

Tracking Ultrafast Ion Diffusion Dynamics in AgCrSe₂ Superionic Conductor

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(Received 7 November 2025; accepted 24 March 2026; published 1 May 2026)

Superionic conductors (SICs) exhibit liquidlike ionic diffusivities while maintaining a periodic crystalline lattice, making them promising candidates for applications in fuel cells, solid-state electrolytes, and thermoelectric materials. The transient local structures of mobile ions and their cooperative interactions with the host lattice are of pivotal importance regarding both the ion and heat conduction in SICs. However, accurately capturing the structural evolution of mobile ions remains a significant challenge due to the inherent complexities involved. Here, we employed ultrafast electron diffraction (UED) with femtosecond-temporal and angstrom-spatial resolution to resolve the structural evolution of mobile Ag⁺ ions in AgCrSe₂. Our experiments identify a critical process originating from localized Ag⁺ vibrations at the long-range-ordered lattice sites to a formation of short-range-correlated Ag⁺ trimer structures through a drastic contraction of the Ag⁺—Ag⁺ bond from approximately 3.68 to approximately 3.00 Å in 1.97 ps. Combining real-time time-dependent density-functional-theory and molecular dynamics simulation, we further reveal the crucial role of these contracted trimer structures in enabling fast Ag⁺ diffusion by opening up excess free volume and reducing local energy barriers. Such an intimate relation between fast diffusion and local lattice variations is not exclusive and can be extended beyond AgCrSe₂ to materials such as Li₁₀XP₂S₁₂ (X = Si, Ge, Sn). The ability to track ion diffusion with UED also provides new avenues for exploring the atomistic mechanisms of fast ion diffusion in next-generation solid-state electrolytes, fuel cells, and ion transport membranes.

DOI: [10.1103/s6rh-7219](https://doi.org/10.1103/s6rh-7219)

Subject Areas: Materials Science, Physical Chemistry

I. INTRODUCTION

Superionic conductors (SICs) exhibit unusually high ionic diffusivities comparable to those of liquids while still maintaining a periodic crystalline lattice [1]. Because of their superior ionic conductivities, SICs serve as

promising candidates for various technological applications such as fuel cells [2], supercapacitors [3], intercalation MXenes [4], and as electrolytes in lithium-ion [5,6] and other solid-state batteries [7,8]. In addition to high ionic conductivity, the low-lattice thermal conductivities of SICs endow them with excellent thermoelectric properties [9,10].

Ion and heat conduction in SICs are fundamentally governed by their instantaneous local structures and cooperative interactions with the host lattice. Optimizing the host lattice and its interactions with mobile ions is crucial for advancing next-generation solid-state electrolytes. Techniques including inelastic neutron scattering [11,12], nuclear magnetic resonance (NMR) [13], electrochemical impedance spectroscopy [14], density functional theory (DFT) [15], and *ab initio* molecular dynamics (AIMD) [16]

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have elucidated key factors that facilitate ion transport, such as lattice softness and polarizability [17], rattling modes [18], and phonon anharmonicity. However, comprehensive studies of local dynamic structures during the diffusion process, particularly those combining both sub-picosecond temporal resolution and atomic spatial resolution, remain limited. For instance, optical pump-probe methods [19], while reaching a temporal resolution from femtosecond to picosecond, cannot probe local bond length variations and correlation lengths of collective ion motion. Inelastic and quasielastic neutron scattering [20,21], which can measure a broad range of momentum and energy transfer, lacks temporal resolution and is also limited in resolving spatial correlations of ion motion. Meanwhile, although AIMD simulations provide very rich structural information, such as temperature-dependent Ag bond distributions in AgCrSe₂ [21], and the liquidlike, collective ionic dynamics in superionic conductors [22], direct comparisons with experimental results should be approached with caution, considering the inherent computational limitations on timescales and system sizes.

To address this limitation, an MeV ultrafast electron-diffraction (UED) technique [23,24] was employed to investigate sub-picosecond-scale Ag⁺ ion dynamics in a model SIC system AgCrSe₂ by delivering ultrafast heating pulses to drive the material from its ordered phase to the disordered superionic conducting phase using a femtosecond laser [16,25]. The high temporal resolution provided by the double-bend achromat compressor, combined with the broad momentum space accessible with MeV electrons, enables direct visualization of local atomic dynamics across diverse stages of ion diffusion. Specifically, we observed a fast transition (approximately 1.97 ps) of the Ag⁺ sublattice from long-range order to a dynamic short-range-ordered (SRO) structure with an average longitudinal correlation length of 6.16 Å and an unexpected substantial reduction of Ag⁺–Ag⁺ bond lengths from 3.68 to approximately 3.00 Å. By combining real-time time-dependent density-functional-theory (rt-TDDFT) calculations and molecular dynamics (MD) simulations, it was further demonstrated that these emergent SRO structures not only effectively mitigated diffusion energy barriers, but also created large free volume for diffusion, thus resulting in the liquidlike fast Ag⁺ diffusion in AgCrSe₂.

