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Copper diffusion rates and hopping pathways in superionic Cu₂Se

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ABSTRACT

The ultra-low thermal conductivity of Cu₂Se is well established, but so far there is no consensus on the underlying mechanism. One proposal is that the fast-ionic diffusion of copper suppresses the acoustic phonons. The diffusion coefficients reported previously, however, differ by two orders of magnitude between the various studies and it remains unclear whether the diffusion is fast enough to impact the heat-bearing phonons. Here, a two-fold approach is used to accurately re-determine the diffusion rates. *Ab-initio* molecular dynamics simulations, incorporating landmark analysis techniques, were closely compared with experimental quasielastic/inelastic neutron scattering. Reasonable agreement was found between these approaches, consistent with a diffusion coefficient of $3.1 \pm 1.3 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ at 675 K and an activation barrier of $140 \pm 60 \text{ meV}$. The hopping mechanism includes short 2 Å hops between tetrahedral and interstitial octahedral sites. This process forms dynamic Frenkel defects. Despite the latter processes, there is no major loss of the phonon mode intensity in the superionic state, and there is no strong correlation between the phonon spectra and the increased diffusion rates. Instead, intrinsic anharmonic phonon interactions appear to dictate the thermal conductivity above and below the superionic transition, and there is only subtle mode broadening associated with the monoclinic-cubic structural transition point, with the phonon density-of-states remaining almost constant at higher temperatures.

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1. Introduction

Liquids have almost no resistance to transverse shear stresses and this permits them to flow freely at the macroscopic scale. For a similar reason, the transverse elastic waves in a liquid are strongly suppressed, at least at long wavelengths. This is reflected in the reduction of the heat capacity from the Dulong-Petit law to below the standard value found in solids ($C_V \sim 3k_B N$) [1]. A subject of great interest is the situation in superionic conductors, which constitute an unusual class of matter with features of both solids and liquids. In such materials (e.g. β -Cu₂Se), one atomic species (Cu) undergoes rapid ionic diffusion, whereas the other species

(Se) forms a stable crystal lattice [1]. These rare compounds generally feature mobile silver, lithium or copper ions in spacious crystal structures, and they have attracted interest as potential solid electrolytes for battery technology. The anomalously low thermal conductivity found in some superionic semiconductors also enables superb thermoelectric performance. For example, β -Cu₂Se offers a thermoelectric figure-of-merit (zT) in the range 1.0 – 2.5 which approaches the highest values ever reported for any thermoelectric [2]. This is linked to the “phonon-liquid-electron-crystal” state, which offers low thermal conductivity in tandem with high electrical conductivity [1]. Yet the origin of this novel state, and its connection with the superionic behavior, is still debated [3].

One theory is that this is a direct consequence of the rapid diffusion of copper in the superionic phase, which has an onset at 405 to 410 K, the temperature at which stoichiometric α -Cu₂Se

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transforms to β -Cu₂Se [1,4]. By analogy to liquids, it was proposed that copper motion suppresses the transverse phonons, thereby reducing the thermal conductivity [1]. However, the role of the rigid Se lattice is yet to be clarified. An alternative hypothesis is that strongly anharmonic cation-anion interactions are the critical factor as this causes increased phonon scattering across a broader temperature range, independently of the diffusion behavior [3]. This general question has been raised in several related materials [5,6]. The apparent deviation from the Dulong-Petit law at high temperature in Cu₂Se may favor the first viewpoint although the measurements of heat capacity do differ between different studies [1,7]. On the other hand, a recent inelastic neutron scattering study concluded that the phonon spectrum is effectively constant from 300 – 900 K whilst the copper diffusion coefficient is low [3]. However, the diffusion coefficients determined in the latter work differ by two orders of magnitude from the earlier determinations by Danilkin *et al.* [8,9] and Horvatić *et al.* [10,11]. The latter also reported that the value depends critically on the Cu stoichiometry in Cu_{2-x}Se. Clearly, further work is required to resolve these issues.

Here we report experimental neutron scattering data and *ab-initio* molecular-dynamics simulations (AIMD), and provide some simple geometrical arguments to support a unified model for copper diffusion in Cu₂Se. Our neutron data are similar to those reported by others, but we show that the data are complex to interpret, and our conclusions are different. Essentially, while it is not possible to distinguish between two hopping pathways with frequencies that are both similar in energy scale to the resolution of the experiment, it is possible to place upper and lower bounds. The AIMD is much more definitive and there is very clear evidence for a major role involving tetrahedral–octahedral and tetrahedral–tetrahedral site hops. This is supported by geometrical arguments resulting from the intrinsic structure of the anti-fluorite lattice, as well as X-ray diffraction data. The model is qualitatively different from those previously proposed for diffusion in Cu₂Se, and for the first time, we end up with a unified self-consistent picture that respects the evidence from simulation, neutron scattering, and the measured bulk *T*-dependent diffusion constants. Furthermore, this model self-consistently explains the intrinsic hopping mechanism in stoichiometric Cu₂Se without the need for Cu vacancies, which remained unexplained in past models. It also correctly reproduces the overall vibrational density of states.

2. Methods

Theoretical: AIMD simulations and nudged-elastic band calculation (NEB) were performed using density functional theory (DFT) in the Vienna Ab Initio Simulation Package (VASP) [12–14]. To analyze the ionic transport properties of Cu₂Se, simulations were performed in the canonical ensemble (N,V,T) using the generalized gradient approximation (GGA) to the exchange-correlation energy due to Perdew *et al.* (GGA-PBE)[32]. The projector augmented-wave method was used to represent the ionic cores [12–14], and the electronic states Cu 4s–3d and Se 4s–4p were considered as valence. Wave functions were represented in a plane-wave basis and the cut-off energy was 500 eV. To model the effect of Cu vacancies in Cu_{2-x}Se, additional simulations were performed by removing a single copper atom from the cell.

Landmark decomposition of the molecular dynamics: Landmark analysis of the DFT results was performed to accurately track the ionic motion of Cu through the lattice, and extract residence times for the different types of Cu hopping motions. Two variants of landmark analysis were performed: one using spherical landmarks, and the other using Voronoi landmarks using the recently developed SITATOR toolkit developed by Kahle *et al.* for “unsupervised” Voronoi landmark analysis [15]. Further detail on the DFT and landmark analysis is given in the supplementary material.

Visualization of the molecular dynamics and corresponding neutron spectral functions: The Visualization for Electronic and Structural Analysis (VESTA) software was used to plot the average structure and copper density maps [16]. VMD was used to plot the trajectories and time-lapse images from the molecular dynamics simulations [17]. The MD trajectories were used to simulate the neutron spectroscopy dataset by deploying the approach implemented in the nMoldyn (v3) software [18–20].

