Phonon spectra and phase transitions in van der Waals ferroics MM’P₂X₆

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ABSTRACT

For CuInP₂S₆ ferroelectrics by Brillouin spectroscopy, the temperature dependence of the longitudinal hypersound velocity was investigated for the acoustic phonons propagated in plane of the crystal layers. Pronounced softening of acoustic phonon branch is observed in the paraelectric phase below Tᵣ ≈ 330 K at cooling to temperature Tᵣ ≈ 312 K of the first order phase transition into ferrielectric phase. Below Tᵣ the hypersound velocity growth in correlation with spontaneous polarization rise and its temperature anomaly is similar to earlier observed temperature behavior of longitudinal ultrasound velocity for acoustic wave propagated normally to the structural layers. Determined anomalous part of the CuInP₂S₆ crystal thermal conductivity in the vicinity of the ferrielectric transition also demonstrates lowering of the heat transferring phonons group velocity with cooling from Tᵣ to Tᵣ. Observed acoustic softening obviously is induced by flexoelectric coupling of relaxational soft polar optical and acoustic branches that is related to an inhomogeneously polarized state appearing between the paraelectric and ferrielectric phases.

KEYWORDS

Acoustic phonons; Brillouin scattering; CuInP₂S₆; flexoelectric coupling; frustrations; thermal conductivity; van der Waals ferroics

1. Introduction

For van der Waals family of CuInP₂S₆ crystals with ferrielectric ordering below Tᵣ ≈ 312 K earlier the possibility of spontaneous polarization switching in samples with a thickness of several structural layers was discovered [1,2]. This discovering has opened a new direction of basic and applied research in the field of nanoelectronics based on van der Waals multiferroics [2–8]. The range of application of CuInP₂S₆ crystals is also widened by their ionic conductivity – here Cu⁺ cations are involved in both lattice spontaneous polarization normally to the structural layers and charge transfer mostly along with the directions in the plane of layers [9].

The ferrielectric polarization of considered crystals is determined by opposite shifts of Cu⁺ and In³⁺ cations out of the structural layers that are built by (P₂S₆)₄⁻ anionic structural groups. Such structural ordering below Tᵣ can be presented as the freezing of Cu⁺ cations in multiwell potential at temperature lowering. Similarly, displacive/order-disorder phase transition occurs in Sn₂P₂S₆ ferroelectric crystals with three-well local potential for spontaneous polarization fluctuations [10]. In the case of CuInP₂S₆ crystals,
the four-well (or quadruple) local potential can be involved in the description of the ferrielectric ordering. The origin of such a complicated potential landscape for copper atoms moving inside the crystal lattice elementary cells can be related to the second-order Jahn-Teller (SOJT) effect destabilizing the $d^0$ Cu$^{+}$ cations in positions in the middle of the structural layers [11].

For AgInP$_2$S$_6$ and AgInP$_2$Se$_6$ compounds, the Ag$^{+}$ cations create stronger covalent bonds inside the chalcogenide octahedra preventing SOJT effect and the transition into a polar state when temperature lowered [12]. But, in AgBiP$_2$S$_6$ and AgBiP$_2$Se$_6$ compounds, the physical origin of anharmonicity can also be traced to the existence of the stereochemically active $s^2$ lone pair of Bi$^{3+}$ cations [13]. The s electron shell of Bi is easily deformed by lattice vibrations, resulting in a strong anharmonicity.

In the case of CuBiP$_2$Se$_6$ crystal the Cu$^{+}$ ions move off-center of the octahedral sites [12] and create dipole moments. However, the Bi$^{3+}$ ions within the same layer displace in the opposite direction as Cu$^{+}$ ones and create an almost equal but opposite dipole moment. This gives rise to antiferroelectric arrangement and as results an intraslab dipole moment cancelation [13]. The reasons for the differences in behavior of CuBiP$_2$Se$_6$ (antiferroelectric) and CuInP$_2$Se$_6$ (ferrielectric) could be traced to the existence of the stereochemically active $s^2$ electron lone pair of Bi$^{3+}$. The inability of $d^0$ In$^{3+}$ cations to behave similarly allows by Cu$^{+}$ created dipole moments to induce the ferrielectric state in CuInP$_2$Se$_6$ crystal.

Data of Raman scattering investigations [14] 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$_2$S$_6$ crystal anharmonic lattice dynamics, we performed DFT calculations of its electron spectra and phonon spectra in the GGA approach with considering of s, p, and d valence orbitals of atoms constituting the crystal lattice [15].