II. RESULTS AND DISCUSSION

A. Probing dynamic Ag⁺ ion diffusion in AgCrSe₂ through femtosecond electron diffraction

Figure 1(a) displays the atomic structures of the low-temperature- (LT) ordered phase and the high-temperature- (HT) disordered phase of AgCrSe₂. In the LT phase, only one of the lattice sites, e.g., the α site, caged by the Se tetrahedra is occupied by Ag⁺ ions, while both α and β sites are randomly occupied above the order-disorder phase

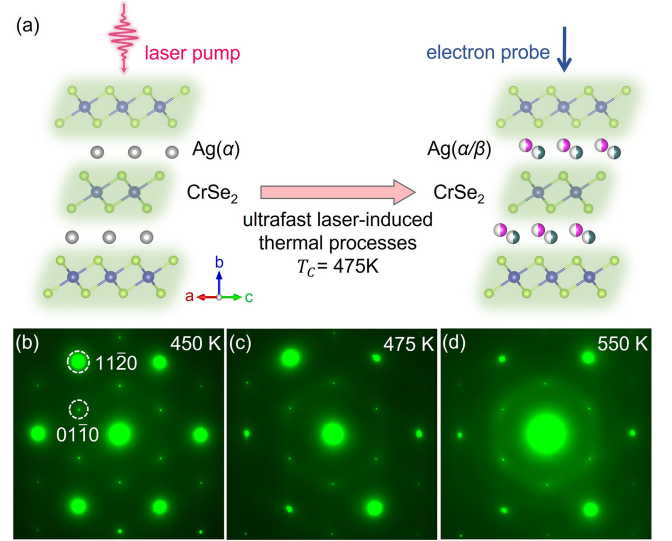


FIG. 1. Tracking the diffusion of Ag⁺ ions in AgCrSe₂ by femtosecond electron diffraction. (a) Schematic of the ultrafast-electron-diffraction pump-probe setup used to measure the ultrafast-laser-induced phase transition of AgCrSe₂. The left panel depicts the low-temperature-ordered phase in which Ag atoms exclusively occupy α sites, and the right panel illustrates the high-temperature-disordered phase wherein Ag atoms randomly occupy both α and β sites. (b)–(d) *In situ* heating selected-area electron-diffraction patterns of AgCrSe₂ acquired on a 200-kV transmission electron microscope at 300, 475, and 550 K, respectively.

transition temperature $T_C \sim 475$ K. Note that the random disorder structure above T_C is an oversimplified time- and spatial-averaged model. The exact local dynamic structures, particularly the spatiotemporal correlations between multiple Ag⁺ ions, remain elusive.

To investigate the order-disorder phase transition, we first conducted *in situ* heating experiments on AgCrSe₂ from 300 to 550 K using a 200-kV transmission electron microscope (see Supplemental Material Sec. I for experiment details [26]). At and above the phase transition temperature $T_C \sim 475$ K, a ringlike diffuse scattering pattern appeared around the $\{10\bar{1}0\}^*$ Bragg diffractions [Figs. 1(b)–1(d)], implying a spatial correlation among mobile Ag⁺ ions [106]. However, these static experiments provided only time-averaged local structural information, and UED experiments were motivated to better capture both the spatial and temporal information of these structures.

Next, we performed a UED experiment, and the experiment setup is schematically shown in Fig. 1(a), where the LT phase was pumped to the HT phase stroboscopically by an 800-nm femtosecond laser pulse. Structural changes were then probed using an MeV electron pulse at various time delays (see Sec. IV for details). Figures 2(a)–2(c) display the representative differential electron diffractions $\Delta I(t) = I(t) - I(0)$ at time delays of 0.95, 4.95, and