Experimental: Commercially obtained Cu₂Se (99.99%) was crushed into a fine powder and processed by spark plasma sintering (SPS; Thermal Technology SPS model 10-4) at 772 K for 10 min under a pressure of 40 MPa in a vacuum. Inelastic neutron scattering experiments were conducted on the PELICAN time-of-flight neutron spectrometer [21] at the Australian Nuclear Science and Technology Organisation. The Cu₂Se powder sample was placed in an annular aluminum sample can. The instrument was optimized for scans using $\lambda = 4.74$ Å incident neutrons, affording energy resolutions approximated by a Gaussian full-width-at-half-maximum (FWHM) of 135 μ eV at the elastic line. Complementary high-temperature X-ray powder diffraction was conducted at the Australian Synchrotron at a wavelength of $\lambda = 0.58973$ Å. Thermal conductivity was measured by the laser flash method using a Linseis LFA 1000. Further experimental details are provided in the supplementary material.

3. Results

3.1. Geometric analysis

Copper selenide possesses the anti-fluorite structure, with the Fm-3m spacegroup (#225), as illustrated in Fig. 1. The structure is identical to the fluorite structure (e.g. CaF₂) except that the anion and cation sites are reversed. The selenium atoms form a rigid lattice and occupy the *a*-Wyckoff site at the (0,0,0) and symmetry-equivalent positions. The mobile copper atoms have their highest occupancy at the tetrahedral “T-sites”, the *c*-Wyckoff position, with fractional coordinates (1/4, 1/4, 1/4). For long-range diffusion to occur, Cu must navigate between the various T-sites. Assuming the jumps occur directly between the T-sites, the hopping vectors are shown in Fig. 1(a) with the nearest-neighbor hop corresponding to ~ 3 Å. We label these as T \leftrightarrow T transitions. Recent work has focused exclusively on the role of T \leftrightarrow T transitions for mediating diffusion [3]. However, several past XRD and near-edge X-ray absorption spectroscopy (NEXAFS) studies have also identified that a smaller fraction of the Cu occupies the interstitial octahedral “O-sites” [8,9]. The lightly-occupied O sites are, on average, centered on 8b site at the (1/2, 1/2, 1/2) position, although some reports may indicate they are slightly offset (e.g. 1/2 \pm δ , 1/2 \pm δ , 1/2 \pm δ , within the closely related 32f sites). In either case, if these O-sites are included in the Cu network, this enables a new set of hopping pathways as illustrated in Fig. 1(b) which include shorter hopping vectors ~ 2 Å. We label these as T \leftrightarrow O transitions. The hop from T \rightarrow O can be considered to generate a Frenkel defect pair [22], consisting of the vacant tetrahedral site, and the copper in the interstitial O-site. Long-range diffusion via T \leftrightarrow O transitions is also possible because a T \rightarrow O transition followed by an O \rightarrow T transition can move a Cu away from its original T-site to a neighboring tetrahedral vacancy. To assess the likelihood of T \leftrightarrow O versus T \leftrightarrow T transitions, an analysis of the steric hindrance for different hopping vectors is presented in Table 1. This shows that the closest-approach for a Cu-Se pair is 0.354*a* for a T \leftrightarrow T jump, where *a* is the cubic lattice constant. In contrast, T \leftrightarrow O hops allow for greater clearance between the Cu-Se pairs (0.408*a*). Intuitively T \leftrightarrow O transitions, therefore, seem very likely, given the larger channel width, yet the octahedral and tetrahedral environments are quite different (Fig. 1(c) and (d)) and thus the internal energy differences may make one

Table 1
Summary of nearest Cu-Se hopping distances, vectors and closest approach distances in terms of the cubic lattice constant (a), as expressed in Ångstroms, assuming a = 5.83 Å.

Label	Description	Closest approach for Cu-Se pair	Hopping distance between sites
(T-T) _i	Hopping along <100> directions between nearest-neighbor T-sites positions	0.354 a	0.5 a = 2.92 Å
(T→T) _{ii}	Hopping along <110> directions, between next-nearest neighboring tetrahedral to tetrahedral sites.	0.250 a	0.7 a = 4.13 Å
T→O	Hopping along <111> directions between tetra-octa sites	0.408 a	0.43 a = 2.529 Å
O→O	Hopping along <110> directions from octahedral to octahedral sites.	0.354 a	0.7 a = 4.13 Å

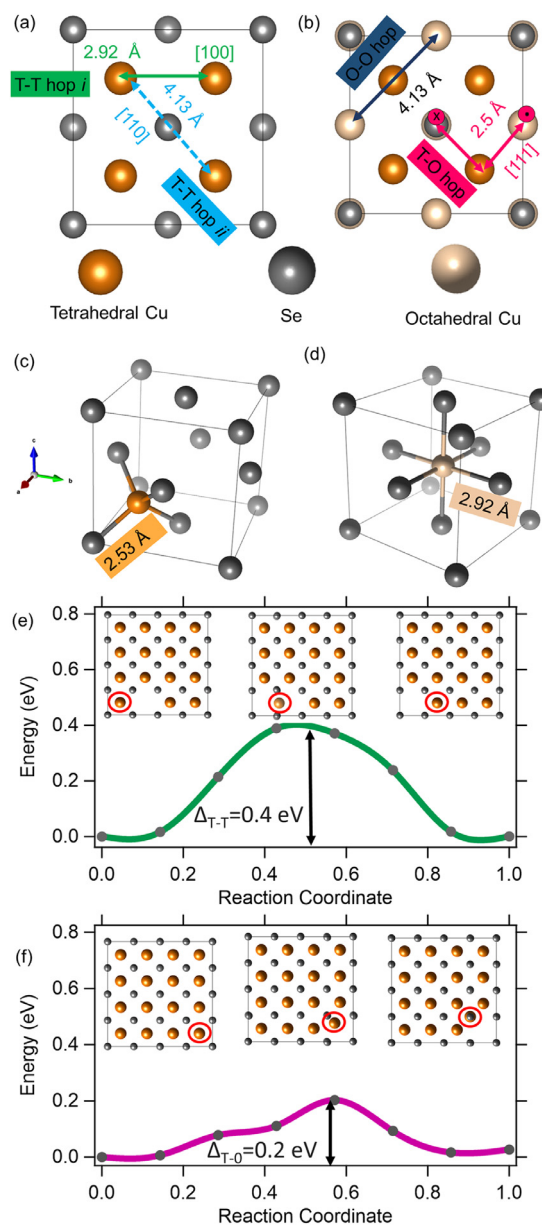


Fig. 1. (a) The time-averaged crystal structure of cubic Cu_2Se consists of a FCC selenium lattice, with copper primarily located in the tetrahedral positions. Hopping between nearest-neighbour Cu positions corresponds to $[100]$ vectors. (b) The lightly occupied octahedral sites in the lattice provide another potential hopping route along the $[111]$ directions, with a shorter hopping length. Note that $[111]$ vectors contain out-of-plane components. While the distances are given assuming idealized positions in the antifluorite structure, there can be considerable variation (± 0.4 Å) if the non-idealised positions are used. (c) Illustration of the copper in the tetrahedral (b-site) position. (d) Illustration of copper at the octahedral O-site (c-Wyckoff position). (e) Energy profile calculated via DFT for copper undergoing a T-T hop. (f) Energy profile calculated via DFT for copper undergoing a T-O hop. The inset figures show the pathway taken by the copper atom.

