Comment on ''Infrared study of the low-temperature phase transitions in incommensurate Cs$_2$HgBr$_4$''

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Jorio *et al.*, in their recent paper [Phys. Rev. B **59**, 11 251 (1999)], published results of infrared studies of Cs$_2$HgBr$_4$ single crystal in the temperature region 10–300 K. In spite of four structural phase transitions occurring on cooling, the authors observed only two new infrared active modes in the low-temperature spectra. Results of our infrared measurement clearly show much more dramatic changes in the spectra with temperature. Activation of many new modes in our spectra of all three polarizations is connected with the lowering of crystal symmetry at the phase transitions and particularly with the doubling of the unit cell below 85 K. Therefore we can conclude that Jorio *et al.* either used inaccurate temperature control or their sample exhibited a different sequence of phase transitions.

Cs$_2$HgBr$_4$ crystal has the β-K$_2$SO$_4$ structure at room temperature (RT) [phase I, space group *Pnma*, $Z=4$ (Ref. 1)]. In the temperature range between $T_I=245$ K and $T_C=232$ K it shows the incommensurate phase (phase II) modulated in the **x** direction with the wave vector $\mathbf{k}_i \approx 0.15\mathbf{a}^*$.[2–4] The lock-in phase transition (PT) of the first order at T_C occurs in the ferroelastic phase (phase III, $P2_1/n11$, $Z=4$) at the Brillouin zone center.[4] On cooling, Cs$_2$HgBr$_4$ undergoes further PT's at $T_{L1}=165$ K (second-order PT) and $T_{L2}=85$ K (first-order) into the triclinic proper ferroelastic phase (phase IV, $P\bar{1}$, $Z=4$) and the improper ferroelastic phase (phase V, $P\bar{1}$, $Z=8$) with a doubled lattice parameter in the **y** direction, respectively.[3,4]

Our Cs$_2$HgBr$_4$ crystal was grown from the melt by the Bridgman method and the crystallographic axes were determined by x-ray diffraction. Near-normal polarized far-infrared (FIR) reflectivity measurements (17–600 cm^{-1}) were performed using a Fourier transform interferometer Bruker IFS 113v (same as in Ref. 5) at 15 different temperatures between 10 K and RT using a continuous-flow Oxford CF104 cryostat. On cooling, a rate of 4 K/min was applied, with a dwell time of 20 min at each temperature before the corresponding spectra were taken. A liquid-helium-cooled Si bolometer operating at 1.5 K was used as an infrared detector.

The FIR reflectivity spectra taken in phases I, III, IV, and V for all three polarizations $\mathbf{E}\|\mathbf{x},\mathbf{y},\mathbf{z}$ are shown in Fig. 1. The spectra were fitted using the same factorized form of the dielectric function as in Ref. 5 and both experimental (points) and fitted curves are presented in Fig. 1.

Temperature dependence of different symmetry transverse optical (TO) mode frequencies evaluated from the FIR reflectivity spectra is presented in Fig. 2. The values of the TO and longitudinal optic (LO) frequencies obtained for marginal temperatures (RT and 10 K) are shown in Table I.

The RT FIR spectra correspond with the spectra published by Jorio *et al.*[5] It suggests that both samples are chemically similar and well oriented. However, in order to get a satisfactory curve fit of RT $\mathbf{E}\|\mathbf{y}$ and $\mathbf{E}\|\mathbf{z}$ polarized spectra, we

have introduced extra modes at 39 and 37 cm^{-1}, respectively. The latter weak mode is also seen in $\mathbf{E}\|\mathbf{z}$ spectrum in the previously published paper,[5] but is not presented in Table II of Ref. 5.

Factor-group analysis in phase I gives (after subtraction of acoustic modes) $12B_{1u}(z)$, $7B_{2u}(y)$, and $12B_{3u}(x)$ optical modes active in the $\mathbf{E}\|\mathbf{x}$, $\mathbf{E}\|\mathbf{y}$, and $\mathbf{E}\|\mathbf{z}$ polarized infrared (IR) spectra, respectively. However, we did not distinguish all these modes in our spectra because of high damping and overlapping of the most modes.