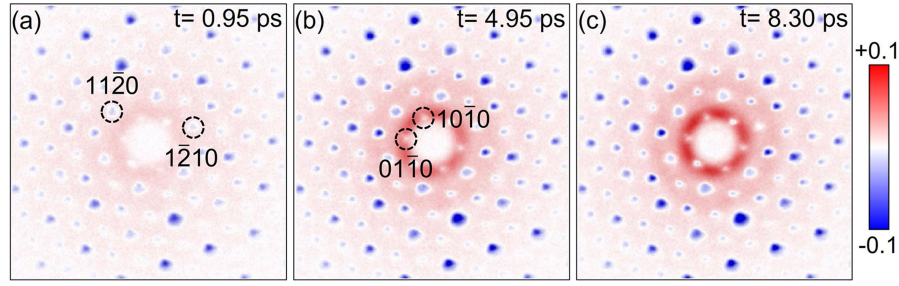


FIG. 2. Differential electron diffractions at (a) 0.95, (b) 4.95, and (c) 8.30 ps, following photoexcitation with an 800-nm, 7.60 mJ cm^{-2} laser pulse at 340 K. Bragg diffractions are labeled by their Miller indices, with blue indicating lower intensity compared to the diffraction pattern at $t = 0$ ps and red indicating increased intensity.

8.30 ps for a 50-nm-thick sample following the photoexcitation with a 7.60 mJ cm^{-2} laser pulse at 340 K. At a short timescale of $t = 0.95$ ps, a clear attenuation of the Bragg peaks was observed, accompanied by a weak diffuse background due to laser heating. At $t = 4.95$ and 8.30 ps, a characteristic diffuse ring pattern, which is consistent with the static electron-diffraction patterns [Figs. 1(b)–1(d)] and also similar to those observed in liquid [107] or amorphous materials [108], appeared around the first-order $\{10\bar{1}0\}^*$ Bragg diffractions. This ring feature indicates laser-induced thermal activation of Ag^+ ion diffusion well above T_C .

To further substantiate the thermal origin of the diffuse ring pattern after photoexcitation, we also conducted a UED control experiment at 100 K with identical laser fluence of approximately 7.60 mJ cm^{-2} (see Supplemental Material Sec. II for details [26]). As clearly shown in Fig. 3 (complete data provided in Supplemental Material Video 1 [26]), the diffuse ring pattern was absent even up to a time delay of 14.80 ps. Therefore, the possibility of nonthermal processes can be ruled out. Moreover, according to our calculations of the sample temperature after photoexcitation (Supplemental Material Sec. III [26]), the maximum change of the sample temperature ΔT is estimated to be about 328 K for an experiment laser fluence of 7.60 mJ cm^{-2} . This ΔT would raise the sample temperature well above T_C for an initial temperature of 340 K, while still below T_C when the sample temperature was 100 K. This result further supports our interpretation that the diffuse ring is due to laser-induced heating.

B. Quantification of the ultrafast diffuse ring patterns

The diffuse ring pattern provides invaluable local structural information, particularly the instantaneous local Ag^+ structures and their short-range correlations during diffusion. Figure 4(a) schematically displays the reference $(33\bar{6}0)^*$ Bragg diffraction and the regions used to extract the diffuse ring intensities following photoexcitation at a fluence of 7.60 mJ cm^{-2} at 340 K. As shown in Fig. 4(b) (top panel), the Bragg peak intensities decay exponentially with a time constant $\tau_{33\bar{6}0} \sim 2.71 \pm 0.11$ ps, which can be attributed to the Debye-Waller effect. This time constant is

indicative of the equilibration time for the entire lattice system. Concurrently, the diffuse ring intensities exhibited a gradual increase over the course of approximately 10 ps [Fig. 4(c); also see Supplemental Material Video 2 for full data [26]]. In addition, a discernible shift of the peak position (labeled as k_c) toward a lower scattering angle k was also observed.

Further quantitative spatial and temporal information is obtained by fitting the diffuse intensity with a Gaussian function $A \exp\{-(k - k_c)^2 / (2\sigma^2)\} + B$ [fitting results shown in Fig. 4(c)], and the results are summarized in Figs. 4(b) (bottom panel) and 4(d). Similar to the Bragg

