

Excitation of lines in the infrared spectrum of Hg_2Cl_2 crystals due to cell doubling with a phase transition

A. A. Kaplyanskii, M. F. Limonov, and Yu. F. Markov

A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR

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Excitation of new lines in the infrared spectra of crystals due to doubling of the unit cell accompanying a structural phase transition (for improper ferroelastics Hg_2Cl_2) is observed for the first time. The number and polarization of lines excited for $T < T_c$ coincide with the predictions of a group-theoretical analysis. The dispersion of optical branches is determined experimentally from the critical orientation $\Gamma \rightarrow X$ of the Brillouin zone of the paraelectric phase.

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It is well known that phase transitions in improper ferroelectrics and ferroelastics are accompanied by a transfer of the critical point from the boundary of the Brillouin zone (BZ) of the paraelectric phase into the center of the BZ of the ferroelectric phase, which makes it possible to observe for $T < T_c$ lattice vibrations from the boundary of the BZ of the paraelectric phase in the first-order optical spectra. The effect was observed previously for excitation of new first-order lines for $T < T_c$ in Raman scattering spectra (RSS) of light. In this work, the excitation of new lines in the infrared (IR) spectra of crystals is observed for the first time.

We have investigated Hg_2Cl_2 crystals which undergo a structural phase transition $D_{4h}^{17} \rightarrow D_{2h}^{17}$ when cooled to $T_c = 185$ K involving a doubling of the unit cell, induced by an acoustic soft mode from the X point of the BZ of the paraelectric phase (improper ferroelastic).¹ As a theoretical analysis showed,¹ the transfer of the X point of the BZ of the paraelectric phase (D_{4h}^{17}) into the Γ point of the BZ of the ferroelectric phase (D_{2h}^{17}) must lead to the appearance of four new lines in the IR spectra of the ferroelectric phase (see Table I). They are genetically related to oscillations from the X point of the BZ of the paraelectric phase, corresponding to even (at the Γ point) optical branches that appear in first-order RSS. The vibrational spectrum of Hg_2Cl_2 for $T > T_c$ contains four even fundamental vibrations: two degenerate vibrations with symmetry E_g and two completely symmetrical vibrations with symmetry A_{1g} .² Vibrations belonging to the E_g branches at the X point of the BZ of the paraelectric phase split into two vibrations with symmetry B_{2g} and B_{3g} (wave vector group D_{2h} , column 2). One of them (B_{2g}) transforms with the phase transition into the IR active vibration B_{1u} , while the other (B_{3g}) transforms into the inactive vibration A_u (representations of the D_{2h} group of the ferroelectric phase). The oscillations of the two A_{1g} branches at the X point of the BZ have A_g symmetry and with a phase transition transform into the IR active vibrations of the type B_{3u} . Therefore, after the transfer $X \rightarrow \Gamma$, two lines with symmetry B_{1u} and two lines with symmetry B_{3u} should be excited in the IR spectra of the ferroelectric phase. The polarization of these lines (along the axes of the rhombic ferroelectric phase) is shown in column 3. The frequencies of the lines excited

TABLE I.

D_{4h}^{17} , $T = 300$ K		D_{2h}^{17} , $T = 100$ K			Dispersion of branches D_{4h}^{17} , $T = 300$ K
Point Γ	Point X	Point Γ (from X)	ν	α , cm^{-1}	
1	2	3	4	5	6
$\nu_1 (E_g)$, 40	$B_{2g} (43) + B_{3g}$	$B_{1u} (z) + A_u$	45, 5	15	0.08
$\nu_2 (E_g)$, 137	$B_{2g} (143) + B_{3g}$	$B_{1u} (z) + A_u$	148, 0	60	0.04
$\nu_3 (A_{1g})$, 167	$A_g (160)$	$B_{3u} (x)$	163, 0	50	-0.04
$\nu_4 (A_{1g})$, 275	$A_g (280)$	$B_{3u} (x)$	288, 0	10	0.02

Frequencies in columns 1, 2 and 4 are given in cm^{-1} .

in the IR spectra will evidently differ (with $T = T_c$) from the frequencies of the corresponding lines in the first-order RSS by the magnitude of the dispersion of the optical branches along the direction $\Gamma \rightarrow X$ in the BZ of the paraelectric phase.

The IR spectra of Hg_2Cl_2 (absorption in powder³ and reflection by single crystals^{4,5}) were previously investigated over a wide temperature range, including $T_c = 185$ K; however, no changes related to the phase transition could be observed in Refs. 3-5. In this work, the IR absorption spectra of Hg_2Cl_2 were studied using a long-wavelength IR spectrometer with a novel design in the spectral range 20-330 μm (500-30 cm^{-1}). Single-crystalline plates with thickness varying from 0.1 to 1 mm were studied. The tetragonal z axis lay in the plane of the specimens, which permitted performing the measurements in polarizations $E \parallel z$ and $E \perp z$.