of the sites unstable, or metastable. To confirm the latter points, density-functional theory calculations were performed to compare the T→O and T→T activation barriers, using the nudged elastic band method. The results are shown in Fig. 1(e) and (f). As anticipated, the T→O transition has a significantly lower barrier (0.2 eV) compared to the T→T transition (0.4 eV). Furthermore, the octahedral site appears as a metastable point in the pathway. This explains the low occupancy found on the O-site experimentally. Consequently, if any T→O transition occurs, it will generally be followed by a subsequent O→T transition, and the Frenkel defects

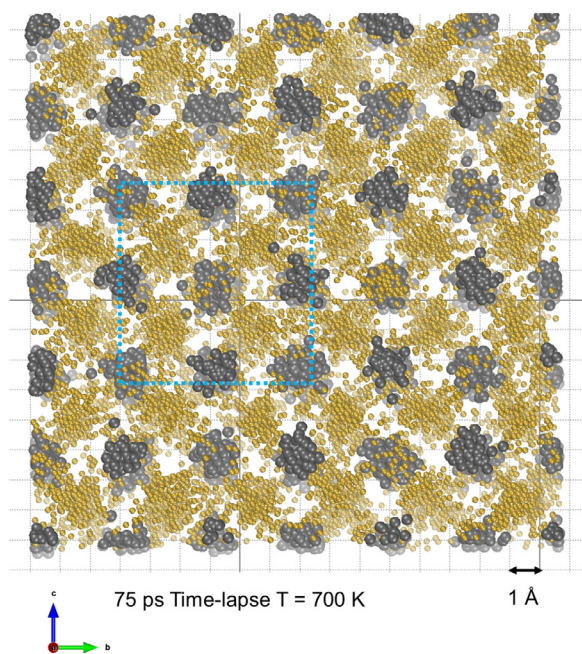


Fig. 2. Time-lapse image showing that the selenium atoms form a thermally agitated FCC lattice, whereas the copper atoms are delocalized across the crystal structure, albeit with a high probability of being located at the tetrahedral sites of the cubic lattice. The image is constructed using the trajectories from the 700 K *ab-initio* molecular dynamics with each still image taken 150 fs apart, and then superimposed on each other.

will be short-lived and dynamic. Nevertheless, the short-lived vacancy generated by an O→T transition is an important mechanism to allow hopping and avoid double occupancy on the tetrahedral copper sites. For example, if one assumes that 1% of the T-sites contain dynamic or extrinsic vacancies, there is a 23% chance that a Cu which undergoes a T→O hop can find a different tetrahedral vacancy available for its next O→T hop. A more detailed explanation of the underlying statistical argument is given in the supplemental materials. One important consequence is that this analysis naturally explains how copper can hop in stoichiometric Cu₂Se *without any extrinsic copper vacancies* because the T↔O hops dynamically generate the vacancies required to avoid a “Cu traffic jam” on the T-site, allowing Cu to shuffle past each other using the O-site as a bypass. In the following sections, we discuss molecular dynamics calculations and quasielastic neutron scattering (QENS) measurements which reveal that the latter picture is essentially correct, and that T↔O transitions dominate overall.

3.2. *Ab-Initio* molecular dynamics

Ab-initio molecular dynamics simulations are a powerful tool to study the motion of an ensemble of Cu and Se atoms self-consistently, with a realistic depiction of the internal energy landscape and atomic forces including anharmonic interactions. For Cu₂Se, AIMD simulations show that both the Se and Cu sublattices are thermally agitated and that the atoms move considerable distances from their idealized position, as illustrated in the time-lapse image taken at 700 K in Fig. 2 which shows the same features identified in past work [23]. In agreement with experiment, the simulations also predict long-range ionic diffusion for the Cu, whereas the Se atoms are trapped near their initial site positions (below 900 K). The mean-square displacements of the Cu during the simulation (Fig. 3(a)) indicate long-range diffusion, where the slope is related to the diffusion coefficient via the Einstein relation:

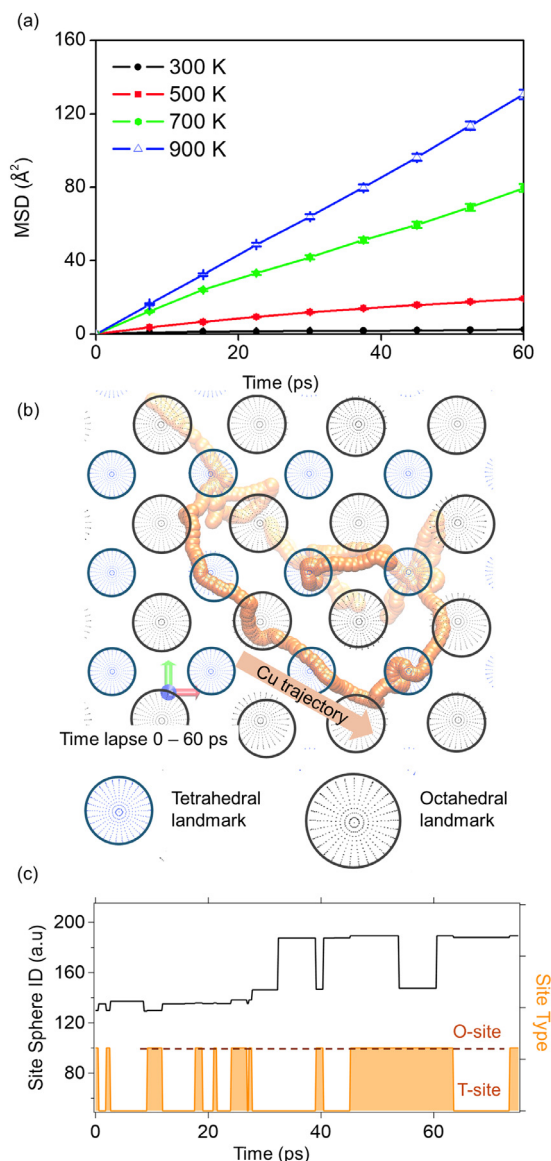


Fig. 3. (a) The mean-square displacements calculated from the AIMD trajectories at various temperatures. (b) A time-lapse image of the motion of a single copper atom shows the hopping motion of the ion as it navigates through the T-site and O-site landmarks. The time-lapse is from the 700 K trajectory over a period of 60 ps with each frame visualized 100 fs apart. The brightness of the copper indicates its height in z, into or out of the page. (c) Landmark analysis showing residence periods for a copper ion as it moves between tetrahedral and octahedral landmark sites during the trajectory.

$$D = \lim_{\tau \rightarrow \infty} \frac{MSD(\tau)}{6\tau} \quad (1)$$

The error bars for the mean-square displacements were estimated using the method discussed in Ref. [24]. The values for the diffusion coefficients show good agreement with the most reliable experimental values, as discussed in detail later.