Comparative analysis [15,16] of DFT calculated phonon spectra and thermal conductivity investigations [16,17] for the layered compounds Cu(Ag)InP$_2$(Se)$_6$, AgBiP$_2$(Se)$_6$, and CuBiP$_2$Se$_6$ presented a detailed explanation of the thermal properties as ions are substituted, showing the role of disorder, electronic levels hybridization, ions coordination and size on SOJT effect. It was shown that in some of compounds the thermal conductivity has very low values due to the enhancement of phonon scattering events, expressing a strong anharmonic behavior, which is justified based on interactions among optical and acoustic phonon branches as well as the presence of electron lone pairs.

Additional information on lattice dynamics and dipole ordering peculiarities can be found in consideration of acoustic phonon spectra and the temperature dependence of the sound velocity. Earlier the ultrasound properties of CuInP$_2$S$_6$ crystals in detail were investigated [18]. Here we present for CuInP$_2$S$_6$ crystal the Brillouin scattering data with the information about the temperature dependence of hypersonic and analyze its thermal conductivity anomaly in the vicinity of the transition between the paraelectric and ferrielectric phases.

2. Experimental results

For grown by Bridgeman method CuInP$_2$S$_6$ layered crystals [19] the Brillouin scattering spectra at different temperatures were investigated with earlier described [20]
equipment. By analysis of Brillouin spectra involving acoustic phonons with oriented along CuInP$_2$S$_6$ crystal layers wave vectors (an example is shown in Fig. 1) the temperature dependence of hypersound velocity for longitudinal (LA) and transverse (TA) waves were found. For LA phonons at 100 K the hypersound velocity $v_{LA} \approx 5330$ m s$^{-1}$ (Fig. 2a). The measured value of $v_{LA}$ agrees with the calculated velocity of LA phonons propagating in the XY plane along crystal layers (Fig. 3b). DFT calculations of phonon spectra, with early described methodology [15], predict small elastic anisotropy of CuInP$_2$S$_6$ crystal in the plane of layers, but this anisotropy appears at deviation out of layers (Fig. 3a) – in normal to the layers direction the longitudinal sound velocity decreased till 3500 m s$^{-1}$. Ultrasound data [18] about longitudinal sound velocity normally to structure layers of CuInP$_2$S$_6$ crystal (Fig. 2b) confirm high elastic anisotropy.

At heating in the ferrielectric phase the longitudinal hypersound velocity monotonously decreases and rapidly drops above room temperature demonstrating a sharp minimum with the minimal value $\approx 5050$ m s$^{-1}$ near first-order phase transition with $T_c \approx 312$ K (Fig. 2a). The minimum of $v_{LA}(T)$ dependence has pronounced asymmetry into the high-temperature side what is similar to ultrasound velocity anomaly (Fig. 2b). In the ferrielectric phase this velocity rapidly rises till $\approx 5150$ m s$^{-1}$ at 300 K. Such nontrivial shape of $v_{LA}(T)$ anomaly with unexpected acoustic softening in wide temperature range ($312 - 330$ K) of the paraelectric phase cannot be related to the order parameter developed fluctuations or influence of the defects. The presence of some polar clusters above $T_c$ in CuInP$_2$S$_6$ crystal is supported by the second optical harmonic generation [21] indicating the crystal lattice eccentricity. The $^{31}$P NMR spectral data is also illustrate [22] some residual nonequivalence of phosphorous atoms inside P$_2$S$_6$ structural groups in range $312$ K – $330$ K as a result of their eccentricity.

The thermal conductivities of MM$^\prime$P$_2$S(Se)$_6$ compounds with layered crystal structure have been investigated by means of an ac photopyroelectric calorimetry [16,17]. In this work we analyze the thermal transport properties of the crystals in the vicinity of the ferrielectric phase transition. Thermal conductivity has been fitted by the known

![Figure 1. Brillouin spectrum for CuInP$_2$S$_6$ crystal at 295 K with light scattering geometry involving acoustic phonons propagating in the plane of crystal layers (a). The spectral lines of longitudinal (LA) and transverse (TA) acoustic phonons fit by Lorentz peak function (b). Lorentz contour of relaxation dynamics and elastic scattering Gaussian peak are also shown.](image-url)
\[ \kappa(T) = \frac{A}{T} + B, \]

where \( A/T \) is related to the three-phonon scattering processes and \( B \) is the so-called lowest possible thermal conductivity in the Cahill-Pohl model \[23\]. Such equation describes well the thermal conductivity in the vicinity and above of the Debye temperature in the case of absence of the structural phase transitions. Example of the fitting with the parameters: \( \Theta_{\text{Debye}} = 64 \text{ K} \), \( A = 109.9 \text{ W m}^{-1} \text{C}^{-1} \) and \( B = 0.298 \text{ W m}^{-1} \text{K}^{-1} \text{C}^{-1} \) is shown in Fig. 4 for AgInP\(_2\)Se\(_6\) crystal which does not demonstrate the structural phase transitions \[16\].

