

# Features of thermal transport processes in van der Waals chalcogenides

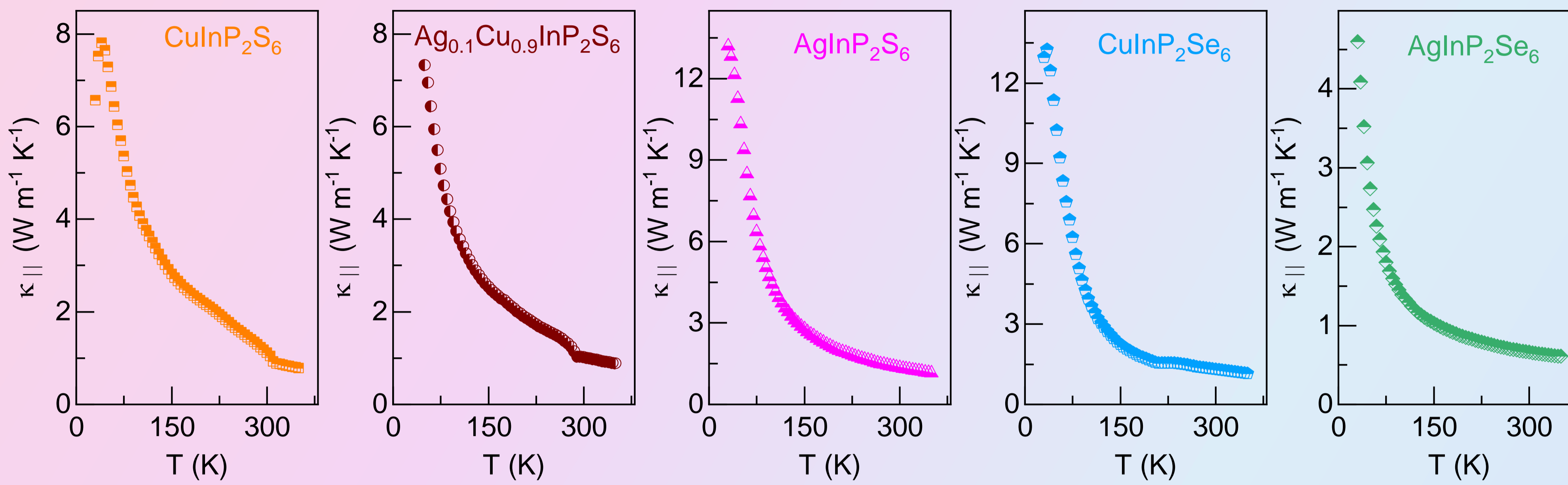


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## Outline

Quaternary phosphorus chalcogenides of the type  $MM'P_2S(Se)_6$  ( $M = Cu, Ag; M' = In, Bi$ ) represent a family of layered materials, down to the nanoscale, exhibit intriguing characteristics related to ferroelectricity and accompanied by ionic conductivity [1]. Previous studies of the thermal properties of these materials [2-3] have elucidated that heat transfer in metal phosphorus chalcogenides occurs through phonon processes and is strongly influenced by anharmonicity. This anharmonicity is attributed to various factors, including disorder, hybridization of electronic levels, ion coordination, and size, which influence the second order Jahn-Teller (SOJT) effect. However, for certain compounds, the temperature dependence of thermal conductivity has been observed to deviate significantly from the predictions of three-phonon processes. In [4], we investigated the intricate interplay between the indium and copper cationic sublattices in the genesis of ferroelectricity. The study has demonstrated that indium plays a pivotal role in the polar ordering of  $CuInP_2S_6$  crystals. This finding suggests the possibility of additional mechanisms influencing heat transfer properties.

