Soft mode from the boundary of the Brillouin zone in the Raman-scattering spectrum of the paraphase of Hg_2Cl_2 and Hg_2Br_2

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Using the extrinsic ferroelastics Hg_2Cl_2 and Hg_2Br_2 as an example, we have observed, for the first time in phase transitions, the appearance of a soft mode from the boundary of the Brillouin zone (BZ) in the Raman scattering spectrum (RSS) of the paraphase ($T > T_c$). The singularities of the RSS show it to be a first-order spectrum induced by structural disturbances of the lattice.

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In phase transitions in extrinsic ferroelectrics and ferroelastics, the actual soft mode corresponds to lattice vibrations with wave vector $\mathbf{q}_{max}$ on the BZ boundary of the high-temperature ($T > T_c$) paraphase. To observe this mode, neutron-scattering methods are used (see, e.g.,[1]). Observation of the mode from the BZ boundary in optical spectra of first order in the paraphase is forbidden by the selection rules with respect to the momentum $\mathbf{q}$, and is possible only in the ferrophase ($T < T_c$) after the point $\mathbf{q}_{max}$ is transferred to the center ($\mathbf{q}=0$) of the new BZ of the ferrophase.[2] In the present study we succeeded, for the first time, in observing the soft mode from the BZ boundary in the RSS in the *paraphase* at $T > T_c$ (using the extrinsic ferroelastics Hg_2Cl_2 and Hg_2Br_2 as examples[3,4]). The behavior of the RSS favors the interpretation of this spectrum as being of first order and as being induced by static or dynamic disturbances of the regularity of the lattice.

The high-temperature phase Hg_2X_2 (X=Cl, Br) is tetragonal (D_{4h}^{17}) and a structural transition into ferroelectric orthorhombic phase D_{4h}^{17} takes place after cooling to $T_c = 185$ K (Hg_2Cl_2) and $T_c = 143$ K (Hg_2Br_2). This transition was investigated mainly by the RSS method.[3,4]

In the present study, the RSS of single crystals of the tetragonal phase were investigated at a 90° scattering geometry in polarized light in a wide range of temperatures, from high ones ~400 K (a limit imposed by the onset of sublimation of Hg_2X_2) down to the phase-transition point T_c. The use of a triple monochromator ("Spex Ramalog") with an argon laser ($\lambda = 4880$ Å, $W = 500$ mW) made it possible to investigate in detail the RSS region near the exciting line. As a result, a weak (~100 times weaker than the fundamental RSS of the first order of the paraphase) low-frequency with a characteristic temperature dependence was observed in the RSS in the case of polarization in the "basal" plane *xx*, *yy*, or *xy*.

Figure 1 shows the RSS of Hg_2Cl_2 in the Stokes and anti-Stokes regions. A peak is observed at Ω_{SM} with a frequency that decreases only as $T \to T_c^+$. We were able to trace a decrease of the frequency Ω_{SM} from 14 to 4.7 cm^{-1} (see Fig. 2b). In the temperature interval 265–195 K, the frequency squared behaves like $\Omega_{SM}^2 \propto (T - T_c)$. When the temperature is changed, the intensity decreases and the shape of the peak changes. In a certain intermediate temperature interval, a shoulder appears distinctly on the low-frequency slope of Ω_{SM} (arrows on Fig. 1d), and attests to the presence of a second peak Ω' in the RSS. All the indicated singularities were observed in the RSS of Hg_2Br_2, where the frequency Ω_{SM} shifts from 12.4 to 5.4 cm^{-1} when the temperature changes from $T = 350$ K to T_c.

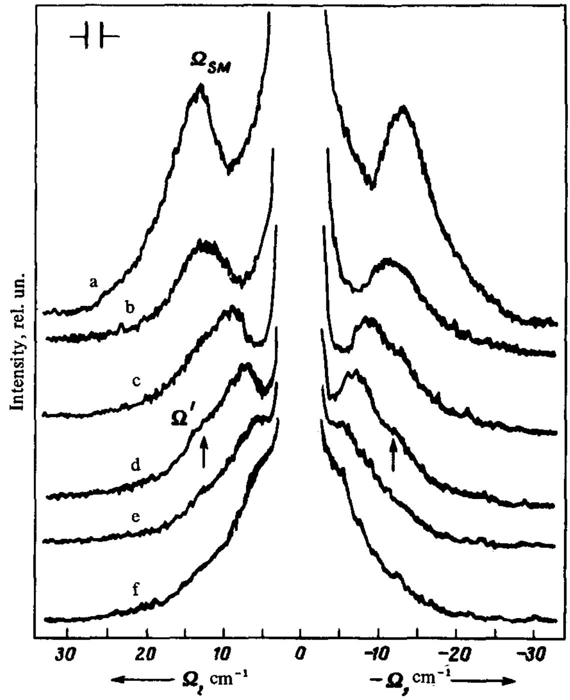

FIG. 1. Low-frequency RSS of Hg_2Cl_2 at various temperatures: a—$T=327$ K, b—$T=294$ K, c—$T=274$ K, d—$T=221$ K, e—$T=210$ K, f—$T=202$ K.

