the Brillouin zone has been observed for the first time. This manifestation of the soft mode, which is forbidden in the first-order optical spectra by the selection rules, is induced by long-range static distortions created by substitution defects and composition inhomogeneities of the mixed $\text{Hg}_2(\text{Cl}, \text{Br})_2$ crystals.

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Pure (Hg_2Cl_2 and Hg_2Br_2) and mixed [$\text{Hg}_2(\text{Cl}, \text{Br})_2$] halides of monovalent mercury undergo a structural phase transition corresponding to the shift $D_{4h}^{17} \rightarrow D_{2h}^{17}$, to a ferroelastic state with a doubled unit cell.^{1,2} The phase transition is induced by a soft transverse acoustic (TA) mode from the boundary of the Brillouin zone at the x point. Observation of this mode in the paraelectric phase ($T > T_c$) in the first-order Raman scattering spectra is forbidden by momentum selection rules. Soft modes with wave vector $q \neq 0$ are usually studied by inelastic neutron scattering. Evidence of a soft-mode vibration has been found previously³ in the Raman scattering spectra of the paraelectric phase of Hg_2Cl_2 and Hg_2Br_2 . It has been concluded from direct measurements of the frequency of the $\text{TA}(x)$ mode in these crystals by neutron scattering⁴ and from theoretical results⁵ that the line observed in Ref. 3 corresponds to a harmonic of the soft mode which is allowed by the selection rules in the Raman scattering spectrum of the paraelectric.^{6,7} A soft mode from the boundary of the Brillouin zone has not previously been observed in the first-order optical spectra.

In this letter we are reporting a study of the low-frequency Raman spectra of the mixed crystals $\text{Hg}_2(\text{Cl}, \text{Br})_2$ in the paraelectric ($T > T_c$) and in the ferroelectric ($T < T_c$). The Raman spectra were measured in polarized light with oriented single crystals with a Spex-Ramalog-5 triple Raman spectrometer with an argon laser ($\lambda = 4880 \text{ \AA}$, $P = 500 \text{ mW}$).

Figure 1 shows the Raman spectra of crystals of one of the intermediate concentrations, specifically, $\text{Hg}_2(\text{Cl}_{0.5}\text{Br}_{0.5})_2$, at $T > T_c$. The most intense line in the low-frequency region of the Raman spectra of all the mixed crystals is the soft-mode harmonic $2\nu_{sm}$ (the x point of the Brillouin zone), which has been detected previously in pure Hg_2Cl_2 and Hg_2Br_2 . The frequency of this line varies with the $\text{Hg}_2(\text{Cl}, \text{Br})_2$ composition at $T = 293 \text{ K}$, from 11.2 cm^{-1} (Hg_2Br_2) to 12.1 cm^{-1} (Hg_2Cl_2). As the temperature is lowered ($T \rightarrow T_c^+$), a softening of the harmonic ($2\nu_{sm} \rightarrow 0$) is observed in the Raman spectra of the crystals of all intermediate concentrations. On the high-frequency wing of the harmonic we can see a slight maximum ν' (Fig. 1), whose fre-