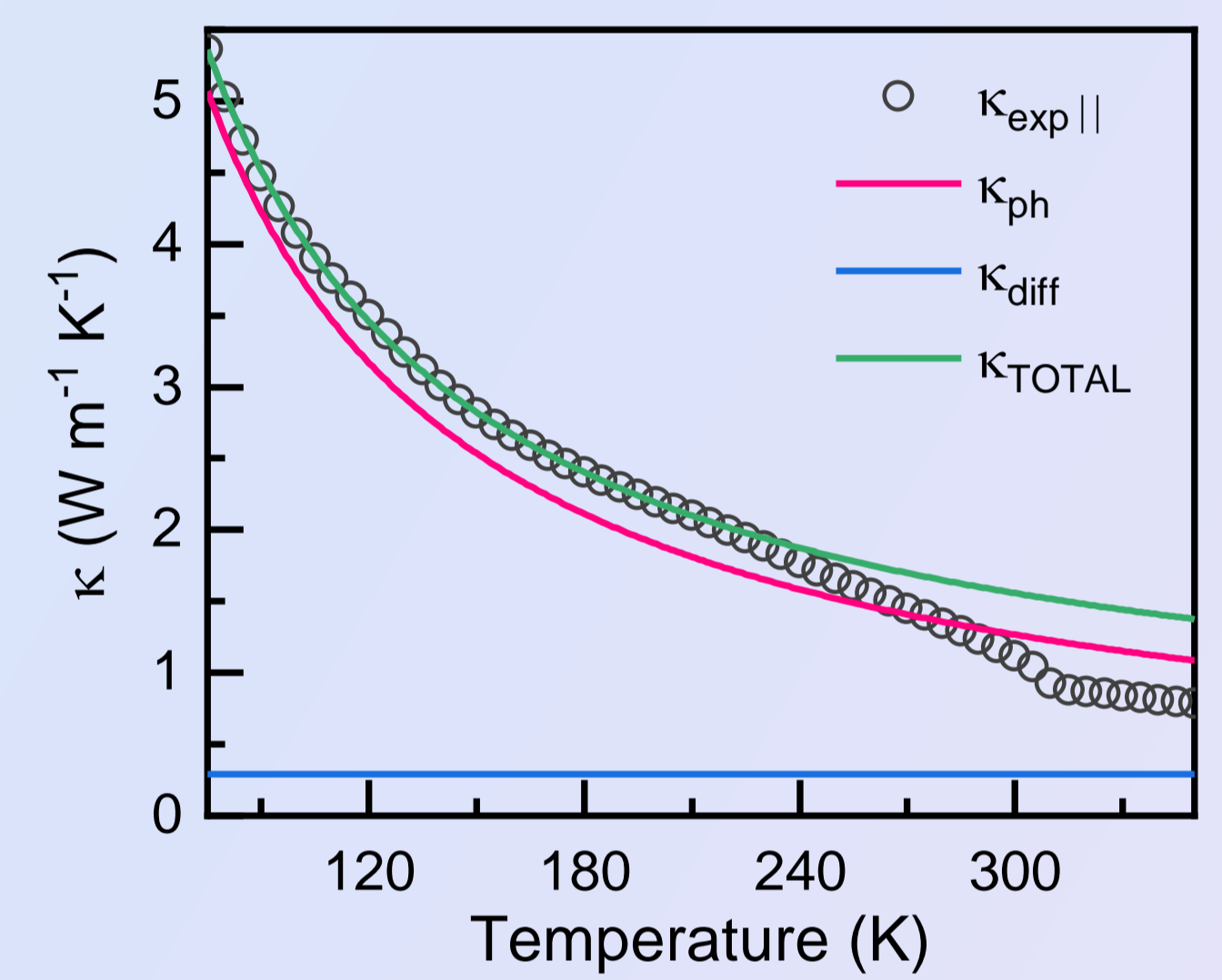


**Figure 1.** Temperature dependence of thermal conductivity  $\kappa$  for  $(Cu,Ag)InP_2(S,Se)_6$  van der Waals chalcogenides measured in direction parallel ( $\parallel$ ) to the structural layers [1].

