Hopping timescales and the phonon-liquid electron-crystal picture in thermoelectric copper selenide

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The suppression of transverse phonons by liquid-like diffusion in superionic conductors has been proposed as a means to dramatically reduce thermal conductivity in thermoelectric materials [H. Lui *et al. Nat. Mater.*, **11**, 422 (2012)]. We have measured the ion transport and lattice dynamics in the original phonon-liquid electron-crystal Cu_2Se using neutron spectroscopy. We show that hopping timescales are too slow to significantly affect lattice vibrations and that the transverse phonons persist at all temperatures. Substantial changes to the phonon spectrum occur well below the transition to the superionic phase, and the ultra-low thermal conductivity is instead attributed to anharmonicity.

Thermal transport is a crucial operational criterion in many technological applications, and thermal conductivity (either high or low) often sets limits to device performance [1]. A prime example of this is the case of thermoelectrics, where the device efficiency is captured by its dimensionless figure of merit $zT = S^2 T \frac{\sigma}{\kappa}$ where S is the Seebeck co-efficient, T the temperature, σ the electrical conductivity and κ the thermal conductivity [2]. Thermoelectric devices currently have zT around unity, and modest improvements in efficiency would dramatically enhance prospects for practical applications [3]. Advances such as nanostructuring [4, 5], reduced phonon velocities [6] and anharmonicity arising from lattice or electronic instabilities [7, 8] have reduced κ to glass-like values. Recently, a new mechanism to obtain even lower κ was proposed, the so-called phonon-liquid electron-crystal (PLEC) model, first used to describe Cu_2Se [9].

Cu_2Se ranks among the best current thermoelectric materials with a peak $zT > 2$ due to its very low $\kappa < 1$ Wm^{-1}K^{-1} [10]. In the low-temperature β-phase Cu_2Se is fully ordered in a monoclinic structure, space group $C2/c$ [11]. There is a phase transition at $T = 414$ K [12] to the superionic α-phase with the anti-fluorite structure, space group $Fm\bar{3}m$, where the fully ordered Se ions occupy a rigid face-centred-cubic lattice. The disordered Cu sites are split into tetrahedra, see figure 1a, and one Cu ion occupies each tetrahedron with the site chosen at random [13]. Within the α-phase the Cu ions have liquid-like mobility [12]. It is proposed in the PLEC model that because liquids do not propagate transverse modes, this leads to an even lower κ than for glasses [9]. However, the question of whether diffusion actually affects phonon modes depends critically upon the timescales involved [14]. If the time between atomic jumps from one equilibrium position to another in a liquid is shorter than the vibrational period, waves do not propagate. If instead the residence time τ is much longer than the phonon period, then waves propagate in the same way as in a solid [15].

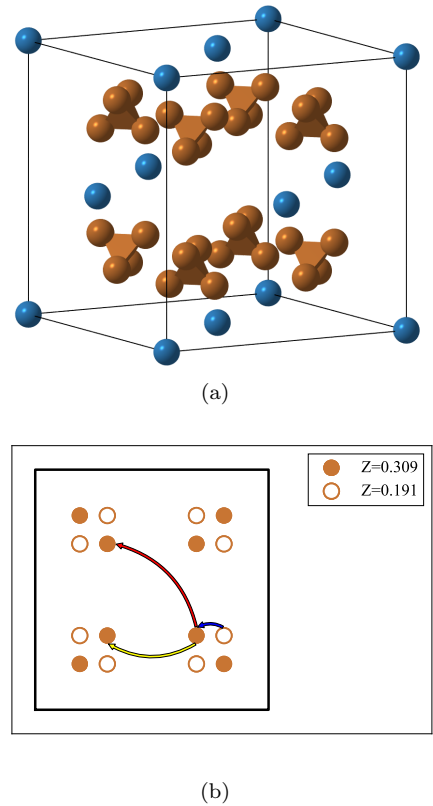Neutron spectroscopy can be used to probe both diffu-

(a)

●	Z=0.309
○	Z=0.191

(b)