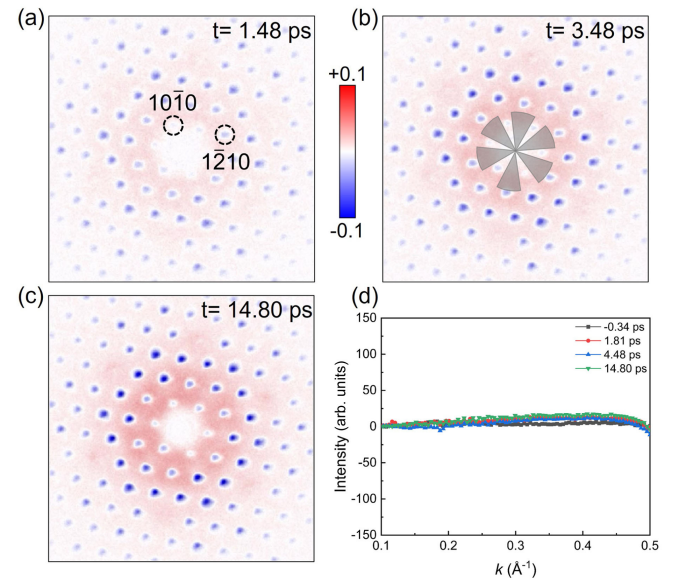


FIG. 3. Quantification of diffuse scattering intensity following photoexcitation with an 800-nm, 7.60 mJ cm^{-2} laser pulse at 100 K. (a)–(c) Differential diffraction patterns recorded at 1.48, 3.48, and 14.80 ps, respectively. Bragg diffractions are labeled by their Miller indices, with blue indicating lower intensity compared to the diffraction pattern at $t = 0$ ps and red indicating increased intensity. The gray-shaded sectors in (b) indicate the regions used for quantification. (d) Azimuthally averaged line profiles of the diffuse scattering at various time delays, showing the absence of the characteristic diffuse ring.

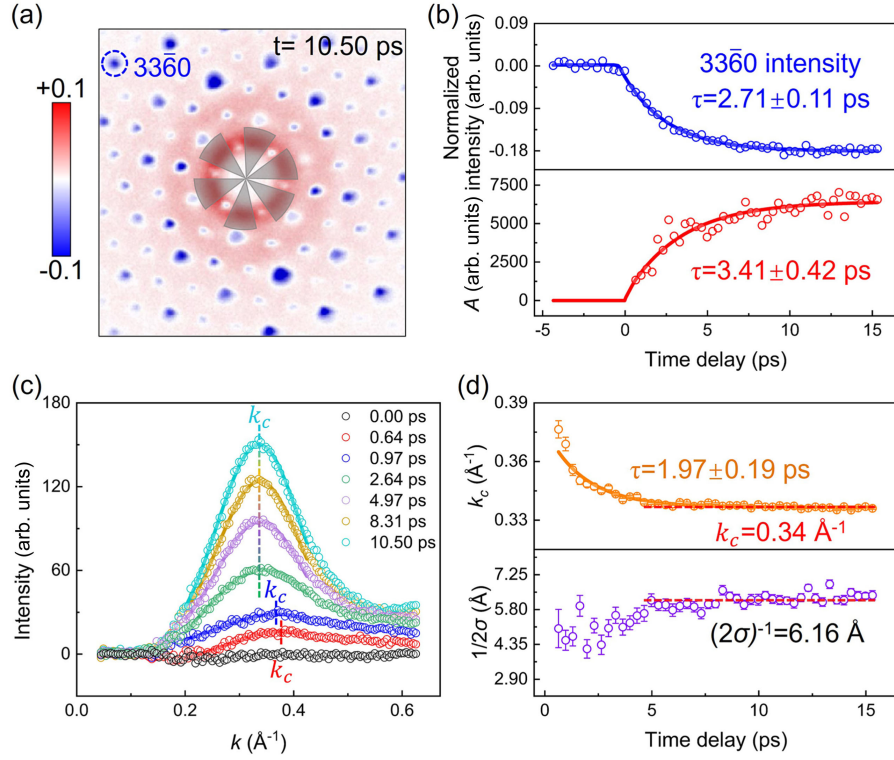


FIG. 4. Quantification of diffuse ring patterns and Ag^+ ion dynamics. (a) Differential diffraction pattern at $t = 10.50$ ps, where the gray sectors and the blue circle indicate the regions used for the quantification of the diffuse ring and the $(33\bar{6}0)^*$ Bragg diffraction, respectively. (b) Intensities of the $(33\bar{6}0)^*$ diffraction peak (top panel) and fitted peak height A determined by fitting the diffuse ring intensity profiles to the Gaussian function $A \exp \{ -[(k - k_c)^2 / (2\sigma^2)] \} + B$ (bottom panel). The solid curves indicate the fitted single exponential functions used to obtain the relaxation time. (c) Raw intensity profiles and Gaussian function fitting results. Azimuthally averaged line profiles of the diffuse ring at various time delays, with the peak positions labeled as k_c . The superimposed solid curves indicate the fitted Gaussian functions used to quantify spatial and temporal information of Ag^+ dynamics. (d) Time evolution of the fitted parameters k_c and $(2\sigma)^{-1}$, where the former indicates a fast equilibration to an inter- Ag^+ distance of 3.00 $\text{\AA}$, and the latter suggests a buildup of an average correlation length up to approximately 6.16 $\text{\AA}$ at approximately 5.00 ps.

peak, the fitted intensity parameter A could also be described by a single exponential function with a relaxation time τ_A of approximately 3.41 ± 0.42 ps. The relatively slower time constant τ_A , in comparison to $\tau_{33\bar{6}0}$, further supports the thermal activation nature of the diffuse scattering and ion diffusion.