For CuInP\(_2\)S\(_6\) compound, with the Debye temperature \( \Theta_{\text{Debye}} = 129 \text{ K} \), the fitting of earlier found \[17\] temperature dependence of thermal conductivity by equation \( \kappa(T) = \frac{A}{T} + B \) in both cases, at heat transfer along and normally to the structural layers

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Temperature dependence of longitudinal hyperson sound velocity with the acoustic phonons propagated in the plane of the crystal layers (a), and longitudinal ultrasound propagated normally to the crystal layers \[18\] (b) for CuInP\(_2\)S\(_6\) crystal.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{DFT calculated for CuInP\(_2\)S\(_6\) ferrielectric phase sound velocity angle dependencies in Cartesian plane YZ oriented normally to crystal layers (a) and in coincided with crystal layers plane XY (b).}
\end{figure}
The deviation $D_j$ of the calculated dependence (red curve at Fig. 6) from the experimental data is similar for both parallelly and normally oriented thermal flows and has the shape of asymmetric minimum that is positioned at $T_c$ (Fig. 7). These deviations can be compared with the temperature dependencies of the optical birefringence increment $D_n(T)$ [24] and with the square of a spontaneous polarization $P_s^2$ of the ferrielectric phase [25]. Temperature anomaly of the longitudinal ultrasound velocity in normal to the crystal layers direction [18] and determined by Brillouin scattering spectroscopy temperature anomaly of the longitudinal hypersound velocity, propagated in the plane of the crystal layers, are also compared with thermal conductivity deviation related to the ferrielectric phase transition.

(Fig. 5), deviates in the temperature vicinity of the ferrielectric phase transition, a.e. at approaching to $T_c \approx 312$ K.

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3. Discussion of results

Anomalous lowering of thermal conductivity in CuInP₂S₆ crystal together with the decreasing of the ultrasound and hypersound velocities can be considered as the evidence of a heat transferring acoustic phonons group velocity decrease in the paraelectric phase at cooling to T_c. Observed temperature dependence of longitudinal ultrasound
and hypersound below $T_c$ correlates with the square of spontaneous polarization and agrees with Landau – Khalatnikov theory for acoustic anomalies at ferroelectric ordering [26]. Lowering of sound velocity in a wide temperature range of the paraelectric phase at cooling to $T_c$ can be related to the longitudinal acoustic phonon branch suppression by softened optical relaxational modes of spontaneous polarization fluctuations in the case of order - disorder type of the phase transition occurring in CuInP$_2$S$_6$ crystal. Such overdamped (relaxational) optical mode is clearly observed by dielectric microwave investigations [18]. The linear interaction of optical and acoustic phonon branches is determined by flexoelectric coupling and can be described by taking into account the Lifshitz like invariants in thermodynamic potential for the monoclinic symmetry of CuInP$_2$S$_6$ crystal, similarly, as was done at the analysis of sound velocity anomalies near the Lifshitz point (LP) on temperature – composition diagram of Sn$_2$P$_2$(Se$_x$S$_{1-x}$)$_6$ ferroelectrics [27].

In the case of Sn$_2$P$_2$(Se$_x$S$_{1-x}$)$_6$ ferroelectrics the development of space inhomogeneous fluctuations of spontaneous polarization at cooling to the edge of the paraelectric phase stability is related to the incommensurate phase appearance between the paraelectric and ferroelectric phases for compositions $x > x_{LP}$ [27]. For layered ferrielectrics CuInP$_2$S$_6$ the acoustic and thermal conductivity investigations show that some specific temperature region between $T_c \approx 312$ K and $T^* \approx 330$ K is inclined between the paraelectric and ferrielectric phases. Here the cooperative behavior may be envisioned in terms of dipole - dipole correlations developing with freezing of random In$^{3+}$ d$^{10}$ cations motions and with ordering of Cu$^+$ d$^{10}$ cations random positions. If the dipoles are part of and orthogonal to the CuInP$_2$S$_6$ crystal plane, the appearance of long-range order would involve antiparallel displacements which minimize the electrostatic and elastic energy costs of ordering.