FIG. 1: **Crystal structure of α-Cu_2Se.** (a) Unit cell with Se shown in blue and Cu in orange with each Cu site split into tetrahedra. (b) Possible jumps, as described in the text. Local hops are shown in blue, nearest-neighbour hops in yellow, and next-nearest-neighbour hops in red.

sion through incoherent quasi-elastic scattering (QENS) and lattice dynamics through coherent inelastic scattering [16]. Cu has a significant incoherent cross-section and the phonon intensity scales approximately as the square of the neutron momentum transfer, Q. This means that at low Q, QENS dominates the scattering, enabling the
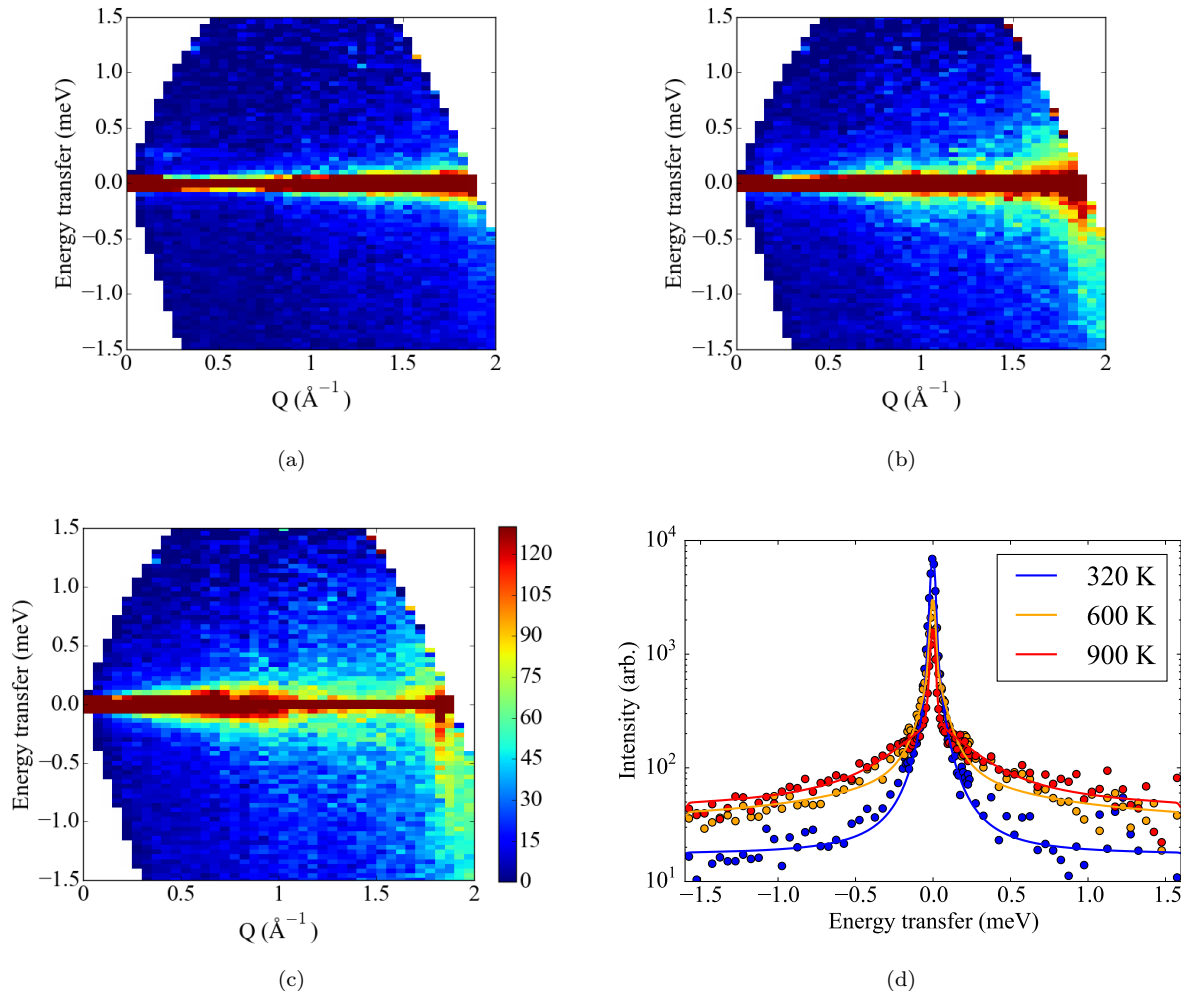
FIG. 2: **QENS intensity observed on LET.** (a) $T = 320$K, (b) $T = 600$K and (c) $T = 900$K. All plots use the same color scale. (d) Scans of energy transfer at fixed $Q = 1.3 \mathring{A}^{-1}$. The solid lines are fits of the Chudley-Elliott model, as described in the text.