As shown in Fig. 4(d), the peak position k_c sharply decreases from approximately 0.38 to approximately 0.34 $\text{\AA}^{-1}$ with a time constant $\tau_{k_c} \sim 1.97 \pm 0.19$ ps, while the inverse of the peak width $(2\sigma)^{-1}$ increases from approximately 5.08 to approximately 6.16 $\text{\AA}$. Unlike the Bragg diffraction intensity or the parameter A , which is primarily associated with individual lattice or mobile ion subsystems, the meaning of k_c and $(2\sigma)^{-1}$ in the non-equilibrium state is less evident. Here we shall first focus on the values of k_c and $(2\sigma)^{-1}$ near equilibrium, as they are directly related to the average interatomic distance d_{Ag} and the longitudinal correlation length ξ of local structures by $d_{\text{Ag}} = k_c^{-1}$ and $\xi = (2\sigma)^{-1}$ [109], which has been exemplified in liquids [107] and amorphous materials

[108]. Using $k_c = 0.34$ $\text{\AA}^{-1}$, we obtained an average d_{Ag} of approximately 3.00 $\text{\AA}$, which is significantly shorter than its value in the ordered phase (approximately 3.68 $\text{\AA}$) and suggests a highly distorted structure with a lattice variation of approximately 18%. Importantly, this distorted structure does not correspond to a static crystallographic distortion of the average lattice. Instead, it reflects a dynamic, local distortion of the Ag sublattice arising from correlated Ag^+ displacements. Specifically, the shortened average Ag-Ag distance can be understood as the combined effect of large off-site displacements of Ag^+ ions from their ideal α -site positions and the transient formation of locally correlated Ag pairs or small clusters with substantially contracted Ag-Ag separations.

Specifically, the experimentally observed diffuse scattering exhibits an intrinsic isotropic ringlike feature in reciprocal space, indicating that the Ag-Ag correlations are statistically isotropic and lack any preferred orientation. If significant anisotropic motifs were present, such as bent trimers or branched motifs with preferred orientations,

anisotropic diffuse features would be expected. The absence of such features therefore constrains the correlated structures primarily to longitudinal Ag-Ag arrangements. Moreover, the experimentally determined average correlation length $\xi \sim 6.16$ Å provides a further geometric constraint. This length is roughly twice d_{Ag} , indicating that the correlated structure typically extends over two Ag-Ag spacings. This result suggests a unique short-range-ordered Ag^+ structure consisting of three Ag^+ ions aligned in a row, or more concisely, transient linear Ag^+ trimers with a highly contracted bond length of approximately 3.00 Å. Importantly, this interpretation does not rely on assuming strictly linear motifs but instead reflects the characteristic correlation length extracted from the diffuse scattering. Similar results were obtained in a separate experiment with higher laser fluence at 340 K as well, (see Supplemental Material Sec. II, Figs. S1 and S2, and Video 3 for details [26]), demonstrating the consistency of the experiments.

C. rt-TDDFT and nonequilibrium MD simulations of the pump-probe process

The SRO Ag^+ trimers, as revealed by our UED experiments, are in stark contrast with the conventional understanding of disordered structures in SICs, as exemplified by the schematic atomic structure shown in Fig. 1(a). Furthermore, the dynamic evolution of the diffuse ring, particularly the changes of k_c and $(2\sigma)^{-1}$, remains to be elucidated.

To gain further understanding of the dynamic structural evolution, we first carried out rt-TDDFT calculations using the software package PWMAT [110,111]. As clearly shown in Fig. 5(a), with the partial density of states (DOS) of photoexcited electrons and holes projected onto Ag, Cr, and Se atoms, together with their charge distribution at selected time intervals in Fig. 5(b), the laser pulse mainly excites the highly localized Cr $3d$ orbitals, while those around Ag^+ are negligible. Thereby, the complicated photoexcitation pump process can be simplified as an excitation or heating of the CrSe_2 sublattice through electron-phonon coupling, while the Ag sublattice remains almost intact. Later on, the “cold” Ag sublattice is heated by the “hot” CrSe_2 sublattice through phonon-phonon interactions (see Figs. S3–S6 for details [26]). Furthermore, we carefully compared the DFT ground-state electronic structure (Supplemental Material Secs. 4 and 5 [26]) with the rt-TDDFT calculation results, and it was found that the Ag^+ ions were weakly dependent upon the electron temperatures (see Supplemental Material Sec. VI for detailed results and further discussion [26]). Hence, the dynamics of the Ag^+ ion after laser excitation could be approximated by its dynamics at the ground state.

