Experimental report

30/05/2024

Proposal: 7-03-215 **Council:** 10/2022

Title: Probing the effect of copper-ion mobility on the thermal conductivityof Cu2ZnGeSe4

Research area: Materials

This proposal is a new proposal

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Samples: Cu2ZnGeSe4

Instrument	Requested days	Allocated days	From	To
IN5	4	3	19/06/2023	22/06/2023

Abstract:

Thermoelectric devices enable the conversion of thermal energy into electrical power. The development of new materials is essential to enable large scale implementation of thermoelectric technology. Diamond-like quaternary chalcogenides, including Cu2ZnGeSe4, are attracting considerable interest for their potential for thermoelectric energy recovery, as well as absorbers for solar cells.

Cu2ZnGeSe4 exhibits an electronic transition at 473 K. Our analysis of variable-temperature neutron diffraction data (J. Mater. Chem. A, 2021) has revealed that an order-disorder transition, accompanied by the onset of copper ion mobility, occurs at this temperature. This transition results in a significant reduction in the lattice thermal conductivity of Cu2ZnGeSe4. Here, we seek to gain a better understanding of the effect of copper ionic mobility on the lattice thermal conductivity and the vibrational phonon modes of this material. In particular, we wish to investigate whether transverse vibrational phonon modes are eliminated due to the liquid-like nature of the mobile copper ions, or whether anharmonicity, arising from copper rattling, occurs.

$Cu_2ZnGeSe_4$ exhibits an electronic transition at 473 K. Our analysis of variable-temperature neutron diffraction data has revealed that an order-disorder transition, accompanied by the onset of copper ion mobility, occurs at this temperature.[1] This transition results in a significant reduction in the lattice thermal conductivity of $Cu_2ZnGeSe_4$.

In this experiment, we sought to gain a better understanding of the effect of copper ionic mobility on the lattice thermal conductivity and the vibrational phonon modes of this material.

We collected data on a powder sample of $Cu_2ZnGeSe_4$ between 300 and 550 K, using two incident energies (1.278 and 3.55 meV). In sharp contrast with copper-rich tetrahedrites, for which copper-ionic mobility results in a marked QENS signal,[2] QENS is not evident in the data collected on $Cu_2ZnGeSe_4$ above the order-disorder transition. This is likely to be related to the atom percentage of mobile copper ions in $Cu_2ZnGeSe_4$ when compared to copper-rich tetrahedrites ($Cu_{12+x}Sb_4S_{13}$). However, the copper vibrational modes in the INS data change with increasing temperature.

Figure 1 shows a comparison of the calculated phonon Density of States (DOS) and the experimentally-determined DOS, using data collected on IN5 at 295 K, which are in reasonably good agreement. The main contributors to the low-energy region (4-12 meV) are the Cu and Se atoms.

(a) (b)

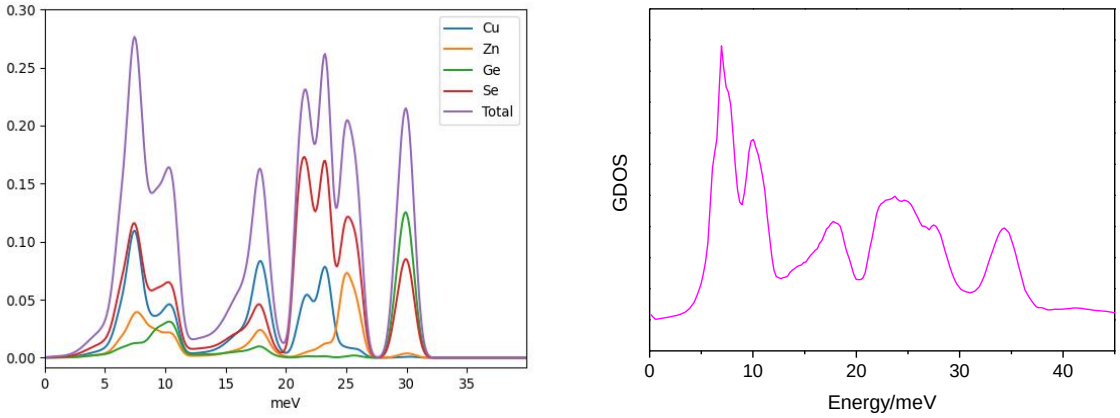

Figure 1. (a) Calculated partial and total DOS for $Cu_2ZnGeSe_4$. DFT calculations were performed by Dr Grau-Crespo (University of Reading), and the resulting force constants matrix was processed using Euphonic, in order to include instrumental broadening and neutron weighting. (b) Experimentally-determined phonon DOS for $Cu_2ZnGeSe_4$ at 295 K.

