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Polar Domain Walls and Orientational Disorder in Incommensurate Cs_2HgBr_4

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The low temperature phases of Cs_2HgBr_4 have been studied by Raman scattering and infrared reflectivity. The anomalous behavior of the ν_1 Raman modes and the increase of the oscillator strength of the infrared modes polarized along the y -direction are discussed in terms of the orientational disorder of the HgBr_4 tetrahedra and the presence of layered structure of polar domain walls at low temperatures.

Keywords: orientational disorder; polar domains; incommensurate phase

INTRODUCTION

The Cs_2HgBr_4 crystal belongs to the A_2BX_4 family, which exhibits a large variety of structural phases and different physical properties such as ferroelectricity, ferroelasticity and incommensurability^{1,2}. The high temperature structure (phase I) belongs to the Pnma ($Z = 4$) space group and below $T_1 = 245$ K it exhibits an incommensurate structure (phase II), that is characterized by a constant wave vector $q \approx 0.16 a^*$. At the lock-in phase transition ($T_C = 232$ K), the modulation wave vector jumps to zero, yielding a commensurate structure (phase III), belonging to the monoclinic space group $\text{P2}_1/n$ ($Z = 4$), without the appearance of superstructure. The crystal undergoes two other phase transitions, at about $T_{L1} = 165$ K and $T_{L2} = 80$ K. Phase IV

(80 K < T < 165 K) belong to the triclinic space group $P\bar{1}$ ($Z = 4$) and phase V (T < 80 K) belong to the same space group, with $Z = 8$.¹

In this work we present results of a Raman and Infrared study of the low temperature phases of Cs_2HgBr_4 . The anomalous behavior of the A_g -symmetry ν_1 mode and the important increase at T_1 in the oscillator strength of the y -polarized modes are attributed to the orientational disorder of the HgBr_4 tetrahedra at high temperatures and the presence of a layered structure of domain walls at low temperatures.

EXPERIMENTAL DETAILS

Single colorless crystals of Cs_2HgBr_4 were grown by H. Arend (ETH, Zurich) using the Bridgman method. The Raman spectra have been recorded between 90 and 290 K with a triple-monochromator spectrometer (DILOR XY) equipped with a multi-array detector (GOLD) and excited with a $\lambda = 514.5$ nm line of an Argon laser (COHERENT INNOVA 70). Infrared reflectivity spectra have been recorded using a Bruker spectrometer (IFS 307), from 10 K up to room temperature.

RESULTS AND DISCUSSION

The correlation diagram for the internal modes of Cs_2HgBr_4 can be found in reference [3]. Since all the low temperature phases are centro-symmetric, the Raman modes observed in the diagonally polarized spectra (xx), (yy), and (zz) belong to the A_g representation and, in that case, only one ν_1 mode is allowed by group theory. Besides, at the room temperature structure, the HgBr_4^{2-} tetrahedra are localized in a m_y mirror plane and, therefore, the ν_1 mode is forbidden in the crossed-polarized (xy) and (yz) Raman spectra.

In a recent work³ we showed that the frequency of the Raman peak

associated with the A_g -symmetry ν_1 mode depends on the scattering geometry, that is, the frequency of the peak observed in the (xx) spectra is smaller than those observed in the (yy) and (zz) spectra. Besides, one ν_1 forbidden mode is always observed in the cross-polarized (xy) and (yz) Raman spectra. These results can be explained as due to the presence of the orientational disorder of the tetrahedra about the x -axis^[4,5]. The ν_1 mode is coupled to the relaxation mode associated with the orientational disorder and the coupling shifts the frequency of the Raman peak. The strength of the coupling is not isotropic since rotation occurs preferentially about the x -axis⁵ and, therefore, the frequency of the peak in the (xx) spectrum is shifted with respect to the frequencies in the (yy) and (zz) spectra. Figure 1 shows the temperature dependence of $\omega_{yy} - \omega_{xx}$, where ω_{yy} and ω_{xx} are the frequencies of the ν_1 peaks observed in the $z(yy)\bar{z}$ and $z(xx)\bar{z}$ Raman spectra. The splitting $\omega_{yy} - \omega_{xx}$ (or $\omega_{zz} - \omega_{xx}$) can be seen as a measure of the orientational disorder of the HgBr_4 tetrahedra. We can observe in Fig. 1 a discontinuous decrease in this curve at T_1 and at T_{L1} , showing that the disorder starts to decrease below the

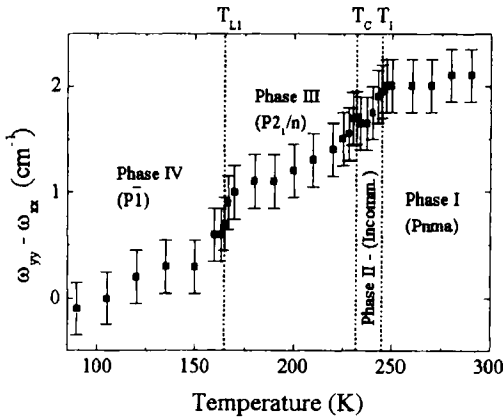


FIGURE 1 Temperature dependence of $\omega_{yy} - \omega_{xx}$.

incommensurate phase transition, and practically disappears in the ordered phase IV (below T_{L1}).