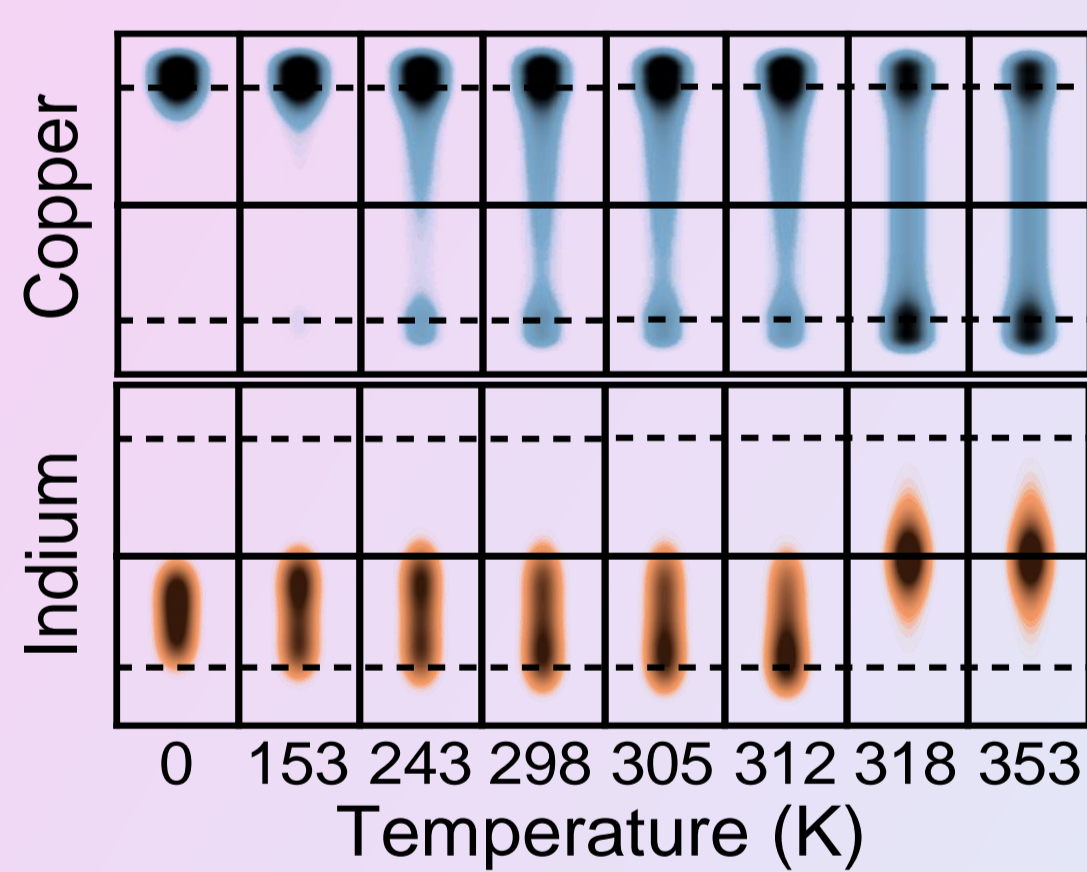
## Results and discussion

According to [5], the thermal conductivity of crystals with a large number of atoms in the elementary cell, which have a multitude of phonon dispersion branches coupling and mixing with increasing wave vector through the Brillouin zone, can be described by considering two channels: a phonon gas and the diffusion channel. The phonon gas contribution follows to the Eucken law, which states that the temperature dependence of thermal conductivity is reciprocal to absolute temperature value due to rise of phonon concentration with heating. In the case of a rich set of phonon branches, the coupling between eigenstates of nearest branches with the same wave vector  $q$  should be possible. Such coupling could be sufficient for capturing the diffusion channel since the Brillouin zone effectively collapses to a single  $q = 0$  point. In result, at high temperatures (above the double Debye temperature), the minimal (glassy-like) value of thermal conductivity can be attained [2,3].

