Phase Transitions in van der Waals ferroics $CuInP_2S(Se)_6$ and their applications

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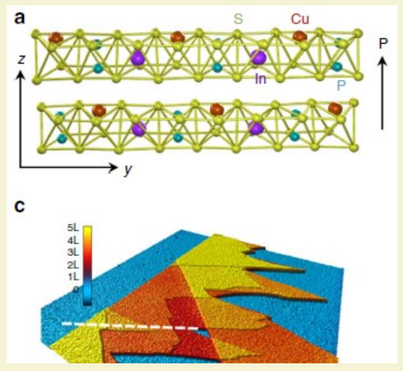


For van der Waals family of $CuInP_2S_6$ crystals with ferrielectric ordering below $T_c \approx 315$ K earlier the possibility of spontaneous polarization switching in samples with a thickness of several structural layers was discovered [1,2]. In case of $CuInP_2Se_6$ crystals observed domain structure confirms coexistence of ferrielectric and antiferroelectric states [3]. These discovering's have opened a new direction of basic and applied researches in the field of nanoelectronics based on van der Waals multiferroics. Up to now, many examples of functional elements are designed with including $CuInP_2S_6$ crystal monolayers or layered sandwiches [4-7]. The range of the application of the $CuInP_2S_6$ crystals also is widened by their ionic conductivity – here the Cu^+ cations are involved in both lattice spontaneous polarization normally to structural layers and charge transfer mostly along with directions in the plane of layers [8].

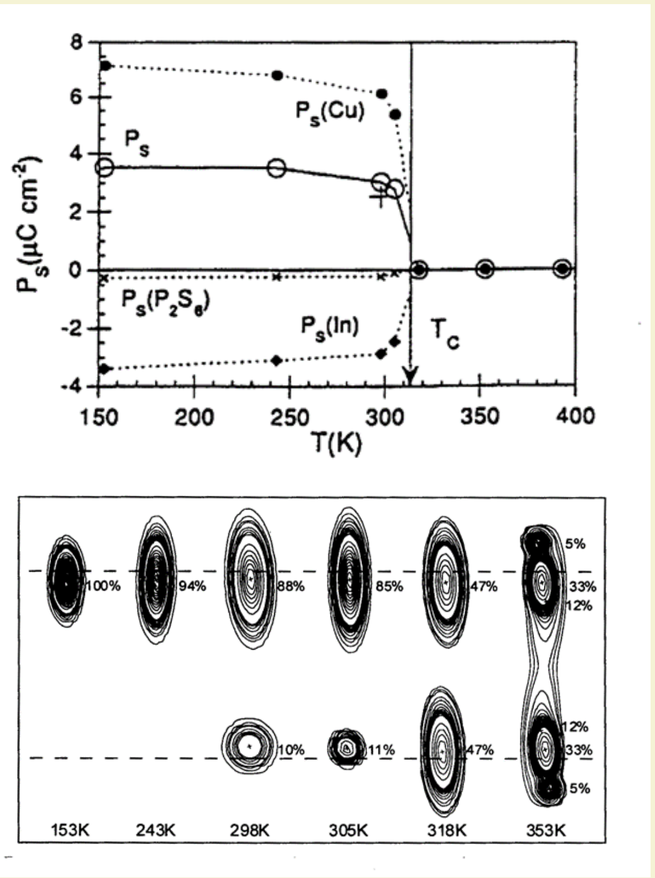
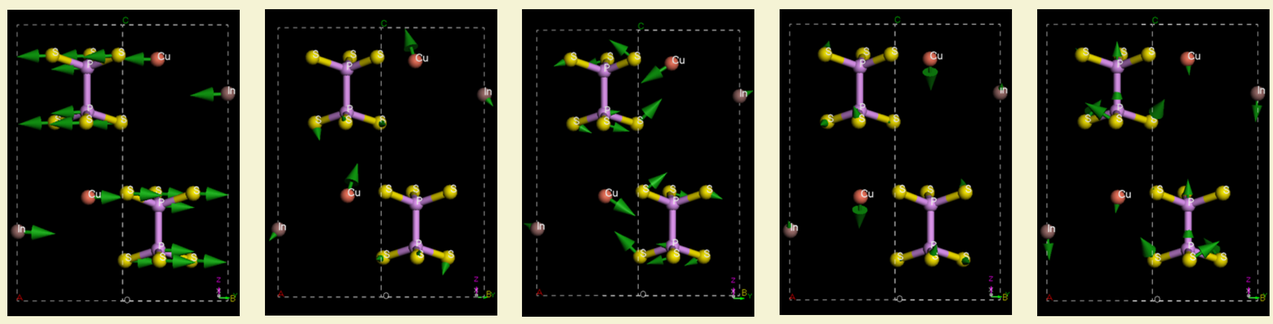


Fig. 1. The spontaneous polarization temperature dependence and thermal evolution of different copper site occupancies and the corresponding probability density contours in $CuInP_2S_6$ crystal [9].