The observed frequency shift $\Omega_{SM}\to 0$ as $T\to T_c^+$ points without doubt to a connection between Ω_{SM} and the soft mode that induces the phase transition in Hg_2X_2. According to[3,4] this transition $D_{4h}^{17}\to D_{2h}^{17}$ is due to condensation of the oscillation of the transverse acoustic branch ω_{TA} ($\mathbf{q}$) on the boundary of BZ of the paraphase at the X point of the BZ. It follows therefore that the Ω_{SM} peak is connected with the oscillations at the X point of the BZ. The appearance of these oscillations in a first-order RSS can be due to disturbances in the regularity of the lattice. It is known[5] that violation of the translation symmetry of the lattice leads to violation of the selection rules with respect to $\mathbf{q}$ and makes it possible for oscillations with $\mathbf{q}$ in the entire BZ to appear in the spectrum; in this case, the maxima of the distribution in frequency $g(\omega)$ appear in the (continuous) RSS.

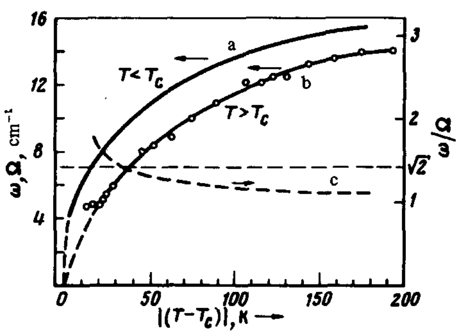

FIG. 2. Temperature dependence of the frequency of the soft mode at $T<T_c$ (a) and $T>T_c$ (b), and of the frequency ratio (c).

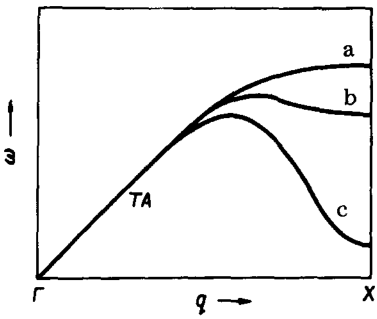

FIG. 3. Acoustic branch at different temperatures $T(a) > T(b) > T(c)$ (scheme).

The quasi-continuous character of the observed RSS (its width is comparable with the frequency) confirms the connection between the spectrum and oscillations from different points of the BZ. We propose that the *predominant contribution to the formation of the singularities* (peaks) of the RSS and to their temperature dependence is made by oscillations of the transverse "soft-mode" acoustic branch $\omega_{TA}(\mathbf{q}_{[111]})$ on the Γ—x line, which is the lowest acoustic branch (with the lowest speed of sound) of Hg_2X_2.[6] Figure 3 shows schematically the evolution of this branch as $T \to T_c^+$, when $\omega_{TA}(X) \to 0$. In the general case, $\omega(\mathbf{q})$ has two extrema ($\partial\omega/\partial\mathbf{q}=0$) in which one can expect a maximum of the function $g(\omega)$. One of them is permanently at the point X with which the peak of the soft mode Ω_{SM} in the RSS is connected. It is seen that as $T \to T_c^+$ the minimum of $\omega(\mathbf{q})$ near X "becomes deeper," and the gently sloping region near X where $\partial\omega/\partial\mathbf{q} \approx 0$ [on which the amplitude of the maximum $g(\omega)$ depends] becomes narrower. This can explain the decrease in the intensity of the Ω_{SM} peak and its narrowing, which are observed in the RSS as $T \to T_c^+$. The second extremum of $\omega(\mathbf{q})$ corresponds to the temperature-dependent maximum inside the zone (Figs. 3b and 3c). It is possible to attribute to it the band Ω' observed in the RSS in a certain temperature interval. The existence of only one relatively narrow Ω_{SM} peak in the RSS at high temperature (Fig. 1a) seems to indicate that the shape of $\omega(\mathbf{q})$ is close to that of curve "a" (Fig. 3).

It is of interest to compare the behavior of the soft mode of Hg_2X_2 in the paraphase at $T > T_c$ with its behavior in the ferrophase at $T < T_c$, when this mode is allowed in the RSS because of the transfer of X to the center of the BZ of the ferrophase.[3,4] Figure 2a shows the temperature dependence of the frequency $\Omega_{SM}(T)$ of the soft mode in the ferrophase of Hg_2Cl_2 according to the data of[3]. It is seen that at a large distance from T_c the frequencies of the soft mode are close to each other in the para- and ferrophases. The same takes place also for Hg_2Br_2. The dashed curve in Fig. 2c shows the ratio ω_{SM}/Ω_{SM} of the frequencies of the soft mode in the ferrophase and paraphase at different $|T-T_c|$.

In a certain temperature region, this ratio is close to the value $\sqrt{2}$ that follows from Landau's phenomenological theory [see formula (25) of[4]].

The proposed connection between the RSS and the first-order spectrum thus explains the principal experimental relations. The assumption that the observed RSS is connected with a second-order spectrum leads to excessively low values of the frequencies $\omega_{TA}(X)$ of the paraphase of Hg_2X_2, which agreed poorly with the acoustic-measurement results[6] and with the RSS of Hg_2X_2.[3,4] The nature of theHg_2X_2 lattice disturbances that induce the RSS of first order remain unclear. Their concentration can be quite low, since the frequency $\omega_{TA}(X)$ is apparently very "sensitive" to factors that lift the forbiddenness in q. This is seen from the anomalously strong peak of the soft-mode line ω_{SM} in the RSS of the ferrophase.[3,4] It is probable that the disturbance is of thermal structural character, either static[7] or dynamic, and can be responsible for part of the temperature-dependent decrease of the RSS intensity as $T \to T_c^+$.

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