Cu diffusion mechanism and rates to be studied. At high Q, the neutron-weighted phonon density of states (PDOS) can be obtained. These two regimes provide all the information required to test the PLEC hypothesis as, τ can be obtained from the QENS and the loss of transverse accoustic modes should be visible in the PDOS. We have studied both the diffusion and lattice dynamics in a powder sample of Cu_2Se (Sigma Aldritch 481629) from 5 to 900 K, with the LET [17] and MERLIN [18] spectrometers at the ISIS facility. The low incident energy on LET allows the quasi-elastic energy broadening to be measured with narrow energy resolution ($E_i = 2.04$ meV with nominal resolution of 36 μeV) while rep-rate multiplication allows the PDOS to be obtained simultaneously with good resolution ($E_i = 18.0$ meV with nominal resolution of 0.69 meV). As the phonon bandwidth is higher than the incident energy, it is only possible to

measure the PDOS with this resolution in neutron energy gain where a large number of phonons are thermally excited at elevated temperature. To cover the full phonon bandwidth (30 meV [19]) at low temperatures it is necessary to excite phonons via neutron energy loss, and here the coarser resolution thermal spectrometer MERLIN was used ($E_i = 60$ meV with nominal resolution of 3.0 meV). All the datasets were reduced with Mantid [20].

Figure 2 presents typical QENS data in the β- and α-phases. At $T = 320$ K in the β-phase, there is relatively weak scattering intensity at energy transfers beyond the resolution-limited elastic scattering, and the energy width grows continuously with Q, suggesting a short jump length. In the α-phase at $T = 600$ K the QENS signal increases dramatically, as expected upon entering the superionic phase. At high temperature, T

= 900 K, a further change to the Q-dependence of the energy width indicates a change in the diffusion mechanism, with broadening at low Q and sharpening at high Q, consistent with the presence of longer range hops.

We have fitted the quasi-elastic energy broadening within the Chudley-Elliott jump-diffusion model [21] over the Q range 0.5 to 1.5 Å^{-1}. Figure 2d compares the fits for typical energy scans at $Q = 1.3$ Å^{-1} for representative temperatures. An analysis of the crystal structure gives the jumps that could be observed using QENS, see figure 1b. We have fitted the data in the β-phase at $T = 320$ K with a single Lorentzian and a jump length, $l = 1.0$ Å, corresponding to localised hops. In the superionic phase it is not possible to fit the data with a single Lorentzian. Over the temperature range $T = 500$-700 K a second length scale $l = 2.2$ Å corresponding to the nearest-neighbour distance between tetrahedra was found to fit the data. At $T = 800$ and 900 K a third length scale, corresponding to next-nearest neighbours (3.2 Å) describes the data well. Molecular dynamics simulations for Cu_2Se [22] and the structurally-related anti-fluorite Li_2O [23] predict a similar diffusion mechanism, initiated by a minority of hops to the octahedral interstitial $(0.5, 0.5, 0.5)$ position, followed by chains of nearest-neighbour vacancy hops, with next-nearest-neighbour hops at elevated temperatures.