Examination of the data collected as a function of temperature shows that the low energy modes between 4-12 meV shift to lower energies upon heating (Figure 2(a)). Using DAVE, it has been possible to model this region using five peaks, as shown in Figure 2(b). Figure 2(c) shows the temperature dependence of each peak, with the largest softening occurring for the 4th and 5th peaks, which are largely Se dominated. Additional data collected on MARI (ISIS) at higher temperatures (600 K) shows a significant reduction in the intensity of the low-energy phonon modes. Calculations on the disordered high-temperature structure are currently underway.

[1] P. Mangelis, P. Vaqueiro, R. I. Smith and A. V. Powell, "The onset of copper-ion mobility and the electronic transitions in the kesterite, $Cu_2ZnGeSe_4$", *J. Mater. Chem A*, **9**, 27493 (2021).
[2] S. Mukherjee, D. J. Voneshen, A. Duff, P. Goddard, A. V. Powell and P. Vaqueiro, "Beyond rattling: tetrahedrites as incipient ionic conductors", *Adv. Mater.*, **35**, 2306088 (2023).

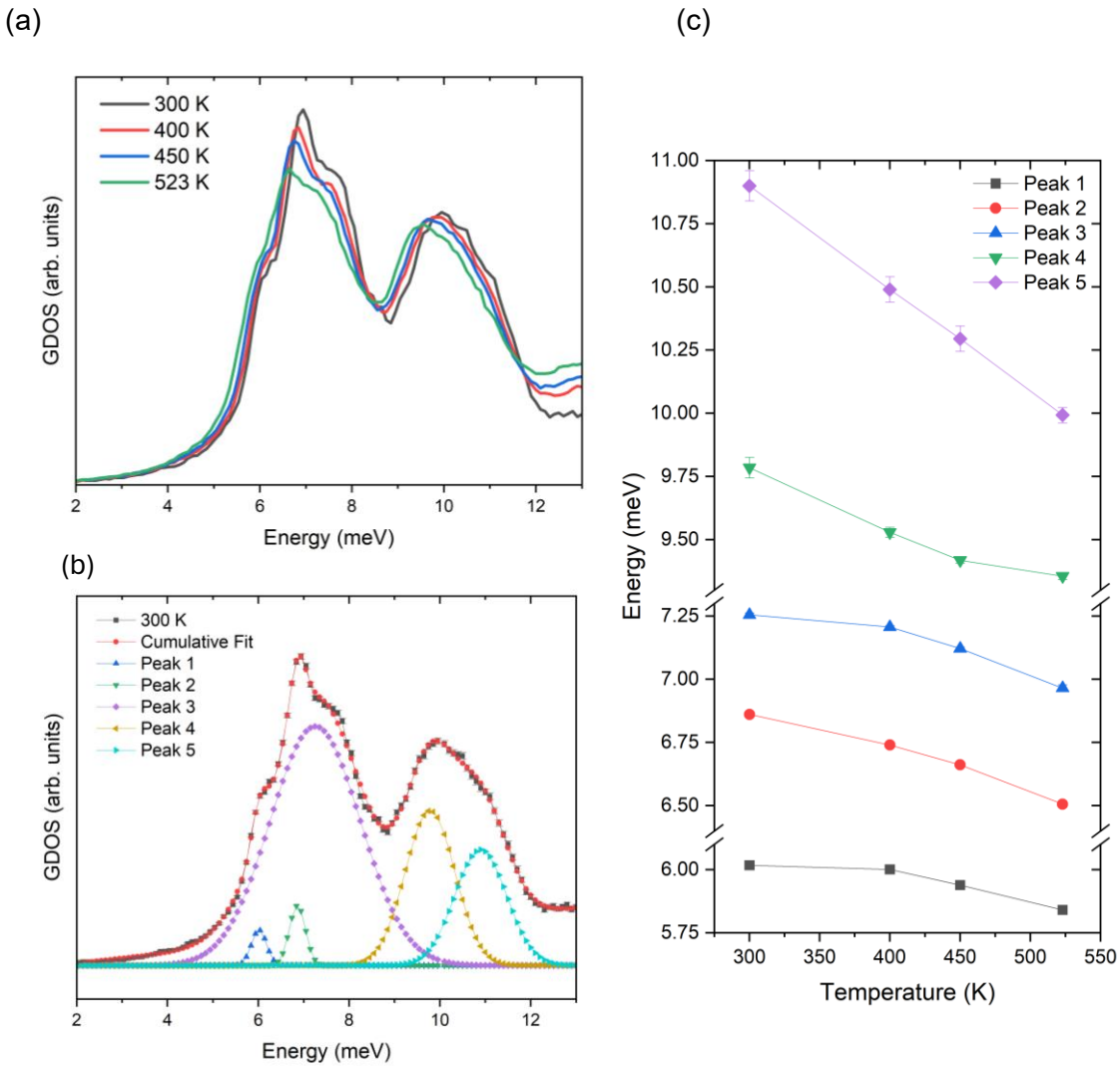

Figure 2. (a) Phonon DOS as a function of temperature over the low-energy region. (b) DAVE fit using data collected at 300 K. (c) Temperature dependence of the peak positions.