The measured transmission spectra (Fig. 1) at $T = 300$ K contain two extremely intense absorption bands which belong to the odd fundamental vibrations, in complete

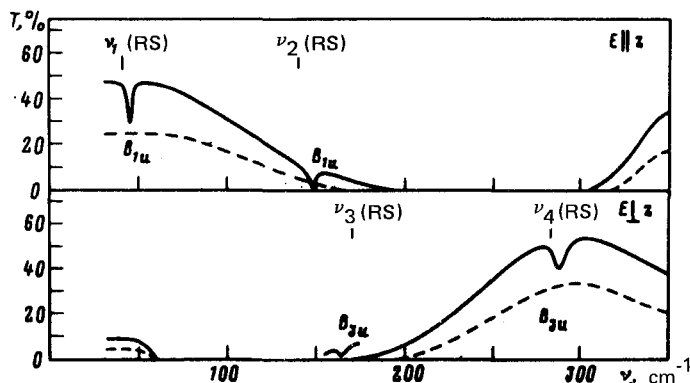


FIG. 1. IR transmission spectra of Hg_2Cl_2 single crystals with a thickness of $d = 0.4$ mm (the region marked with an asterisk is for the specimen with $d = 0.14$ mm). The solid curves are for $T = 100$ K and the dashed curves are for $T = 300$ K.

agreement with the data from a group-theoretical analysis.⁴ One of the bands is observed in the geometry $E||z$ and corresponds to vibrations with symmetry A_{2u} ($\nu_{TO} = 241 \text{ cm}^{-1}$), while the other band is observed in the geometry $E \perp z$ (the vibration E_u , $\nu_{TO} = 69 \text{ cm}^{-1}$).⁵ As the temperature is decreased, the total transparency of the crystals increases, the A_{2u} and E_u bands narrow slightly, but there are no qualitative changes in the spectra down to $T_c = 185 \text{ K}$.

It was possible to observe for $T < T_c$ the excitation of all four theoretically predicted absorption bands in the IR spectra of Hg_2Cl_2 (Fig. 1). The bands $\nu'_1, \nu'_2, \nu'_3, \nu'_4$ are situated in spectral regions close to the position of the four first-order RSS lines $\nu_1, \nu_2, \nu_3,$ and ν_4 , respectively (the position of the latter at $T = 100 \text{ K}^1$ is indicated in Fig. 1 by the vertical marks), and have a polarization that corresponds completely to the results of the group-theoretical analysis (column 3).¹⁾ This permitted identifying the excited bands uniquely. The frequencies of the excited bands and the coefficients of absorption α at their maxima at $T = 100 \text{ K}$ are given in columns 4 and 5 of Table I.

The integrated absorption coefficients $A \sim \int \alpha(\nu) d\nu$ of all three excited bands (ν'_1, ν'_2, ν'_4) approach zero with $T \rightarrow T_c^-$. For the line ν'_4 , it was possible to measure quantitatively the dependence of A on $|T - T_c|$ (see Fig. 2). Figure 2 also shows the dependence of A on the square of the frequency of the soft mode ν_{SM}^2 , observed in RSS with $T < T_c$.¹ Theoretically, $A \sim \eta^2$ (η is the order parameter for the phase transition), so that the linear dependence of A (ν_{SM}^2) indicates that $\nu_{SM} \sim \eta$. In the temperature interval under examination.

The possible effects of excitation in the IR reflection spectra of Hg_2Cl_2 crystals were estimated from the magnitude of the absorption coefficients α at the maximum of the excited bands. The estimate showed that in the most favorable case ($\nu'_2, \alpha \sim 60 \text{ cm}^{-1}$) the excitation of a new IR absorption band must lead to an increase in the reflection coefficient in the region of the band by only $\sim 1\%$. This explains why no manifestations of the phase transition were observed in Refs. 4 and 5 in the IR reflection spectra of Hg_2Cl_2 .

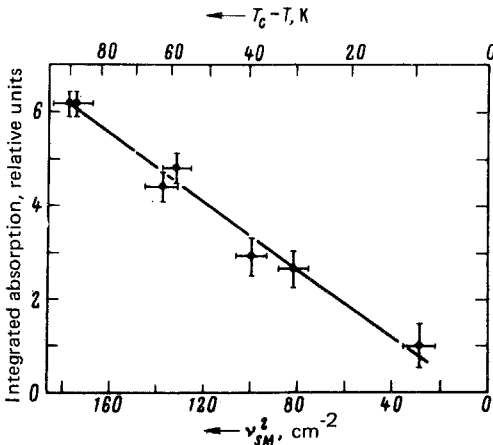


FIG. 2. Integrated absorption of the excited IR line ν'_4 , plotted as a function of ν_{SM}^2 and $(T_c - T)$.

Our measurements of the temperature shifts of the frequencies of the four excited IR lines turned out to be analogous to the temperature shifts of the corresponding lines in RSS.¹ This permitted extrapolating the position of the observed frequencies of the excited IR lines to $T = 300$ K and thus to obtain the frequency of vibrations of the "even" branches at the X point of the BZ of the paraelectric phase. These frequencies $\nu(X)$ are given in brackets in column 2 of Table I. We note that the frequency of the libration branch $\nu_1(X) = 43 \text{ cm}^{-1}$ agrees with the value obtained from the position of the overtone of this vibration $2\nu_1(X) = 89 \text{ cm}^{-1}$ in the second-order RSS of Hg_2Cl_2 .⁶ The values obtained for $\nu(X)$ make it possible to determine the relative dispersion of the "even" optical branches along the direction $\Gamma \rightarrow X$: $n = [\nu(X) - \nu(\Gamma)]/\nu(\Gamma)$ (column 6 in Table I). It is evident that the dispersion is very small for branches of intramolecular stretching (ν_3, ν_4) vibrations and deformational (ν_2) vibrations and are only slightly larger for the branches of the intermolecular (librational) vibration ν_1 . This fact additionally indicates the "quasimolecular" structure of Hg_2Cl_2 crystals.

The results of the investigations of the excited IR lines, together with the results of Ref. 1 on the excitation of new lines in RSS, give a complete spectroscopic picture of the transfer $X \rightarrow \Gamma$ and again convincingly confirm the model of the structural phase transition in Hg_2Cl_2 crystals.¹

¹Because of the strong absorption in the principal IR band E_u , the line ν'_3 is observed only in the thinnest specimens $d < 0.2$ mm. The residual intensity of the ν'_3 band seen in IR spectra for $T > T_c$ could be attributed to the damaged surface layer in such specimens.

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