The ferrielectric polarization of considered crystals is determined by opposite shifts of Cu^+ and In^{3+} cations out of structural layers that are built by $(P_2S_6)^{4-}$ anionic structural groups. Such structural ordering below T_c can be presented as freezing of Cu^+ cations in multiwell potential at temperature lowering [9]. Similar interesting displacive/order-disorder phase transition occurs in the $Sn_2P_2S_6$ ferroelectric crystals with three-well local potential for spontaneous polarization fluctuations [10]. In the case of $CuInP_2S_6$ crystals, the four-well (or quadruple) local potential can be involved in the description of ferrielectric ordering (Fig. 1). The origin of such a complicated potential landscape for the copper atoms moving inside crystal lattice elementary cells can be related to the second order Jahn - Teller effect destabilizing the Cu^+ cations in positions in the middle of structural layers [11].

Data of previous Raman scattering investigations [12] illustrate the temperature-dependent transformation of the low-frequency spectral lines intensity, which is related to Cu^+ cations redistribution between wells of the local potential. For further analysis of $CuInP_2S_6$ crystal anharmonic lattice dynamics, we performed DFT calculations of its phonon spectra in the GGA approach with considering of s, p, and d valence orbitals of atoms constituting the crystal lattice. For the ferrielectric phase in ground state the phonon branches across the monoclinic Brillouin zone and partial phonon densities of states (Fig. 2), and the eigenvectors of long-wave phonons (Fig. 3) were calculated. Also, the Raman spectral intensity at different temperatures was calculated (Fig. 4) and compared with observed Raman spectra temperature dependence (Fig. 6). Such comparison illustrates anharmonic effects – redistribution of spectral lines intensities that can be related to changes of Cu^+ cations population in different wells of quadruple local potential at heating in the ferrielectric phase.

The Raman spectra temperature dependence also is compared with calculated, in the four – well quantum anharmonic oscillators model, temperature transformation of pseudospin fluctuations spectra. The shape of local potential was determined following data [9] about thermal evolution of different copper site occupancies and the corresponding probability density contours in $CuInP_2S_6$ crystal (Fig. 1).



17 cm^{-1} **68 cm^{-1}** **70 cm^{-1}** **72 cm^{-1}** **98 cm^{-1}**

Fig. 3. Eigenvectors of the low frequency optical lattice vibrations at center of Brillouin zone for ferrielectric phase of $CuInP_2S_6$ crystal.

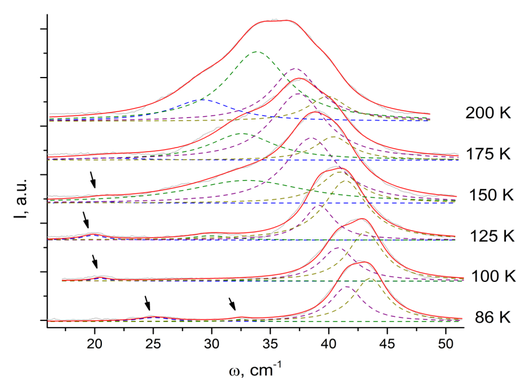


Fig. 5. The low frequency part of Raman scattering spectra for ferrielectric phase of $CuInP_2S_6$ crystal at several temperatures.

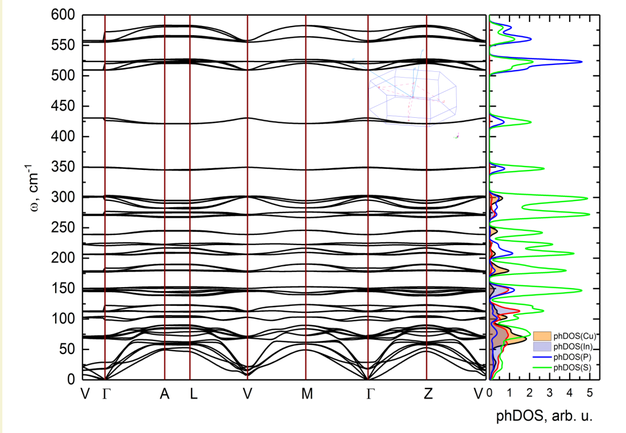


Fig. 2. Calculated in GGA approach phonon branches and partial phonon densities of states for ferrielectric phase of $CuInP_2S_6$ crystal.