According to structural investigations [25] in CuInP$_2$S$_6$ crystal lattice above $T_c$, the cooper cations are disordered around positions at top and bottom of crystal layers with occupation probabilities symmetrical relatively second order symmetry axis $C_2$, which is placed at the middle of the structural layer and oriented along $Y$ (b) axis of monoclinic (C2/c) elementary cell. At this, the indium cations are also distributed among positions that are a little shifted above or below of $C_2$ axis. In the case of antiferroelectric interaction between nearest-neighbor dipoles (in the plane of the given layer) created by indium cations shifts, and at the ferroelectric coupling of the nearest dipoles related to cooper cations positions in neighbor structural layers, some frustrations in the dipole space ordering can appear. Such possibility is supported by dipole glassy type disordering at low temperatures inside the ferrielectric phase of CuInP$_2$S$_6$ crystals [28]. For CuInP$_2$Se$_6$ compound the dipolar frustration was supposed at interpretation of successive phase transitions according to observed temperature dependence of dielectric susceptibility [29]. The frustration was appeared by piezoelectrically active domain walls between competitive ferrielectric and antiferroelectric states [30,31]. Also, the dipole glassy state in the mixed crystal CuInP$_2$(Se$_x$S$_{1-x}$)$_6$ [28] obviously is related to frustration effects at dipole ordering.

The DFT calculations [15] illustrate the hybridization of valence orbitals for Cu$^+$ and In$^{3+}$ cations in d$^9$ nominal state. The local SOJT effect strongly displaces the Cu$^+$ cations from the center of the surrounding sulfur octahedron (such effect is a little
weakened in selenide compound). For the indium cations in $d^0$ electronic configuration, the eccentricity inside chalcogen’s octahedrons is relatively small. But due to the high charge of In$^{3+}$ cations appeared dipoles are big enough for partial compensation of electric dipoles related to the Cu$^+$ position. It can be supposed that at disordering of Cu$^+$ cations above $T_c$, in some temperature interval – till $T_c+30$ K, the antiferroelectric type ordering for In$^{3+}$ sublattice still exists. Such possibility can be described in the mean-field approximation suggesting that an order parameter of the ferrielectric transition in considered crystals interacts with another order parameter, which is related to the structural transition – obviously with some structure modulation. Such interaction is strong enough for CuInP$_2$S$_6$, and here, at temperature decreasing, the second-order and first-order transitions can occur. For CuInP$_2$Se$_6$ crystals named interaction evidently is weak that can determine at cooling in a series of the second-order phase transitions [29].

In the pseudospin quantum anharmonic oscillators model with two sublattices (one of them with Ising like two – well local potential, another with Blume–Emery–Griffith model like three – well local potential at given single-ion anisotropy) and with account of competition between nearest and next nearest neighbors interactions the ground state and the temperature – pressure – composition phase diagram of layered CuInP$_2$S(Se)$_6$ ferri-(antiferro-)electrics can be described, similarly to the description of Sn(Pb)$_2$P$_2$S(Se)$_6$ ferro-(antiferro-)electrics with three-dimensional crystal lattice [32,33].

4. Conclusions

The Brillouin spectroscopy and thermal conductivity investigations confirm earlier received ultrasound data [18] about unexpected elastic softening of the CuInP$_2$S$_6$ layered crystals at the edge of stability of the paraelectric phase – at cooling to the first order transition into the ferrielectric phase. Observed effect at high temperature side of the order – disorder type phase transition can be induced by flexoelectric coupling of relaxational soft polar optical and acoustic branches. Such coupling can induce the inhomogeneously polarized state in temperature region between the paraelectric and ferrielectric phases.

The second optical harmonic generation [21], the $^{31}$P NMR spectral data [22] and nonzero value of the second-order dielectric susceptibility together with mismatch between the temperatures of linear and third-order dielectric susceptibilities maxima [34] clearly indicate that some polarization exists above the phase transition temperature $T_c$ in CuInP$_2$S$_6$ crystals. Also, at calorimetric investigations two anomalies were found by A. Inaba [35] on the temperature dependence of CuInP$_2$S$_6$ heat capacity: at $T_c = 309.35$ K with transition entropy $\delta S = 2.1J K^{-1} mol^{-1}$, and at $T^* = 329.47$ K with $\delta S = 0.79 J K^{-1} mol^{-1}$. Addition diffraction investigations are required for checking of the polarization space distribution in the temperature region between $T_c$ and $T^*$. This peculiarity is very important for CuInP$_2$S$_6$ family ferroic materials, which are already widely integrated into different functional heterostructures, and requires further theoretical and experimental study.

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