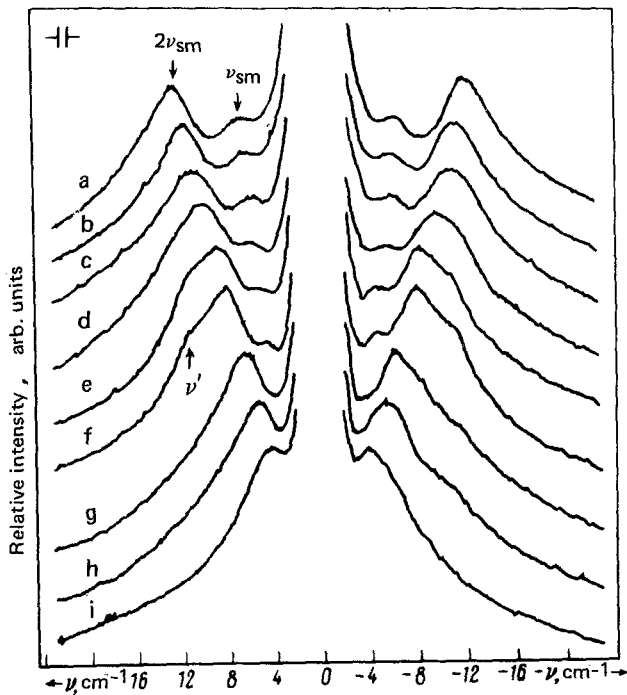


FIG. 1. Raman scattering spectra of $\text{Hg}_2(\text{Cl}_{0.5}\text{Br}_{0.5})_2$ crystals in the Stokes and anti-Stokes regions at the following temperatures: a-293; b-271; c-254; d-230; e-214; f-204; g-174; h-166; i-153 K.

quency is essentially independent of the temperature. By analogy with the pure crystals, the line ν' may be interpreted as a harmonic of the TA branch at the Δ point of the Brillouin zone.^{3,7}

The most interesting result is the appearance of the soft TA branch ν_{sm} in the first-order Raman spectra of the paraelectric phase ($T > T_c$) of the mixed crystals $\text{Hg}_2(\text{Cl},\text{Br})_2$ (Fig. 1). This branch has its maximum intensity in the spectra of the crystals of intermediate concentrations (but even in these cases, its intensity is nearly an order of magnitude lower than that of the harmonic $2\nu_{\text{sm}}$); its intensity falls off toward the extreme concentrations. The line ν_{sm} is not observed at all in the spectra of the pure crystals, Hg_2Cl_2 and Hg_2Br_2 (Fig. 3). The fundamental ν_{sm} , like the harmonic, is polarized in the components XX, YY, and XY. Despite the low intensity of the fundamental ν_{sm} and its proximity to the exciting line, we were able to reliably trace the softening of ν_{sm} by a substantial amount in the limit $T \rightarrow T_c^+$ —from 6.8 cm^{-1} to 4.5 cm^{-1} for $\text{Hg}_2(\text{Cl}_{0.5}\text{Br}_{0.5})_2$, for example (Figs. 1 and 2). It should be noted that at all concentrations the ratio of the frequency of the harmonic $2\nu_{\text{sm}}$ to the frequency of the first-order line, ν_{sm} , retains a constant value of approximately two as the temperature is changed.

The low-frequency parts of the Raman spectra of the pure and mixed mercury halides are qualitatively the same in the ferroelectric phase ($T < T_c$): In both cases, there is a single intense soft-mode line (Fig. 2). This line becomes allowed in the

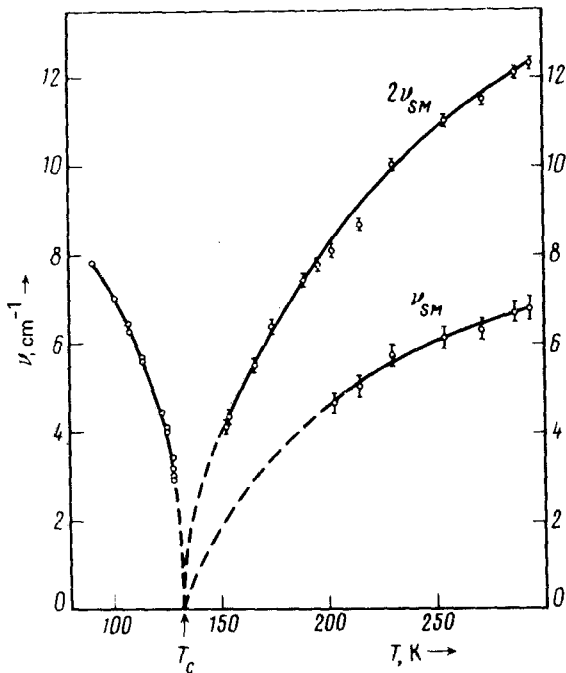


FIG. 2. Temperature dependence of the frequency of the soft phonons in the crystals $\text{Hg}_2(\text{Cl}_{0.5}\text{Br}_{0.5})_2$.

first-order Raman spectrum after the x point of the Brillouin zone of the paraelectric phase moves to the center of the Brillouin zone of the ferroelectric phase (the Γ point, $q = 0$) upon the phase transition.