Figure 3a shows the self-diffusion coefficients from our fits of the Chudley-Elliott model. The diffusion constant is particularly large above $T = 800$ K due to the drop in residence times for nearest-neighbour hops. Our diffusion rate upon entering the α-phase of $D_{QENS} = 5.3(3) \times 10^{-7}$ cm^2 s^{-1} is in agreement with the value obtained from the ionic conductivity measurements of Takahashi $et\ al.$ [12] $D_\sigma = 6.1 \times 10^{-7}$ cm^2 s^{-1} at $T = 423$ K [24]. We note that the value determined by Danilkin $et\ al.$ [25] using QENS at a comparable temperature is over an order of magnitude higher. We suggest that this is due to their fitting a single Lorentzian to their data, corresponding to a single residence time. This will be dominated by the local component which does not contribute to bulk diffusion, leading to a large overestimation of D.

The residence times presented in figure 3b are key to assessing the validity of the PLEC model to Cu_2Se. Only the residence times for hops between tetrahedra contribute towards bulk diffusion, and both τ_{NN} and τ_{NNN} are above 10 ps at all temperatures. Hence only modes with energies below 0.4 meV can be suppressed by diffusion. As seen from the INS data in Fig. 4, these constitute a negligible fraction of the total. Since the maximum energy for transverse acoustic phonons is an order of magnitude larger than this [26], diffusion will have a negligible effect on κ. This is entirely consistent with the thermal conductivity measurements for Cu_2Se, since κ is actually observed to increase across the β to α phase transition and there is no sharp drop associated with the
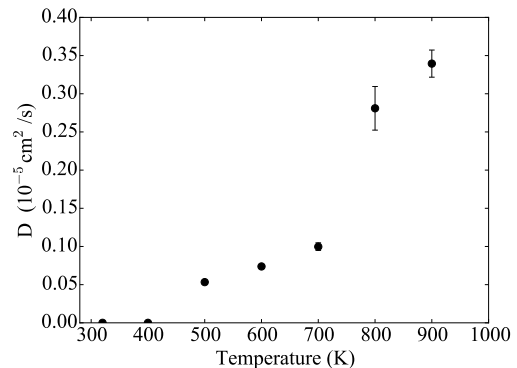

(a)
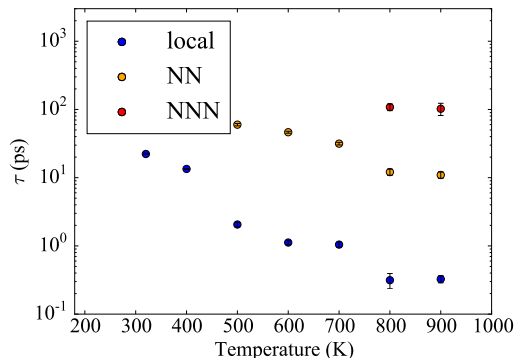
(b)

FIG. 3: **Parameters extracted from fits of the Chudley-Elliott model.** (a) Self-diffusion constant, D, obtained at each temperature. (b) Residence times, τ for each type of hop. See Supplementary Information for details of the calculation of D.

jump in D at $T = 800$ K [9].

The PDOS measured at high temperature and shown in figure 4a directly tests whether the suppression of transverse modes predicted in the PLEC model occurs. There is no dramatic loss of spectral weight accompanying the phase transition from the β-phase to the superionic α-phase between 320 and 600 K, or the dramatic increase in diffusion between 600 and 900 K (see Supplementary Information [24]). At $T = 320$ K while still in the β-phase where diffusion is purely local and rather slow, the PDOS is extremely broad and washed out, with no sharp features remaining. Only on cooling to 200 K (where no QENS signal could be detected) the spectrum begins to sharpen and recover distinct features. The low temperature data measured (figure 4b) shows this, with comparatively sharp features at 5 K, which broaden continuously such that at 320 K they are completely washed out. The only detectable reduction in the low-energy PDOS occurs within the β-phase (see Fig. 4b) where there is no liquid-like diffusion. The in-
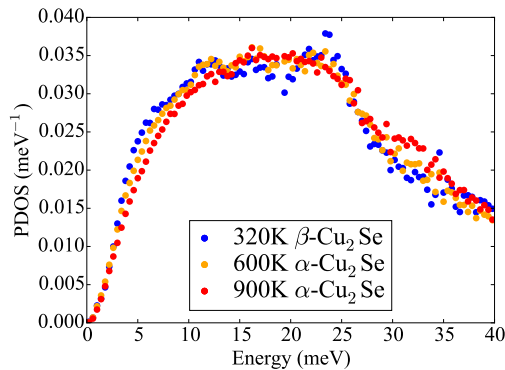
(a)
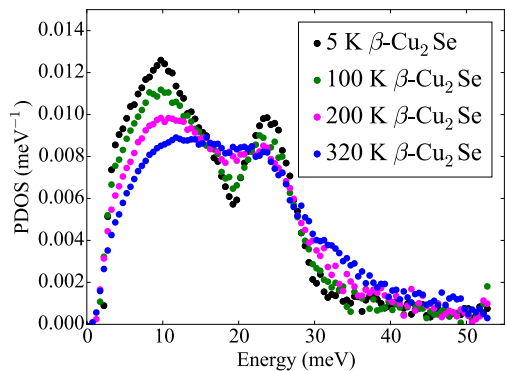
(b)