We have also observed that, at low temperatures, frequency of the $A_g\text{-}\nu_1$ Raman mode depends on the phonon propagation direction.³ Below T_1 , the modes propagating along y -direction have their frequencies larger than those propagating along x and z -directions. In this case, the frequency splitting is similar to a TO-LO splitting for a polar mode, in which the polar character of the mode is given by its effective charge which is proportional to $\omega_{LO}^2 - \omega_{TO}^2$. Figure 2(a) shows the temperature dependence of $\omega_y^2 - \omega_z^2$, where ω_y and ω_z are the frequencies of the ν_1 modes observed in the $y(xx)\bar{y}$ and $z(xx)\bar{z}$ Raman spectra, respectively. Note that the polar character of this mode appears at T_1 and increases within the incommensurate phase. However, according to the X-ray diffraction studies of Cs_2HgBr_4 , all the low temperature structural phases are centro-symmetric^{1,4} and, in that case, the polar modes are not Raman active.

In order to understand the behavior of the polar modes at low temperatures, we have performed an infrared reflectivity (IR) study of Cs_2HgBr_4 between 10 and 300 K. The IR spectra have been fitted using the factorized form of the dielectric constant function, allowing the determination of the frequencies ω , damping constants γ and oscillator strengths $\Delta\epsilon$ for all polar modes. A detailed analysis of this experiment can be found in reference [6]. The infrared dielectric constant ϵ_0 can be obtained from the sum of the oscillator strength of the polar modes, that is, $\epsilon_{0i} = \epsilon_{\infty i} + \sum \Delta\epsilon_{ij}$, where i denotes the crystallographic direction, j denotes the polar modes and ϵ_{∞} is the dielectric constant in the visible. Figure 2(b) shows the temperature dependence of ϵ_0 along the three crystallographic directions x , y and z . Note that the values of ϵ_0 increase below T_1 , but the increase is much more pronounced for the modes polarized along

the y -direction. This effect is mostly associated with the increase of the oscillator strength of the two lowest frequency modes in y -polarized spectra and is due to the appearance of an extra mechanism of polarization along y -direction below T_1 .

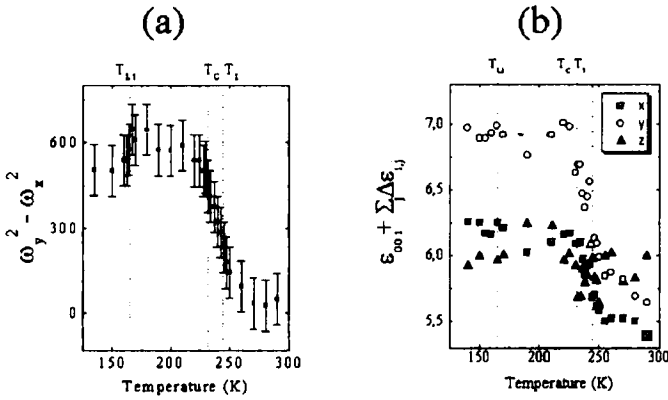


FIGURE 2 (a) Temperature behavior of $\omega_y^2 - \omega_z^2$, where ω_y and ω_z are the frequencies of the ν_1 peaks observed in the $y(xx)\bar{y}$ and $z(xx)\bar{z}$ Raman spectra; (b) Temperature dependence of $\epsilon_{00i} = \epsilon_{00i} + \sum_j \Delta\epsilon_{ij}$ along the three crystallographic directions (x , y , or z).

A possible explanation for the low temperature Raman and IR results is related to the existence of a macroscopic polarization along the y direction associated with the presence of domain walls with y -polar symmetry. The symmetry breaking occurring from phase I to phase III gives rise to two types of twin domains at low temperature^[3]. The domain walls perpendicular to the z -direction have a C_{2v} point group symmetry, with polarization along y . The

polarization is due to the displacement of the Cs(1) atoms that occurs principally along this direction, creating a local electric dipole. The frequency up-shift for the ν_1 modes propagating along the y -direction is related to the existence of a macroscopic electric field in the domain walls that increases the restoring forces and the frequency of the mode propagating parallel to the macroscopic field.

CONCLUSION

The analysis of the Raman and IR spectra of Cs_2HgBr_4 shows that the crystal exhibits an orientational disorder of the HgBr_4^{2-} tetrahedra about the x -axis in the room temperature phase, in agreement to a recent X-ray diffraction study.⁴ The disorder decreases in the incommensurate phase and disappears below the III-IV phase transition. Below T_1 , the crystal exhibits a structure of polar domain walls perpendicular to the z -direction with polarization parallel to the y -direction, and the macroscopic electric field in the polar domain walls increase the frequency of the ν_1 modes propagating along the y -direction.

Acknowledgments

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