In contrast to the result of Jorio *et al.*[5] we observed considerable temperature changes of the FIR spectra below the lock-in PT from incommensurate to the ferroelastic phase III. As one can see from Figs. 1 and 2 three new modes (50, 157, and 178 cm^{-1}) arise in $\mathbf{E}\|\mathbf{x}$ spectra and two new low-frequency modes appear both in the $\mathbf{E}\|\mathbf{y}$ (50 and 69 cm^{-1}) and $\mathbf{E}\|\mathbf{z}$ (49 and 68.5 cm^{-1}) polarized spectra. The considerable enrichment of Raman spectra below 100 cm^{-1} for all scattering geometries at the lock-in PT was also found by Dmitriev *et al.*[6] Note that Jorio *et al.* reported an activation of two new internal stretching modes (157 and 178 cm^{-1}) in the $\mathbf{E}\|\mathbf{x}$ spectrum only in phase IV. We observed the appearance of these modes already in phase III at 205 K.

The activation of new modes in phase III is not strange because it is caused by symmetry lowering at PT to the monoclinic structure. Moreover, the number of theoretically predicted IR active normal modes of $A_u(x)$ and $B_u(y,z)$ symmetry must increase to 20 and 19, respectively, at the I–III PT. It should be noted that the modes of the A_u symmetry, forbidden in IR and Raman spectra in the high-temperature phase I according to the selection rules, activate in the $\mathbf{E}\|\mathbf{x}$ IR spectra in the phase III.

However, more dramatic changes of FIR spectra we found at two lower PT's, especially at the lowest IV–V PT (see Figs. 1 and 2). The III–IV PT into triclinic proper ferroelastic phase (space group $P\bar{1}$) is accompanied by the appearance of new phonon modes in the spectra of all polarizations. There are three new modes (30, 55, and 177 cm^{-1}) in the $\mathbf{E}\|\mathbf{x}$ spectra, one new line at 81 cm^{-1} in the $\mathbf{E}\|\mathbf{y}$
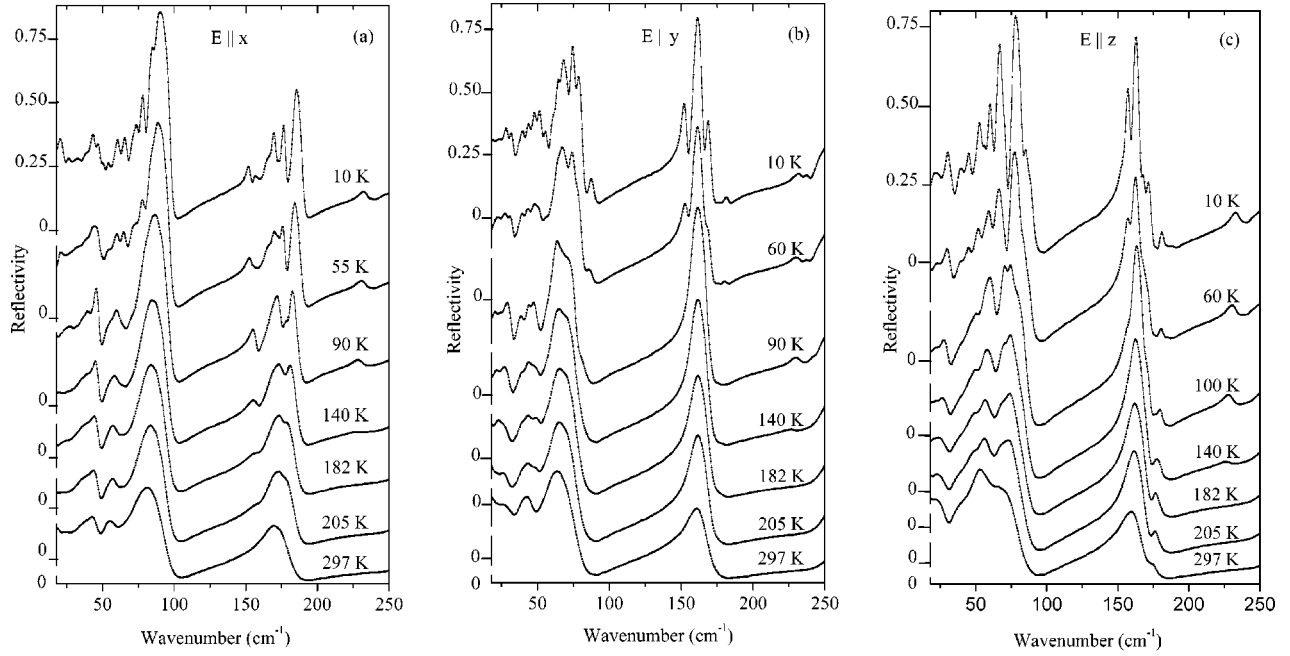
FIG. 1. FIR reflectivity spectra of Cs_2HgBr_4 at different temperatures for (a) $\mathbf{E}\|\mathbf{x}$, (b) $\mathbf{E}\|\mathbf{y}$, and (c) $\mathbf{E}\|\mathbf{z}$ polarizations.