FIG. 4: **Temperature dependence of the PDOS.**
(a) PDOS measured on LET in neutron energy gain,
integrated over a Q range of 1 to 6 Å^{-1} (b) PDOS
measured on MERLIN in neutron energy loss,
integrated over a Q range of 5 to 10 Å^{-1} . The elastic
line has been estimated from vanadium measurements
and subtracted. The MERLIN data has had the empty
instrumental background subtracted. In both cases the
integrated area has been normalized to one and the
error bars are not plotted for clarity.

tensity of the scattering above the maximum of the dispersion increases gradually with temperature consistent with multi-phonon scattering due to anharmonicity.

Although these PDOS data do not yield a clear measurement of phonon linewidths, the broadening even at 320 K is clear despite the coarse resolution of MERLIN (3 meV) and thus must be much greater than the maximum which could be caused by diffusion (which at most would be 0.4 meV at 900 K). Consequently other intrinsic or extrinsic mechanisms also operating in the low-temperature phase must dominate, and are responsible for limiting κ. In the α-phase the local Cu hops are fast ($\tau_{loc} = 0.3 - 2$ ps). However, this local motion is similar to anharmonic vibration arising from the split nature of the local energy

minima at each Cu site rather than translational diffusion. The ions do not move away and, therefore, they do not prevent the propagation of transverse acoustic phonons. The gradual broadening of the phonon scattering and increase in the multi-phonon scattering with temperature is entirely consistent with anharmonicity being at the origin of the low thermal conductivity. It is acknowledged in the x-ray diffraction studies of Cu_2Se that fitting anisotropic displacement parameters is an alternative to placing ions at these interstitial sites of the tetrahedron [27]. This is similar to $Cu_{12}Sb_4S_{13}$ where, the splitting of a Cu site at low temperature leads to anharmonic motion and phonon scattering at elevated temperatures [28].

The anions in fluorite compounds also exhibit liquid-like diffusion well below their melting temperatures and, by symmetry, they may be expected to behave similarly to the anti-fluorites. The phonons in PbF_2 have been studied using single-crystal inelastic neutron scattering, and the transverse acoustic modes are found to persist at all temperatures [29]. There is an increase in phonon scattering rates above the superionic transition due to anharmonicity and Frenkel defects, but phonon scattering from diffusion is an order of magnitude smaller. The lack of inversion symmetry on the site of the mobile ions allows considerable anharmonicity, and this is always likely to be important for κ in this class of materials.

The PLEC concept is unlikely to work for any superionic solids, since the removal of a substantial fraction of the transverse acoustic phonons would be likely to destabilise the crystal structure. Furthermore, the Cu diffusion in Cu_2Se is harmful, as it actually makes the fabrication of practical devices harder [30]. To develop practical thermoelectric devices from Cu_2Se will require this Cu diffusion to be suppressed, perhaps through doping and the QENS technique offers an accurate way to determine not just the diffusion rates, but also the mechanism. The fact that extreme anharmonicity is responsible for the suppression of κ means that further reduction may be possible through the introduction of nanoscale scattering sites, as has been so successful in other thermoelectric materials.

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