Close inspection of the MD also reveals that the individual Cu ions experience three main types of atomistic hopping. To illustrate this, Fig. 3(b) displays a representative trajectory for a single Cu as a time-lapse image. Firstly, the Cu atom undergoes frequent T↔O transitions described in the earlier section, corresponding to hops mainly along the <111> directions. The Cu in the O-site has a finite residency time, indicating that it is a metastable site. Secondly, at high temperature, the Cu occasionally hops directly be-

tween tetrahedral sites (i.e. $T \leftrightarrow T$ transitions), involving hopping along a $\langle 100 \rangle$ direction. Thirdly, the Cu sometimes dwells for longer times in the T/O sites, undergoing confined local diffusion, orbiting to further distances around the average Wyckoff position, within what is still a fairly large “interstitial “cage”. This motion occurs even at a lower temperature when the Cu atoms are not undergoing long-range diffusion. The dynamics for the $T \leftrightarrow O$ and $T \leftrightarrow T$ are consistent with the earlier description in Table 1 and Fig. 1. The only caveat is that the confined diffusion around the T/O-sites introduces a thermal spread of copper positions in the sites, which in turn means that hops are not simply parallel to $\langle 111 \rangle$ or $\langle 100 \rangle$ or exactly 2 or 3 Å, but rather distributed around these average values. As the number of events per Cu is relatively low, it can be misleading to examine a single atom since there is a large statistical variation. Landmark analysis of the entire ensemble is, therefore, a better tool to extract the average behavior.

In the simplest approach, landmarks were manually placed at the T- and O-sites throughout the supercell, where the positions were as defined in the time-averaged structure. As detailed in the supplementary material, any Cu atom within $d_0 = 1$ Å of a landmark site was labelled with that site’s unique ID and type (O or T), and transitions could be tracked by monitoring the site IDs for each atom at each frame (for example, shown in Fig. 3(c)). By performing this procedure for all 144 Cu atoms in the simulation, the average residence time and transition rates between types were extracted. Table 2 presents the average transition rates, at 700 K, for the entire copper ensemble, along with the statistical analysis of the various hopping events. The fractions of the different types of hops extracted is fairly robust, since it did not depend on the cutoff radius d_0 , but the residence times were found to depend strongly on the choice of cut-off size. This reflects that the choice of the spatial region defining a site is somewhat arbitrary, and the copper also spends a considerable amount of time in ‘no man’s land’ in interstitial regions between spherical sites. To cross-check the analysis, we also deployed the unsupervised landmark algorithm recently developed by Kahle *et al.* [15]. Although automated, the algorithm does depend on a range of parameters which specify the spatial and statistical resolution that defines sites. We selected a midpoint as 1, occupancy minimum as 0.2, clustering threshold of 0.9 and an assignment threshold of 0.75 because, with these parameters, the algorithm automatically identified 72 c sites and 215 (out of the total 216) b-sites as hopping residence points. Moreover, the algorithm confirmed the c-sites were tetrahedrally coordinated (T-sites), whereas the b-sites were octahedrally coordinated (O-sites). The residence times extracted using Kahle’s algorithm are shown in Table 2 for comparison, and the agreement between the two methods is good. This shows most transitions are $O \rightarrow T$ hops, or the inverse $T \rightarrow O$ hops (over 80 %). As the vast majority of hops involve $T \leftrightarrow O$ transitions using the O-site intermediary site, this scheme is very similar to that proposed by Danilkin *et al.* [8], although that work did not identify the smaller fraction of $T \leftrightarrow T$ hops (16%). In contrast, Voneshen *et al.* [3] argued that the $T \leftrightarrow T$ hops are the main source of diffusion, but they did not identify the $T \leftrightarrow O$ hops. Nevertheless, the mechanism in the AIMD is broadly consistent with the hopping mechanism known in other fluoride fast-ion conductors (CaF_2) [22,25].

To visualize the hopping pathways, Fig. 4 (a) shows the copper density map calculated from the AIMD at 700 K. The density contains clear regions of high density at the tetrahedral positions and medium density at the octahedral positions. This results in a distinctive “Swiss-cheese” isosurface when viewed along the [001] projection caused by the lower density along $\langle 100 \rangle$ vectors associated with the rarer $T \leftrightarrow T$ transitions. To pinpoint the hopping directions, the density was visualized on 2D slices along the (100) and (11-2) planes are shown in Fig. 4(b)–(d). Transitions between the copper sites appear as blurred intensity connecting two dis-

Table 2
Theoretical residence times extracted from landmark analysis for the 700 K AIMD trajectory. The residence time is defined as average time in a site spent before a hop occurs, whereas the hop rate is the total number of hopping events per picosecond. Detailed balance requires the residence type in the 8c octahedral sites to be half that within the 4c tetrahedral sites owing to the multiplicity of the sites.

The dominant hopping vector direction		Proportion events	Residence time – Spherical landmarks (ps)	Hop rate(ps ⁻¹)	Residence time – Voronoi landmarks (ps)
$T \leftrightarrow T$	[100]	16%	3.9	0.03	4
$O \rightarrow T$	[111]	41%	2.0	0.11	1.6
$T \rightarrow O$	[111]	41%	3.9	0.11	3.2
$O \rightarrow O$	[110]	2%	> 200 ps	0.005	N.A.

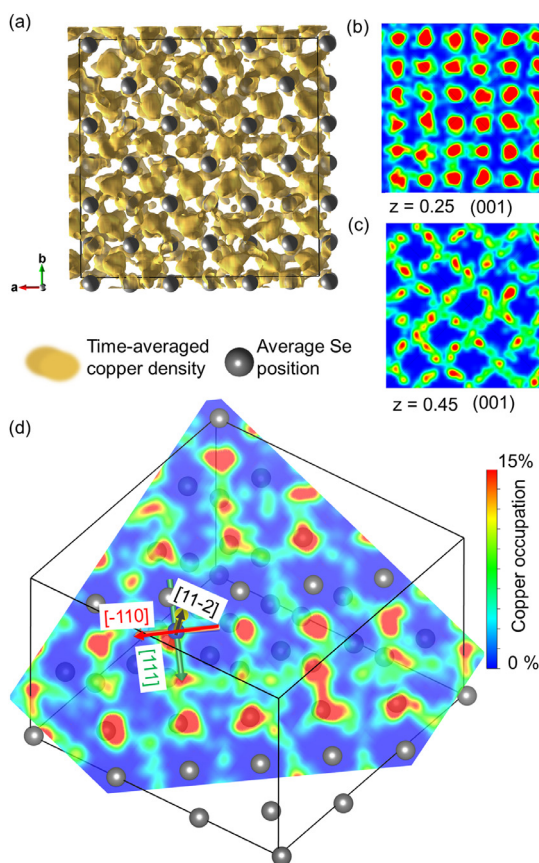


Fig. 4. (a) The copper density map from AIMD is visualized as an isosurface connecting regions where the copper occupation is greater than 5%. (b) A 2D slice of density map on a plane normal to (001) shows the heavily occupied tetrahedral sites at the $z = -0.25$ positions which are generally disconnected from one another indicating low probability of direct $T \leftrightarrow T$ transitions. (c) The (001) slice at $z = 0.45$ shows the transition pathways between the T-sites and O-sites, which appear to be along the [110] directions. (d) A isometric view of the [11-2] slice superimposed on the crystal structure shows the main transition pathways between the $T \leftrightarrow O$ transitions for hopping vectors in the plane along the [111] directions.