spectra, and four new modes (25, 80, 156, and 169 cm^{-1}) appear in the $\mathbf{E}\|\mathbf{z}$ spectra. Jorio *et al.*[5] observed only two new IR modes below T_{L1}, but strong temperature changes of mode activities at III–IV PT's were observed also in the

Raman scattering spectra.[6,7] This is caused by the essential change of the crystal symmetry (the loss of the glide plane) at the III–IV transition. Note the difference between the spectra at 90 K (just above T_{L2}) and at 140 K (just below

TABLE I. Frequencies of TO-LO modes observed in FIR spectra at RT (phase I) and 10 K (phase V), in cm^{-1}.

| $\mathbf{E}\|\mathbf{x}$		$\mathbf{E}\|\mathbf{y}$		$\mathbf{E}\|\mathbf{z}$	
10 K	RT	10 K	RT	10 K	RT
A_u	B_{3u}	A_u	B_{2u}	A_u	B_{1u}
22.8–23.4		22.3–25.2		25.1–25.7	
29.0–29.5		29.3–30.0		31.1–33.0	30.8–31.3
32.5–36.5		31.6–34.0	32.5–34.3	40.9–41.4	37.2–42.0
38.0–39.0		40.0–42.0	39.5–41.6	45.3–46.5	
43.5–45.0	44.6–47.0	43.4–45.7	43.0–47.2	52.9–53.9	51.4–60.7
47.0–49.0		47.5–49.3		56.0–58.0	
50.0–52.0		51.2–52.4		59.3–63.0	
54.5–55.0	55.4–57.4	56.2–57.5		65.3–68.0	
60.6–62.3		60.4–62.6	58.7–80.4	68.2–72.0	66.4–83.7
65.5–67.7		64.0–64.7		75.5–84	
71.0–72.0		67.5–70.6		84.6–85.5	
74.0–75.0		73.5–76.3		88.8–90.8	
77.5–79.7	77.3–96.3	78.0–81.4		156.8–159.7	156.3–170.0
83.0–86.0		87.0–88.5		161.1–166.8	
87.0–98.0		151.5–154.2		167.0–170.0	
153.5–154.4		158.5–165.5	157.2–170.6	171.5–172.3	173.2–175.0
155.0–158.6		167.3–171.0		180.8–181.2	
165.0–166.5		181.7–183.0			
169.3–170.6	167.0–182.8				
176.0–178.0					
183.0–190.0					
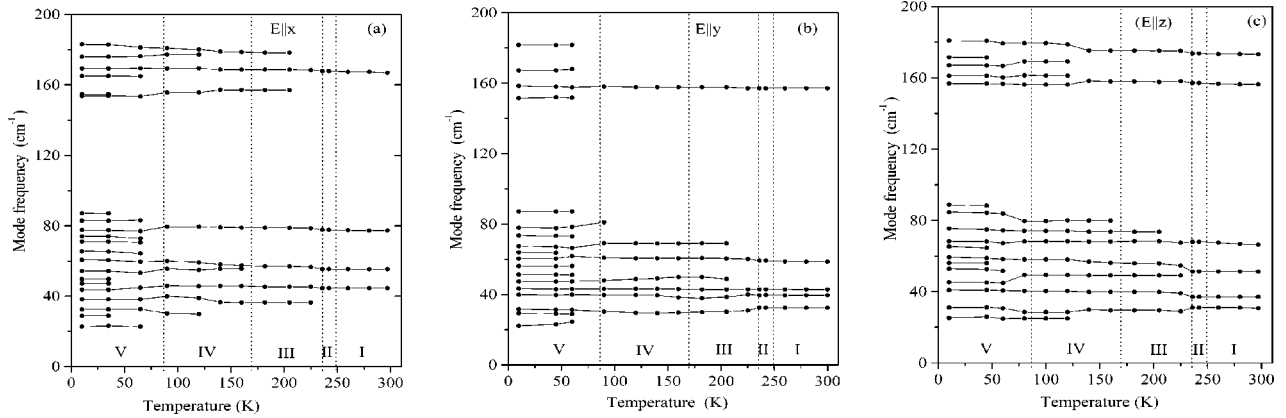
FIG. 2. Temperature dependences of TO phonon frequencies observed in (a) $\mathbf{E}\|\mathbf{x}$, (b) $\mathbf{E}\|\mathbf{y}$, and (c) $\mathbf{E}\|\mathbf{z}$ FIR reflectivity spectra.