Based on this approximation, we performed nonequilibrium MD simulations using the neuroevolution potential (NEP) trained by density functional theory (see Sec. IV for details). The calculation was performed on a model comprising 11 520 atoms with a hot-spot thermostat based

on the generalized Langevin equation (GLE) for 600 ps [112,113]. Using this approach, we obtained a nonequilibrium steady state, whereas the CrSe_2 sublattice was heated to approximately 700 K, the Ag^+ ions were still cold at approximately 340 K. Subsequently, free relaxation to equilibrium in the microcanonical ensemble was performed to simulate the heating of the Ag^+ sublattice. Figure 5(c) compares the kinetic temperature calculated by rt-TDDFT and MD simulations. These two results are in excellent agreement with each other, strongly supporting the validity of our MD simulations.

From the nonequilibrium MD simulations, we extracted a series of structures and calculated their electron-diffraction patterns (see Sec. IV for details). Figure 5(d) shows the total electron diffraction of the initial structures $I(0)$ ($t = 0$ ps), which consists of conventional Bragg diffraction spots and six diffuse scattering patterns situated between the diffraction spots. To further identify the origin of these unique diffuse scattering patterns, we performed further electron-diffraction simulation (Supplemental Material Sec. VII [26]), and as clearly displayed in Figs. S7–S9 of Supplemental Material [26], the diffuse scattering can be attributed to the Ag^+ -dominant low-frequency transverse acoustic phonons. The absence of comparable diffuse scattering patterns in our UED experiments might be ascribed to the much weaker intensity of phonon diffuse scattering compared to those of Bragg diffraction and inelastic plasmon scattering (see Supplemental Material Sec. VIII for further discussion [26]).

Figures 5(e)–5(j) display the structure snapshots and the corresponding differential electron diffractions $\Delta I(t)$ at $t = 0.95$, 4.95, and 8.30 ps, respectively. The displacements of Ag^+ ions determined by their positions at time t and $t = 0$ ps were also provided. The simulation results clearly reveal the dynamic structural changes in both time and space. On a short timescale ($t = 0.95$ ps), only a few Ag^+ ions exhibit substantial displacement from their original positions (marked in light yellow in Fig. 5(e)). These highly localized and independent displacements are a distinctive feature of Ag^+ vibrations in AgCrSe_2 [114]. During this process, there was a decrease in the Bragg peak intensities accompanied by a slight increase in diffuse background. At an intermediate timescale ($t = 4.95$ ps), the displacements of Ag^+ become more pronounced and dimers and trimers spanning two to three Ag^+ ions begin to form [highlighted by the light blue and light green circles in Fig. 5(f); also see Supplemental Material Sec. IX and Figs. S10–S12 for their definitions [26]]. The inter- Ag^+ distances within these SRO regions, as directly measured from the radial distribution functions (Figs. S3 and S13, also see Supplemental Material Sec. X for details [26]) are in excellent agreement with the experimental value $d_{\text{Ag}} \approx 3.00$ Å. Furthermore, the simulated electron diffraction [Fig. 5(i)] also reproduces the characteristic diffuse ring pattern observed in experiments. On a longer timescale