tinct sites. Clearly, there are very few transitions evident between the tetrahedral sites in Fig. 4(b). In contrast, there are clear transitions between $T \leftrightarrow O$ sites in Fig. 4(c). Further inspection in Fig. 4(d), shows that many of these $T \leftrightarrow O$ events occur along $\langle 111 \rangle$ directions, as expected according to the simple model in Section 3.1. Simulations were also run for a slightly non-stoichiometric Cu_{2-x}Se cell with $\text{Cu}_{1.99}\text{Se}$, but the results were qualitatively identical, and are not presented for brevity, although the small shifts in the diffusion coefficient are included in Fig. 8.

In summary, all the available analysis shows that the short $T \leftrightarrow O$ hops are the dominant diffusion pathway in Cu_2Se , and direct $T \leftrightarrow T$ hops are far rarer. In a later section, we show that the quasielastic neutron scattering is consistent with this picture, after correction for complexities arising from the confined diffusion component and coherent acoustic phonons.

3.3. Experiment: Inelastic neutron scattering and X-ray diffraction

Past work has established that off-stoichiometry in Cu_{2-x}Se can strongly affect the obtained diffusion coefficients and phase transition point [26]. To quantify the level of the off-stoichiometry and transition temperature, Fig. 5(a) shows the experimental X-ray diffraction maps which illustrate the phase transition point for Cu_2Se . The low angle (004) peak is a signature of the monoclinic phase. The integrated intensities of the (004) and ($\bar{3}$ 31) Bragg

peaks are shown in Fig. 5(b). To determine the critical temperature, and the “apparent critical exponent”, we have fitted the peak area of the (004) peak to the relationship, $A = \left(\frac{T_c - T}{T_c}\right)^\beta$ and obtained $T_c = 395 \pm 5$ K, $\beta = 0.86 \pm 0.1$. The transition temperature indicates that our sample is stoichiometric to within 1-3% since the phase transition temperature varies as $(T_c = 405 - 2.5x)$ [27,28]. The Rietveld refinement in Fig. 5(c) confirms the expected site occupancies, and that Cu_2Se is in the Fm-3m space group, and the results are consistent with the reported structure (#ICSD 54916). We note that the literature is still divided on whether this is a first or second-order transition, and the uncharacteristically large β exponent suggests that this transition is not reliably described by critical theory. Instead, this phase transition is most likely of first-order but gives rise to “apparent critical phenomena” by virtue of its complex phase diagram [4]. In support of this, there is a smooth evolution of the DOS above, below and across the phase transition (Fig. 5(d)), and there is no strong evidence of soft-phonons. To examine the low energy range of the GDOS, an enlarged region is shown in Fig. 5(e).

Using the correlation functions obtained from the AIMD, it is possible to compare the vibrational density of states with the values measured in the inelastic neutron scattering. Fig. 5(d) compares the generalized density of states in the experiment with those calculated from AIMD. The agreement is almost perfect, indicating the AIMD simulations do an excellent job at capturing the main optical modes in Cu_2Se in the energy range 5 – 20 meV. This leads to excellent agreement with the experimental data over the entire temperature range because the GDOS is almost temperature-independent between 300 – 700 K (Fig. 5(d), see Supplemental). Importantly, the phonon spectrum is similar at all temperatures, with two major peaks at 10 meV and 23 meV in both the low temperature data (300 K) and the superionic phase ($T > 400$ K). The similar overall intensities indicate that there is no major systematic loss of the transverse acoustic modes because, if that was the case, the number states/intensity would be reduced by two thirds. Close examination, however, does show that there are subtle changes in the phonon lifetimes in this temperature range which leads to minor broadening of some modes, particularly in the sub-THz regime (< 4 meV) (Fig. 5(e)). The effects in this region, which are dominated by low energy acoustic phonons, are still relatively minor. Indeed, this is supported by the fact that the thermal conductivity above the phase transition temperature, far away from the transition, is only lowered by about 25% even at the hottest temperature (850 K) compared to the low-temperature phase (Fig. 5(f)), again supporting the notion that the phonon structure is very similar. The partial densities of states for the copper and selenium contributions in the superionic state are included in the supplementary materials, showing a large contribution of copper modes at low frequency.

To go beyond the angular-averaged DOS, Fig. 6(a) shows the measured neutron scattering function $S(\omega, Q)$ for Cu_2Se at 675 K, compared with the theoretical $S(\omega, Q)$ calculated from the AIMD decomposed into its coherent (Fig. 6(b)) and incoherent contributions (Fig. 6(c)), where the total measured $S(\omega, Q) = S_{coh}(\omega, Q) + S_{inc}(\omega, Q)$. The coherent part of the neutron scattering function $S_{coh}(\omega, Q)$ involves the Fourier transform of time-correlation functions of pairs of different atoms’ positions (e.g depending on $R_i(t)$ and $R_j(t)$ where R_x is a position operator for atom x , and i and j are indices for different atoms). The latter includes strong contributions from collective motions such as phonons. In contrast, the incoherent part of the $S_{inc}(\omega, Q)$ is generated by the self-correlation function of a single atom’s time-dependent position (e.g depends on R_i and $R_i(t)$), and is an indication of self-diffusion. The latter generates a distinctive broadening of the elastic line near $\omega=0$, known as the quasielastic contribution, which is a hallmark of diffusive processes. In both the experiment and incoherent theory for