T_{L1}), where the structure remains the same. The strengths of the new modes are generally proportional to the square of the order parameter,[8] therefore they are best seen at lower temperatures.

While the space group is not changed at the first-order IV–V PT, essential enrichment of FIR spectra was observed for all polarizations due to the unit cell doubling along the **y** axes and corresponding folding of the Brillouin zone below T_{L2}. The number of symmetry allowed IR active modes in the spectra for all polarizations theoretically increases up to 81 in phase V. Therefore the considerable change of IR spectra (practically doubling the number of IR active modes both in the $\mathbf{E}\|\mathbf{x}$ and $\mathbf{E}\|\mathbf{y}$ spectra and activation of five new modes in the $\mathbf{E}\|\mathbf{z}$ spectrum) is observed together with significant narrowing of lines in phase V due to the lower phonon damping. Similar behavior was observed in recent FIR spectra of Cs_2CdBr_4 single crystal,[9] which exhibits similar sequence of the PT's. However, no changes were observed in the Jorio et al.[5] FIR spectra below T_{L2}.

Additional anomalies similar to reflection bands appear in the IR spectra of all polarizations (see Fig. 1) at low temperatures and at frequencies above 225 cm^{-1}. They are multiphonon absorptions and/or bands connected with a high transparency of the sample and consequent reflection from the back surface.

In conclusion we have to stress that we have observed considerable temperature changes of the FIR spectra for all polarizations in all low-temperature phase III, IV, and V. Particularly dramatic changes of the spectra (almost doubling the number of the IR active mode) were seen below T_{L2}. The number of IR active modes in the $\mathbf{E}\|\mathbf{x}$, $\mathbf{E}\|\mathbf{y}$, and $\mathbf{E}\|\mathbf{z}$ polarized spectra, taken at RT, increases from 4, 5, and 6, respectively, to 21, 18, and 17 modes, respectively, obtained at 10 K. Such strong temperature evolution of the IR spectra responds to the substantial transformation of the crystal lattice at lock-in PT, two low-temperature PT's, and corresponding changes of mode activities. Our spectra obtained in the phase IV are similar to the Jorio et al. spectra[5] at 10 K. Therefore we can conclude that Jorio et al. either used inaccurate temperature control or their sample exhibited a different sequence of phase transitions.

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