What is responsible for the appearance of the soft mode from the boundary of the Brillouin zone in the first-order Raman spectrum of the $\text{Hg}_2(\text{Cl},\text{Br})_2$ crystals? At low concentrations of the Cl or Br atoms (at $x \ll 1$ or $1 - x \ll 1$, respectively) the structure of the Raman spectrum of the paraelectric phase of the mixed crystals can be studied theoretically in the approximation of noninteracting defects,⁵ under

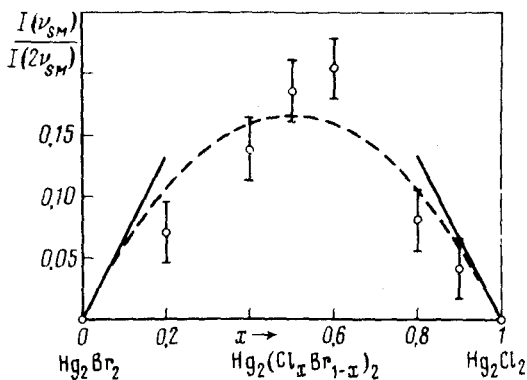


FIG. 3. Concentration dependence of the ratio of integrated intensities of the soft mode and of its second harmonic in $\text{Hg}_2(\text{Cl}_x\text{Br}_{1-x})_2$ at $T = 239$ K. Dashed and solid lines—theoretical results.

the assumption that the corresponding atoms are defects of an ideal lattice. Calculations by the method of Ref. 5 yield not only the second harmonic of the soft mode, which results from second-order scattering by thermal fluctuations of the transition parameter, but also the fundamental component ν_{sm} . This approximation, of course, yields only a linear dependence of $I(\nu_{sm})$ on the concentration x (the straight lines in Fig. 3). The point defects of this type differ from the matrix atom in effective radius; they generate static long-range distortions in the crystal which correspond to the transition parameter. In addition to the elastic scattering of light by these static distortions, there is an inelastic first-order Raman scattering, caused by the defects. The dimensions of the static distortions near an isolated defect increase in the limit $T \rightarrow T_c$, increasing the contribution of the static distortions and causing a temperature dependence of the ν_{sm} intensity: $I(\nu_{sm}) \sim (T - T_c)^{-3/2}$. According to the theory of Ref. 5, the increase in the scattering intensity should weaken toward T_c and also at high defect concentrations.

With increasing defect concentration, the interaction between defects can be determined approximately by a generalization of the average-field method, by assuming that the regions of lattice distortions near individual defect (which are described by an Ornstein-Zernike solution^{5,8}) overlap. This method can be used except in the immediate vicinity of T_c , where there are important nonlinear increments in the solutions of the linearized equations for the distribution of the transition parameter and where the error of the average-field method is large. The local disorder of the arrangement of Cl and Br atoms in the lattice disrupts the translational symmetry, imposing restrictions on the selection rules for the wave vector. As a result, the ν_{sm} line becomes allowed in the Raman spectrum of the paraelectric phase, because of fluctuational inhomogeneities of the composition of the mixed crystal. The dependence of the scattering intensity on the interatomic force constants becomes far more complicated. Figure 3 (the dashed curve) shows the results of numerical calculations which were "tied" to the experimental data in order to eliminate theoretical parameters. We see a completely satisfactory agreement between the results of this simple theory and the experimental results, but this agreement is only qualitative because of the large number of simplifying assumptions.

In summary, first-order Raman scattering by a soft acoustic mode from the boundary of the Brillouin zone has been observed for the first time for phase transitions in mixed $\text{Hg}_2(\text{Cl}, \text{Br})_2$ crystals. The appearance of this mode in the first-order optical spectra of the ideal crystal is forbidden by the selection rules.

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