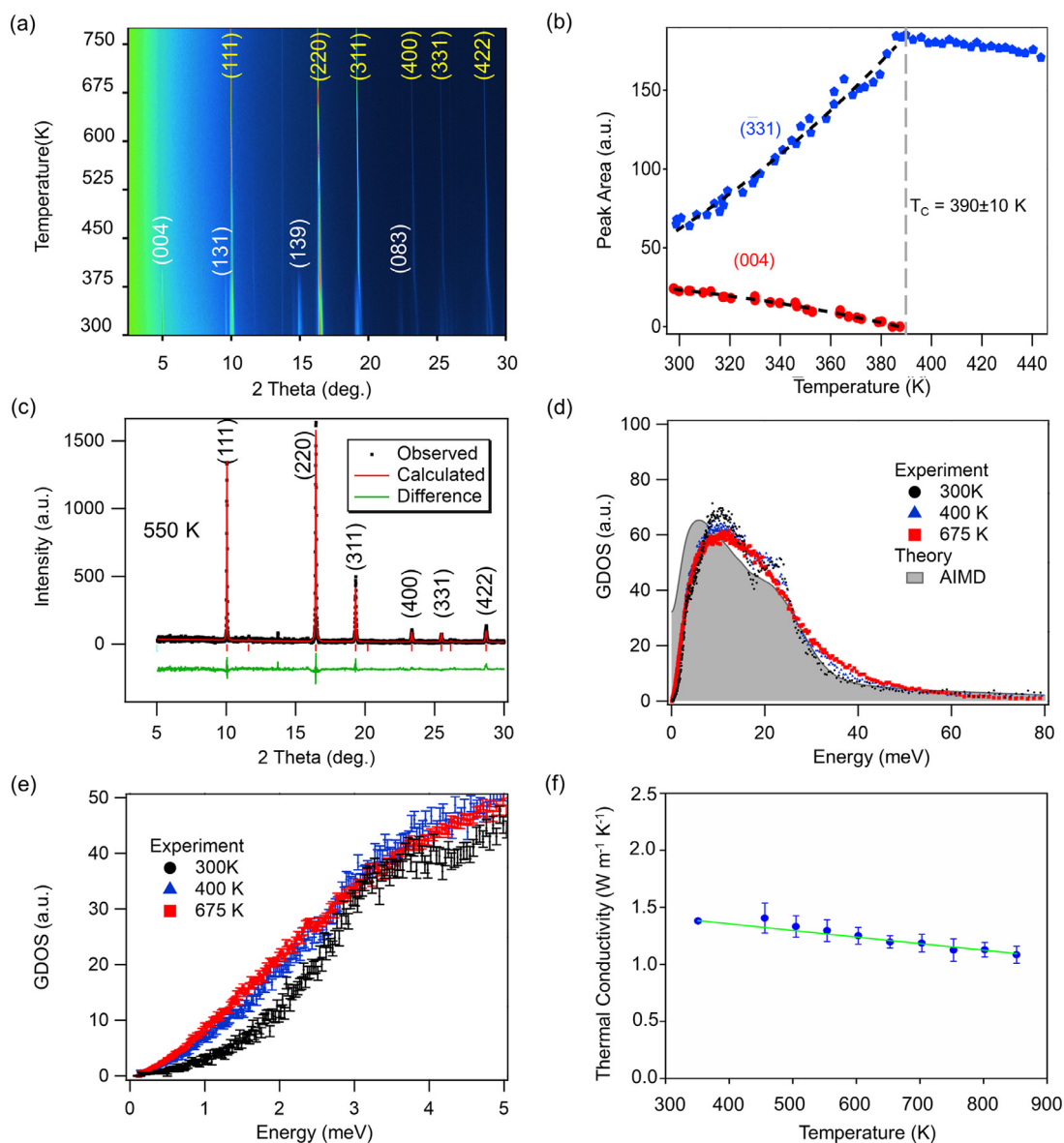


Fig. 5. (a) X-ray diffraction patterns for a temperature sequence stacked in a heatmap. The (004), (131), (139) and (083) reflections are associated with the low temperature phase of Cu_2Se . (b) Integrated peak intensity for the (004) and (331) monoclinic peaks from the XRD (c) Rietveld refinement of the XRD data at 550 K. (d) Experimental generalised density of states in Cu_2Se at 300, 400, and 675 K, compared with the theoretical DOS calculated from the AIMD at 675 K. (e) Enlargement of the low-energy region of the DOS showing subtle changes in the acoustic phonon spectrum above and below the superionic transition. (f) The thermal conductivity of Cu_2Se has an anomaly (not shown) at the 400 K transition temperature, but overall is only weakly temperature-dependent.

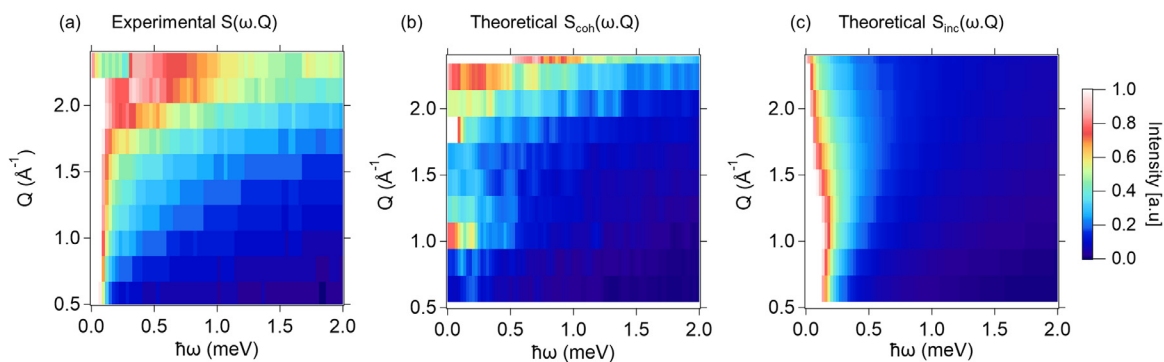


Fig. 6. (a) The total measured experimental $S_{\text{tot}} = S_{\text{coh}} + S_{\text{inc}}$ for Cu_2Se at 675 K. (b) The calculated S_{coh} from the AIMD simulations including low-energy phonons. (c) The calculated S_{inc} from the AIMD simulations which depends on Cu self-diffusion processes.

Cu₂Se, a strong quasielastic broadening is observed at the E=0 line for all Q-values which is an unambiguous indication that diffusion processes are taking place. The linewidth increases with Q as expected for long-range diffusion. But at high Q (~ 2.3 Å⁻¹), the experimental broadening suddenly increases, whereas the theoretical $S_{inc}(\omega, Q)$ does not. The explanation for this can be seen by examining the theoretical pure coherent $S_{coh}(\omega, Q)$ which shows strong intensity at these Q-positions corresponding to acoustic phonons with a high dispersion that survives in the superionic state of Cu₂Se. The excellent qualitative and quantitative agreement with experiment gives us confidence in the other predictions of the AIMD, and next, we examine the low-energy realm in the quasielastic region below 1.2 THz (5 meV).