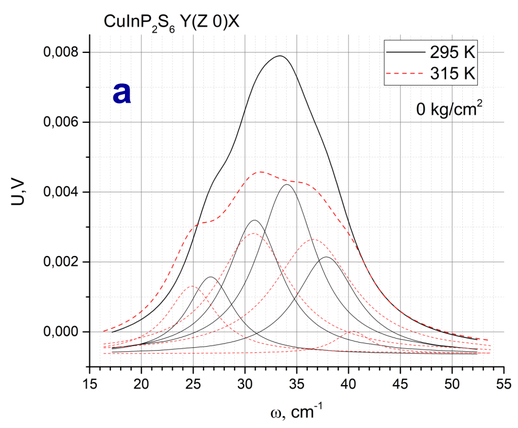


Fig. 6. The low frequency part of Raman scattering spectra for $CuInP_2S_6$ crystal at different temperatures (a) and under uniaxial pressure normally to structural layers (b).

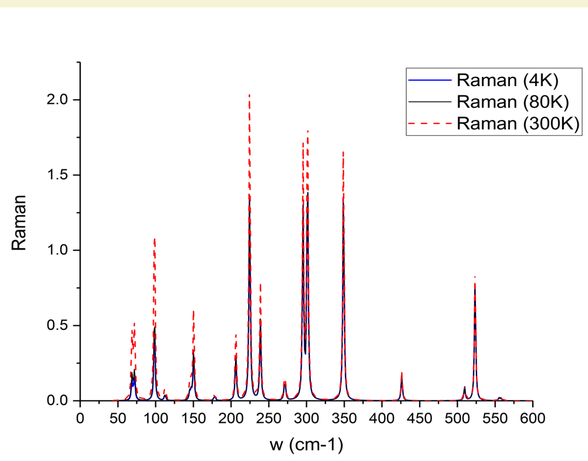


Fig. 4. Calculated in GGA approach Raman scattering spectra for $CuInP_2S_6$ crystal at different temperatures.

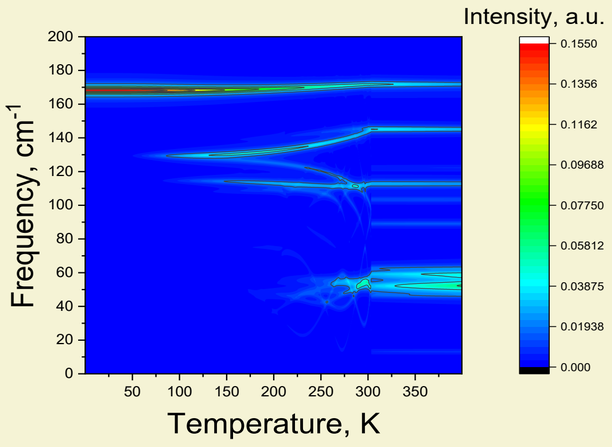


Fig. 9. Calculated in the four – well quantum anharmonic oscillators model temperature dependence of the pseudospin fluctuations spectra intensities.