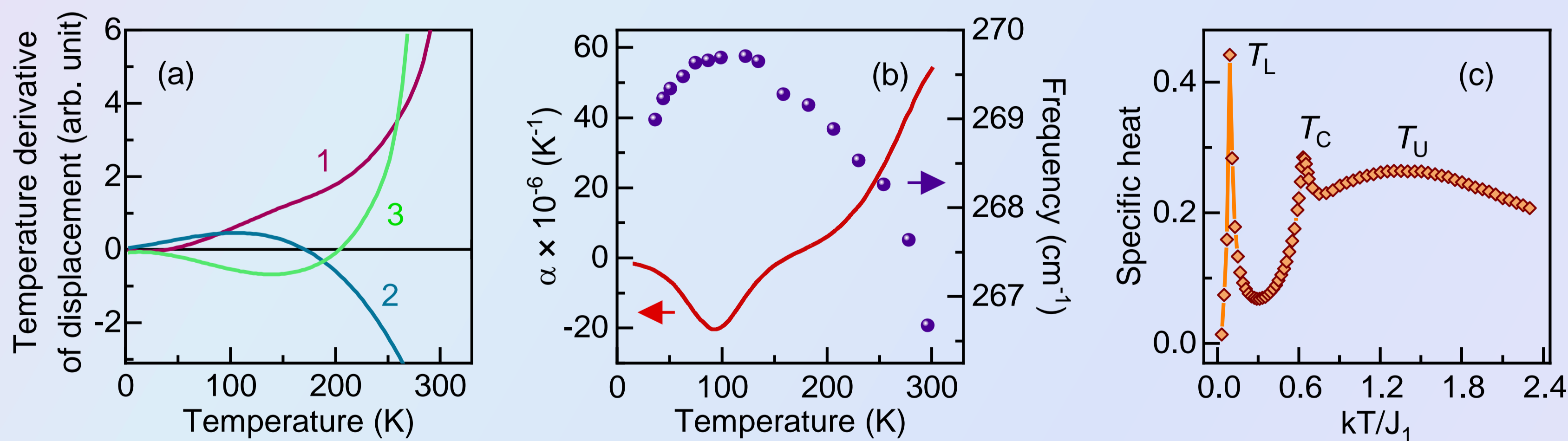
The two-channel heat transfer can be described by the expression:  $\kappa(T) = A/T + B$ . In this equation parameter  $A$  represents the three-phonon scattering mechanism, while parameter  $B$  represents the additional contribution of diffusive transfer. It is seen (figure 2) that for  $CuInP_2S_6$  crystal the best fitting of thermal conductivity curve was obtained in the temperature region of 90-230 K with parameters  $A = 380.2 \text{ W m}^{-1}$  and  $B = 0.29 \text{ W K}^{-1} \text{ m}^{-1}$ . The clear appearance of diffusive-like heat transfer already in the low temperature range of the ferroelectric phase is evidently related to the anharmonic dynamics of  $In^{3+}$  cations. The temperature dependence of  $In^{3+}$  cations space distribution in the  $CuInP_2S_6$  crystal layers (figure 3) was calculated within the quantum anharmonic oscillator (QAO) model [4,6], demonstrating that they are involved in strongly anharmonic relaxations even in the ground state, near 0 K. The  $In^{3+}$  cations experience anharmonic disordering/displacements in the local asymmetric three-well potential. This results in a change in the temperature behavior of the lattice vibrations, which in turn affects the thermal expansion coefficient, causing it to change sign (figure 4). Additionally, a dipole glassy appearance is observed in the deeply cooled ferroelectric phase.



**Figure 2.** Thermal conductivity  $\kappa$  measured parallel to the structural layers of  $CuInP_2S_6$  compound fitted by equation  $\kappa(T) = A/T + B$ .



**Figure 3.** Probability density contours for the spatial distribution of copper (above) and indium (below) cations calculated in the QAO model for  $CuInP_2S_6$  crystal [6].