3.4. Experiment: quasi-elastic neutron scattering

Quasielastic neutron scattering examines the energy region around the elastic line at $S(0+\delta, Q)$ (typically within a few meV in a time-of-flight experiment) and is a well-established technique to determine self-diffusion coefficients in materials, because it offers energy and reciprocal space vector (Q) resolution. The broadening of the elastic line via the quasielastic component can be analyzed to determine the self-diffusion of the ionic species including the length of the jumping vectors involved. QENS has the advantage over DC/AC transport measurements in that no sample contacts are needed, and it is free of geometric artifacts. The disadvantage of QENS is that it is an indirect method which relies on fitting to a model to determine the diffusion coefficient. Although there have been several attempts to measure the diffusion constant of Cu₂Se using both AC/DC transport and QENS, there is considerable disagreement in the reported diffusion coefficients [3,8,9,11,29]. The first reports by Takahashi *et al.* [29] obtained diffusion coefficients using DC transport that were two orders of magnitude smaller than obtained later using similar methods by Horvatić [11]. Subsequent QENS work by Danilkin *et al.* found values broadly consistent with those of Horvatić (marginally higher) [8,9]. However, recent QENS work by Voneshan *et al.* [3] found values closer to those of Takahashi *et al.* [29]. The main difference between the work of Danilkin and Voneshan lies in the quite different models used to fit the QENS data. In this section we present a modified model that can place upper and lower bounds on the diffusion coefficient, and is generally applicable for superionic conductors. In particular we emphasize the coexistence of local “confined” diffusion for copper trapped in a site for long periods, together with sporadic jump events that lead to long-range copper migration. For brevity, the detail of our model and its validity is discussed in the supplemental materials and here we only present the main results.

After restricting the ω/Q range to avoid coherent (phonon-like) contributions (discussed in the supplemental materials), we then fit multiple Lorentzians which describe the confined diffusion and long-range diffusion components which are differentiated by their unique Q dependence of the energy-width. The minimal model that describes the low energy data at 675 K is a sharp elastic peak in combination with two distinct Lorentzian quasielastic peaks centered at zero energy:

$$S(Q, \omega) = A(Q)\delta(\omega) + (1 - A(Q))L_1(\omega) + L_2(\omega, Q)$$

where δ is the Dirac delta function describing the elastic line, $A(Q)$ is the elastic incoherent structure factor, L_1 is a Lorentzian with a fixed Q-independent energy width, and L_2 is a Lorentzian with a Q-dependent width. This is convoluted to include the broadening caused by the instrumental resolution function measured using a vanadium standard. In the supplemental materials, it is shown that both L_1 and L_2 are required to fit the data. As detailed in the supplemental, the first Lorentzian captures the effect of confined diffusion where the Cu is trapped for long periods in a local re-

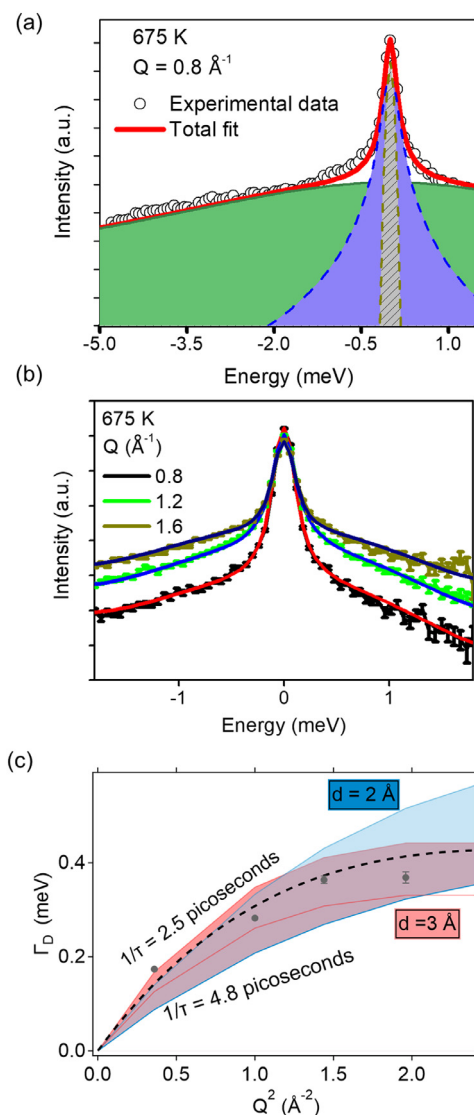


Fig. 7. (a) The low-Q quasielastic neutron spectra and fitting for Cu₂Se at 675 K. (b) Comparison of several Q values at 675 K. (c) Extracted FWHM for the narrower QENS components as a function of Q² at 675 K. The points are the experimental data. The dotted line is the line-of-best fit for $D = 2.79 \text{ \AA}$. The two shaded regions show the limiting behavior for 2 Å and 3 Å hops, which is the bounded range where statistically valid fits can be achieved.

gion of the lattice. The second Lorentzian describes long range diffusion where the Cu moves between adjacent regions in the lattice. Using this model, and accounting for the instrument resolution effects, Fig. 7 shows that the QENS spectra are very well fitted. Fig. 7(b) shows the Q dependency of the data and model. The confined diffusion is tied to high-frequency vibrations thus giving a broader energy width for L_1 , with a full-width-half-maximum of $\Gamma_1 = 3.5 \pm 0.5 \text{ meV}$ that is independent of Q. The long-range diffusion described by L_2 leads to a narrower E-width (Γ_D) that is Q-dependent and increases as Q², at low momentum transfer shown in Fig. 7(c), which is a signature of long range diffusion. It is physically reasonable that Γ_D is an order of magnitude smaller than Γ_1 because an ion will experience many unsuccessful trial vibrations orbiting an average position before finally transitioning to a new crystallographic site, and this is reflected in the lower frequency-width of Γ_D .

Having extracted the key parameter related to long-range diffusion, namely Γ_D , we employ the Chudley-Elliott (CE) model to re-

Table 3
Bounded diffusion coefficients obtained at 675 K for different Chudley-Elliott models.

Model	d (Å)	τ (ps)	D ($\times 10^{-5}$ cm 2 .s $^{-1}$)
T \leftrightarrow T upper limit	3	3.6	4.2
T \leftrightarrow T lower limit	3	4.8	3
T \leftrightarrow O upper limit	2	2.5	3.3
T \leftrightarrow O lower limit	2	4	1.9
Simple best fit	2.79 ± 0.19	3.72 ± 0.12	3.4

late the Q-dependence to the diffusion coefficient [30], where the FWHM from the diffusive component is:

$$\Gamma_D = \frac{2\hbar}{\tau} \left(1 - \frac{\sin(Qd)}{Qd} \right) \quad (2)$$

where τ is the hopping time, and d is the hopping length and the diffusion coefficient is $d^2/6\tau$. This model was selected because it correctly captures the trends in the Q-dependence (see supplemental materials), and allows us to compare hopping times extracted from the *ab-initio* molecular dynamics. A common approach would be to fit the CE model to Fig. 7(c), shown by the dotted line, where the fits give $d = 2.79 \pm 0.19$ Å, $\tau = 1.86 \pm 0.06$ ps. This value of d is intermediate between the values expected for O \leftrightarrow T and T \leftrightarrow T (2Å and 3Å). However, one can note that not all points in Fig. 7(c) are equally well described by the line of best fit. The single-component CE model assumes that all hops occur with a unique jump length, whereas if there is a distribution this could be an oversimplification. If the distribution is sufficiently bimodal to correspond to distinct O \leftrightarrow T and T \leftrightarrow T hops, one would expect an additional Lorentzian (L_3) would be observed experimentally. The fact that this Lorentzian is not observed in practice indicates both types of hop have a similar FWHM making them indistinguishable within experimental resolution – a scenario that is shown to be likely in Fig. S5. Thus, to place bounds on the Cu $_2$ Se data we adopted a different strategy detailed in the supplemental materials. Essentially, we insist that all Γ_D experimental points need to be encapsulated within the shaded regions in Fig. 7(c) determined by using $d = 2$ Å or 3 Å for T \leftrightarrow O or T \leftrightarrow T hops, and upper and lower estimates for τ . The resulting limits for the bounding choices on the CE model are shown in Table 3, giving diffusion coefficients bounded from 1.9 - 4.2 ($\times 10^{-5}$ cm 2 .s $^{-1}$) with an average of 3.1×10^{-5} cm 2 .s bounded in the range of \pm of 1.3×10^{-5} cm 2 .s which agrees well with the *ab-initio* simulations.