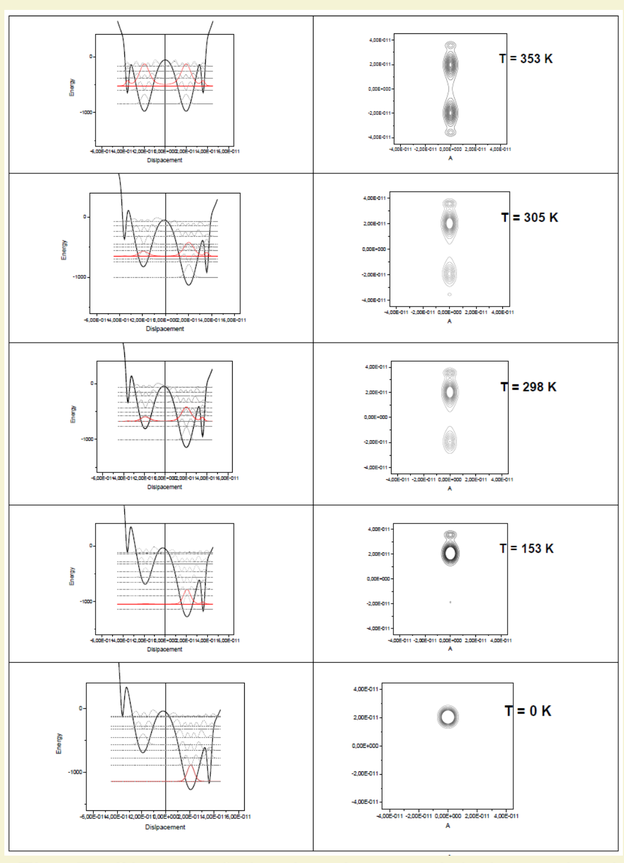


Fig. 7. Shape of the local potential determined following thermal evolution of different copper site occupancies and the corresponding probability density contours in $CuInP_2S_6$ crystal.

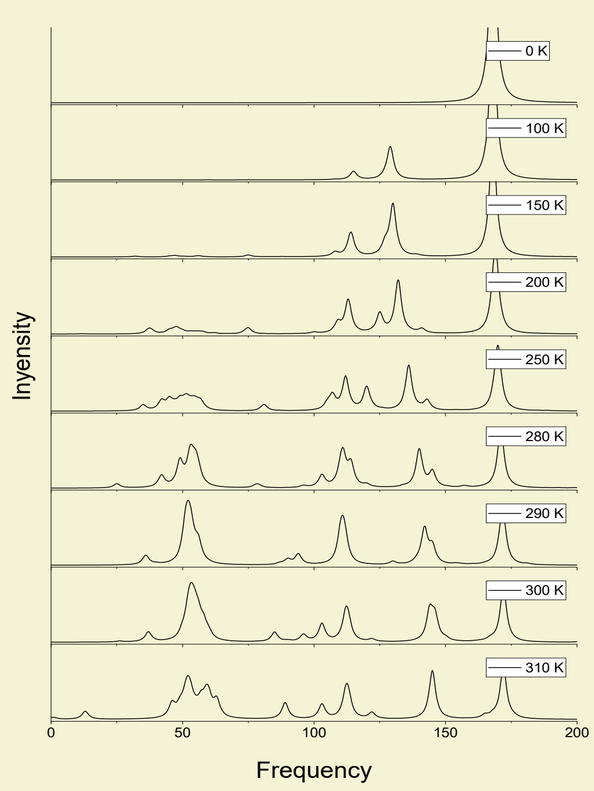


Fig. 8. Calculated in the four – well quantum anharmonic oscillators model temperature transformation of pseudospin fluctuations spectra at shown on Fig. 7 temperature variation of the local potential.

Conclusions: According first principles phonon spectra calculations for monoclinic ferrielectric phase of $CuInP_2S_6$ crystal the lowest energy long wave A' symmetry optical modes have frequencies near 17 cm^{-1}, 68 cm^{-1}, 70 cm^{-1}, 72 cm^{-1}, 98 cm^{-1} and 104 cm^{-1}. At this, placed near 17 cm^{-1} optical mode has exceedingly small Raman intensity and don't appeared in calculated Raman spectra. In experimental Raman spectra intensity of spectral lines in region below 30 cm^{-1} at low temperatures is very small. These spectral lines growth at hating and approaching to transition from ferrielectric into paraelectric phase. Activation of the low energy spectral lines obviously is induced by frequent jumps of Cu^+ ions in multiwell local potential. Disordering of crystal structure provokes destroying of scattering selection rules and reflecting in Raman spectra of phonons with big wave vectors – from segments of Brillouin zone that provide high contribution to the density of phonon states. The low energy region of Raman spectra mostly is determined by optical phonon branches in Γ – V direction in the reciprocal space, which consist vibrations of Cu^+ and In^{3+} cations propagated normally to structural layers. Calculated spectra of pseudospin fluctuation in frame of quantum four – well anharmonic oscillators model reflect observed by Raman spectroscopy nonlinearity of $CuInP_2S_6$ crystal lattice dynamics. Uniaxial compression normally to structural layers increases the phase transition temperature because of the local potential changing, what is observed in by pressure induced variation of the low energy Raman spectral lines.

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