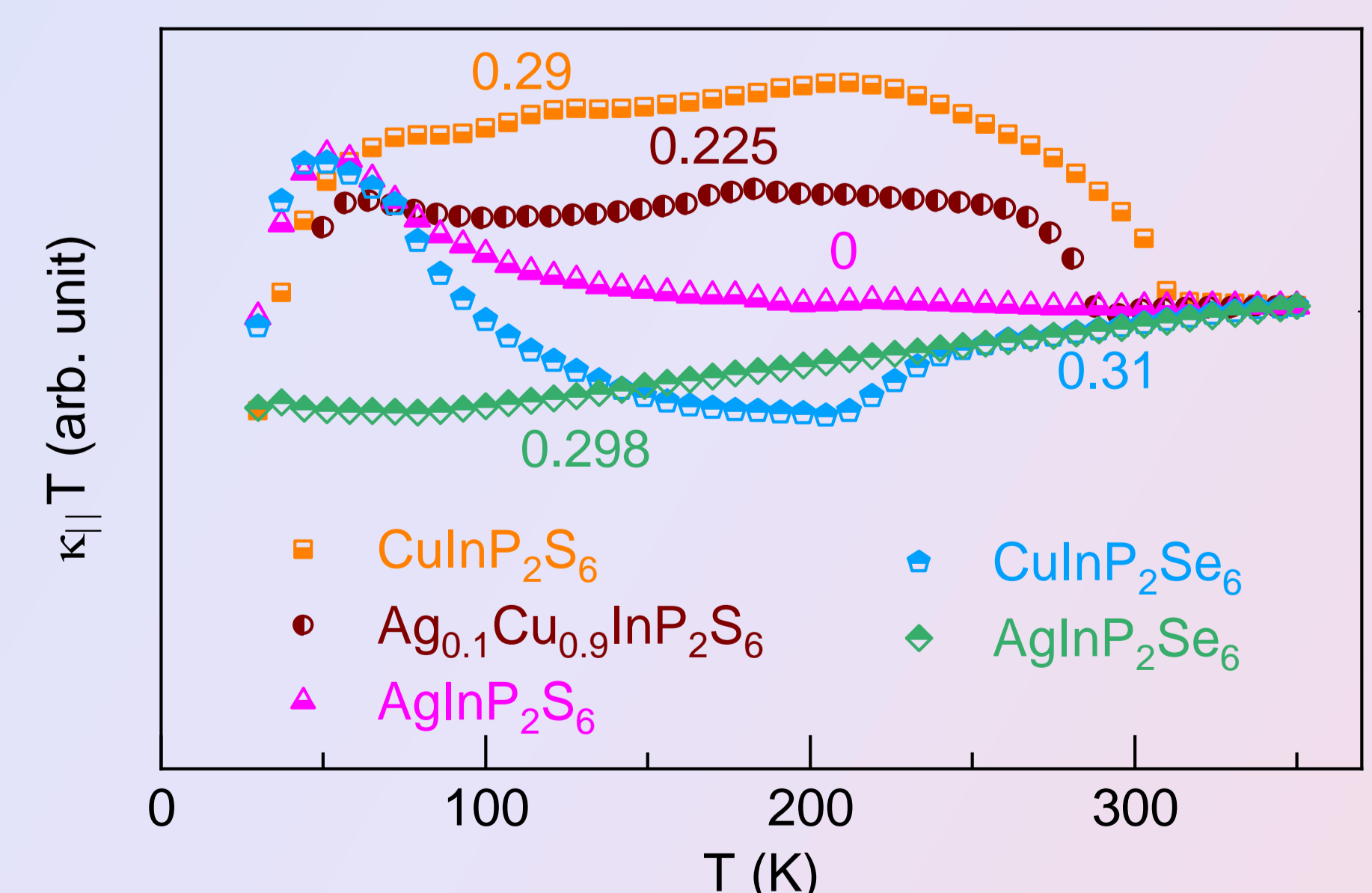
**Figure 4.** (a) Change with heating of the temperature derivatives of the displacements of  $In^{3+}$  cations for the solutions 1, 2 and 3 according to the calculations in the QAO model [6]. (b) Temperature dependence of the linear thermal expansion coefficient  $\alpha$  [7] together with the temperature evolution of the lattice vibration frequency for  $CuInP_2S_6$  crystal [7]. (c) Temperature dependence of the specific heat  $C(T)$  calculated within a mixed Ising model with two non-critical anomalies at temperatures  $T_L$  and  $T_U$ , and a critical anomaly at  $T_C$  related to the phase transition [8].

At temperatures above 200 K, the thermal conductivity is effectively suppressed due to disorder in the copper sublattice (figure 3). This peculiarity is the result of thermal activation of  $Cu^+$  cations in the local double-well potential, which is associated with the SOJT effect. Moreover, the copper disordering contributes to the rise in ionic conductivity in  $CuInP_2S_6$  crystals with heating to the temperature of the ferroelectric to paraelectric phase transition ( $T_C \sim 315 \text{ K}$ ) and in the paraelectric phase.

At partial Cu by Ag substitution, the diffusive contribution is reduced (figure 5). This can be explained by the suppression of indium contribution due to the more covalent Ag bonding and a suppression of the SOJT effect. In  $AgInP_2S_6$ , only the three-phonon contribution has been observed in the high-temperature region. At S by Se substitution, the diffusive component was observed in the paraelectric phase of the  $CuInP_2S_6$  crystal. However, it was not found in the ferroelectric phase, which can be explained by the shallower double-well potential for Cu cations in the selenide compound what leading to a reduction in the phase transition temperature. In the case of the  $AgInP_2Se_6$  crystal, a diffusive contribution is present over a wide temperature range.

## Conclusions

A depth analysis of thermal transport properties in 2D phosphorous chalcogenide of metal cations crystals in the wide temperature region has been performed. Different mechanisms responsible for the obtained values of thermal conductivity have been considered: at low temperatures heat is effectively transferred by phonons and in the high temperature region a diffusive mechanism to the heat transport is observed for all compounds except  $AgInP_2S_6$ .



**Figure 5.** Comparable thermal conductivity of van der Waals chalcogenides, measured parallel to the structural layers, presented in  $\kappa T(T)$  coordinates.

## References

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