3.5. Comparison of diffusion coefficients between AIMD and experiments

Using the approach described above, Fig. 8 compares the diffusion coefficients obtained from AIMD, QENS and transport experiments together with past reports. The Nernst equation was used to convert the measured conductivities in the transport experiments to a diffusion coefficient. The results reported here from AIMD and QENS line up well with the transport experiments of Horvatić *et al.* [10,11] and fall within the green band in the figure. Overall, the new values are only a little smaller than those determined by Danilkin *et al.* [8] but are almost 10^2 times greater than those reported by Voneshen *et al.* [3] and the transport measurements of Takahashi *et al.* [29]. We consider the convergence between our AIMD, our QENS work and that of Horvatić and Danilkin to be satisfactory [31]. It remains unclear why our results differ from Refs. [3] and [29], however, our study has given all of the details of our fitting procedure, explained the uncertainties clearly and compared closely with theoretical calculations for the first time, and we are thus confident in our results. We also note that Ref. [3] contains an error in the expression for the random walk diffu-

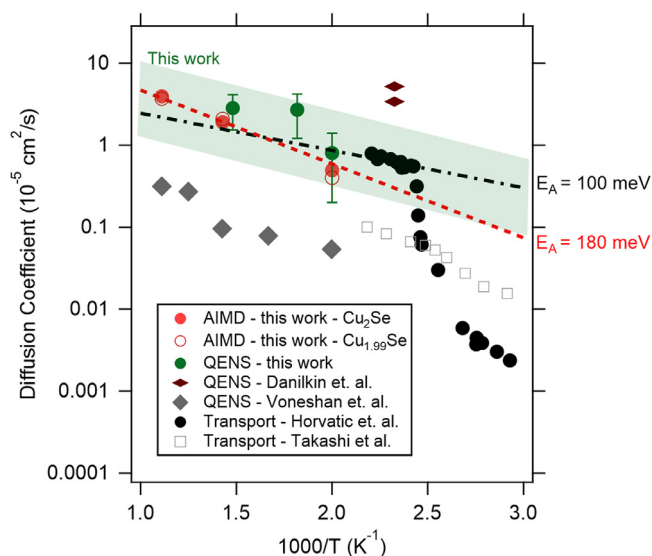


Fig. 8. Diffusion coefficients obtained in this work (encapsulated within the green bar), compared with past reports from both QENS and transport experiments.

sion coefficient described in the supplementary material which has the incorrect dimensions. Meanwhile, Horvatić *et al.* earlier argued [10,11] that geometric factors introduced artifacts into Takahashi *et al.*'s [29] earliest transport measurements. The lack of any sudden increment in the diffusion coefficient in Takahashi *et al.*'s measurements at the monoclinic-cubic transition is also at odds with nearly every other measurement for Cu $_2$ Se, and it is therefore reasonable to query the data above the transition.

Despite the quantitative differences in the absolute diffusion coefficient, there are also similarities between all of the datasets in that they appear to follow a similar Arrhenius law above 400 K such that:

$$D(T) = D_0 e^{-E_A/(k_b T)} \quad (3)$$

with a similar activation energy E_A in the range of 90 - 210 meV (albeit with very different values of D_0). The range of activation energies also agrees with the energies determined electrochemically under isothermal conditions [29] and the AIMD. For example, from the *ab-initio* molecular dynamics, E_A is 210 meV and D_0 is 6.124×10^{-4} cm 2 /s. The barrier derived from the neutron and Horvatić's work is 90 meV. These values are also in reasonable agreement with the barriers expected for the T \rightarrow O hop calculated using the nudged-elastic band method described in Section 3.1

4. Conclusions

Using a combination of simulations and experiments, we have provided a new determination of the diffusion coefficients and pathways for copper motion in Cu $_2$ Se. Careful treatment of the QENS data leads to a value that is in reasonable agreement with the *ab-initio* theory and Horvatić *et al.*'s transport measurements. These insights are essential to understand the analogous effects in more complex nanocomposite forms of Cu $_2$ Se [18]. So, what are the implications for thermal transport in Cu $_2$ Se more generally? It is well established that the contribution of ionic diffusion to the thermal conductivity is negligible compared to the heat transport by phonons. Nevertheless, the standard paradigm is that Cu diffusion does indirectly affect the phonon transmission by introducing scattering or removing certain phonon modes. Contrary to this assumption, the direct experimental evidence shows an almost temperature-independent phonon DOS in our work, as in past work [3], in the window where superionic motion is speeding

up by orders of magnitude. Although the hopping rates do increase exponentially, the hopping timescales are well below the speed limit of the THz phonons which constitute most of the phonon modes in Cu₂Se residing above 10 meV, as originally pointed out by Voneshen et al. [3]. It was proposed that for ionic motion to have a maximal effect on the phonons, the copper hopping rates should be on the same or faster timescale than the heat-bearing phonons. In Cu₂Se, the ionic diffusion does not break the critical speed limit to affect the majority of the phonons. Since copper diffusion is not the main factor determining the low thermal conductivity, we propose that it would be worthwhile to explore chemical approaches which suppress the fast-ionic diffusion. This could potentially solve an important issue because the long-range mobility of the Cu ion in Cu₂Se poses a major technological barrier for real-world applications because prolonged exposure to strong electric fields leads to undesired electromigration and device degradation [19].

As a more subtle point, we have also identified an alternate mechanism for phonon scattering: the dynamic creation and destruction of Frenkel defects. The role of this mechanism on the sub-THz phonons needs to be clarified although the overall effect on thermal conductivity must be rather subtle as the conductivity only varies by 25% between 300 K and 850 K, even as the defect-creation rates (equal to the T-O hopping rates) change by orders of magnitude. Importantly, the dynamic generation of Frenkel defects does not necessarily require long-range copper diffusion, as it is essentially a local motion. In the future, it could be beneficial to adjust the structure-function relationship in new crystal phases derived from Cu₂Se to suppress the long-range diffusion whilst maximizing phonon-scattering.

Declaration of Competing Interest

The authors declare no conflict of interest.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.actamat.2021.117026.

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