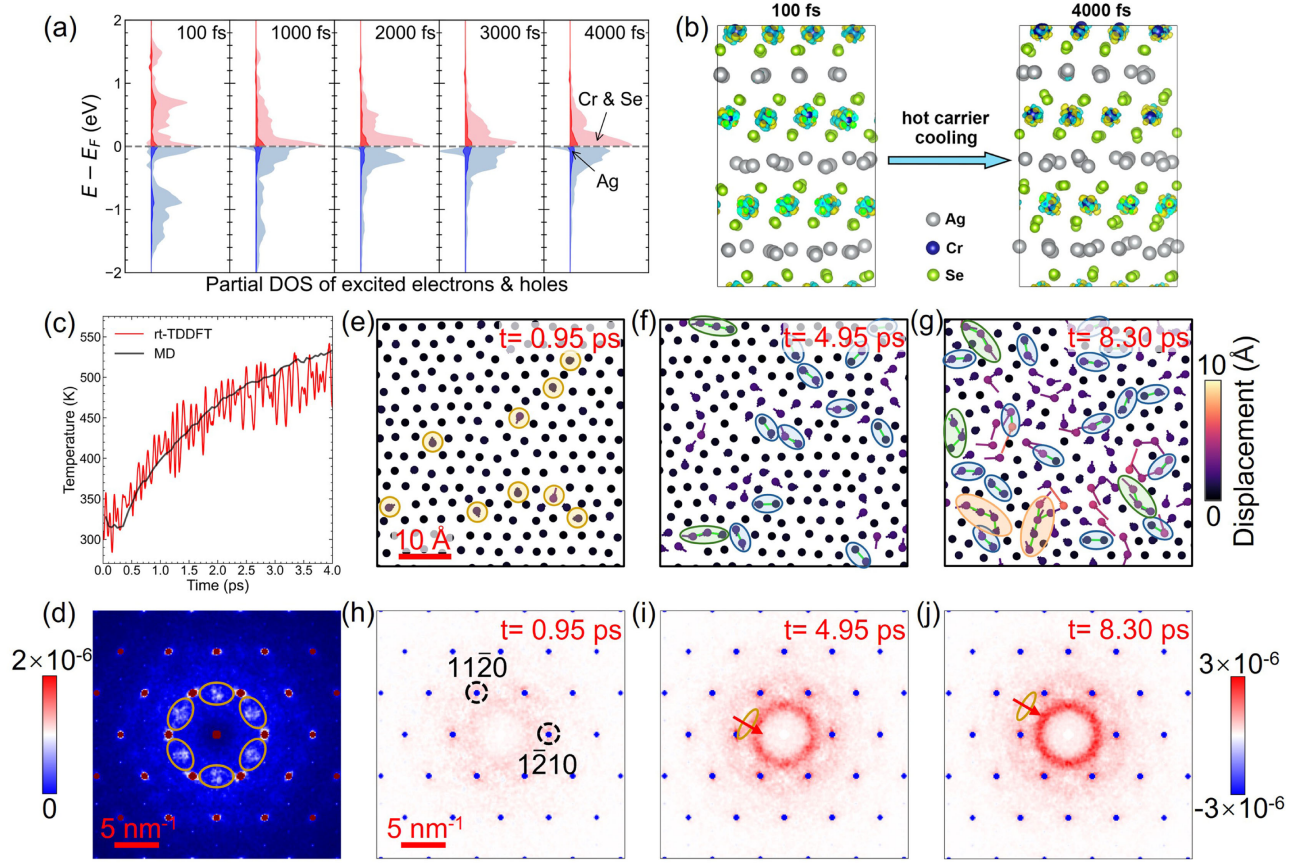


FIG. 5. rt-TDDFT and nonequilibrium MD simulations. (a) Partial DOS of photoexcited spin-polarized electrons and holes projected onto Ag (red and blue) and CrSe₂ (light red and blue) at $t = 100, 1000, 2000, 3000$, and 4000 fs, respectively. (b) The photoexcited electron (yellow) and holes (cyan) charge-density distribution (isosurface level = 1.65×10^{-3}) at $t = 100$ and 4000 fs, respectively. The atomic structure is viewed along the a axis of the hexagonal cell. These photoinduced charges are localized on Cr $3d$ orbitals. (c) Instant kinetic temperature calculated by rt-TDDFT and nonequilibrium MD simulation. (d) Total electron-diffraction intensity I_0 of the structure at $t = 0$ ps. (e)–(g) Instantaneous structures of Ag⁺ ions at $t = 0.95$ ps (e), 4.95 ps (f), and 8.30 ps (g), where the arrows denote the relative displacements of Ag⁺ with respect to their initial positions at $t = 0$ ps and colored circles in (f) and (g) indicate dimers (light blue), trimers (light green), and their combinations (light orange). (h)–(j) Differential electron-diffraction patterns $\Delta I(t) = I(t) - I(0)$ at $t = 0.95, 4.95$, and 8.30 ps, respectively.

($t = 8.30$ ps), the dimers and trimers are interconnected, resulting in the formation of stringlike patterns [Fig. 5(g)] with a longitudinal correlation of approximately two to three Ag⁺ ions. A similar stringlike pattern was also reported in previous work on AgCrSe₂ by MD simulations [115]. However, the predicted correlation length was much longer (approximately $20 \text{ \AA}$) than our results due to lower simulation temperature (250 K) and longer time delay (approximately 337 ps).

As denoted by the arrows in Figs. 5(i) and 5(j), the diffuse ring is positioned more inward with respect to the phonon diffuse scattering pattern. This explains the evolution of k_c and $(2\sigma)^{-1}$ shown in Fig. 4(d). In brief, k_c and $(2\sigma)^{-1}$ are determined by both phonon diffuse scattering and diffuse ring. Their changes indicate a dynamic transition from localized vibrations at the long-range-ordered lattice sites to the onset of local SRO dimers and trimers. We remark that the transition time τ_{k_c} (approximately

1.97 ± 0.19 ps) also provides a rough estimation of the relaxation time of local structure fluctuations. As a comparison, the relaxation time of dynamic Ag⁺ disorder was determined to be approximately 2.29 ps at 520 K by inelastic neutron scattering [25]. This good agreement supports the phonon-triggered diffusion mechanism, as suggested in previous studies of Ag₈SnSe₆ [20] and Ag₈GeSe₆ [116].

D. Origin of short-range-ordered Ag⁺ trimers and its implication for fast ion diffusion

From our experiments and simulations, we discovered SRO Ag⁺ dimers and trimers that are notably incompatible with the host lattice. The origin of the short Ag⁺–Ag⁺ bond and the formation of dimers and trimers can be readily understood from theoretical calculations by NEP, according to which the energy minimum of two Ag⁺ ions, or an Ag⁺ dimer, is exactly at approximately $3.00 \text{ \AA}$ [Fig. 6(a)].

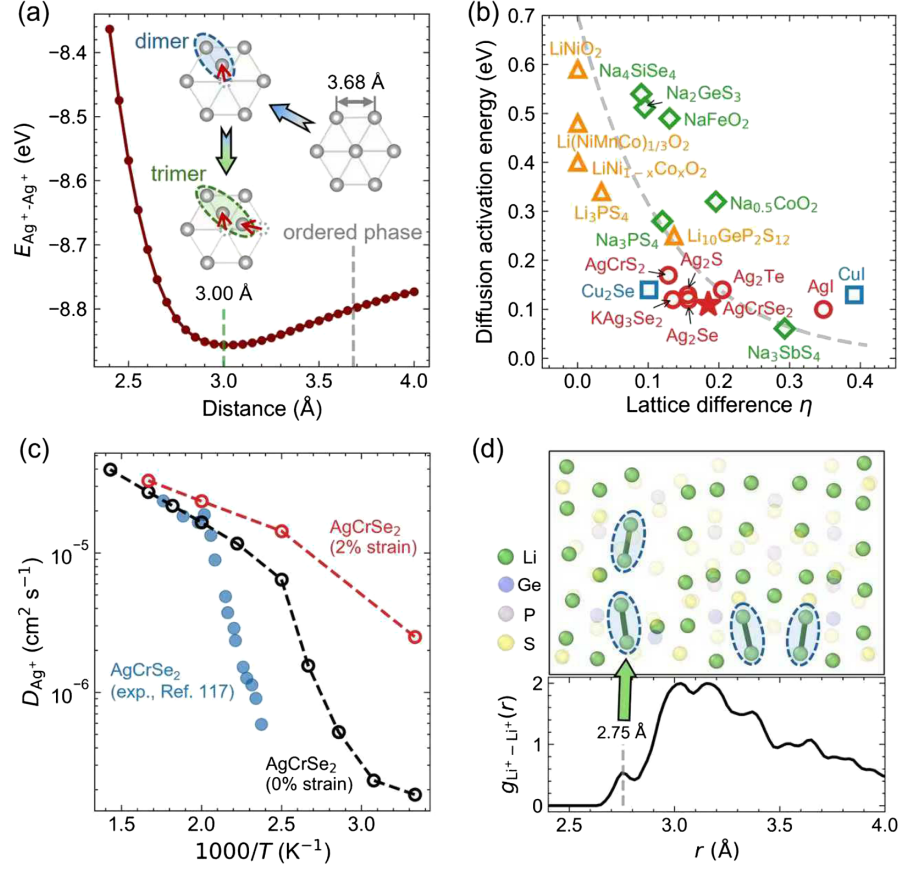


FIG. 6. Origin of dynamic short-range-ordered Ag⁺ structure and fast-ion-diffusion property. (a) The potential energy of two Ag⁺ ions calculated by the neuroevolution potential, indicating an energy minimum at a distance of approximately 3.00 Å. The formation of dimers and trimers by the attractive forces between Ag⁺ ions and open free volume are illustrated schematically in the inset. (b) Diffusion activation energy as a function of the lattice difference η for the Ag⁺-, Cu⁺-, Na⁺-, and Li⁺-based superionic conductors, revealing a general trend: activation energy decreases with increasing η , as indicated by the dashed gray line. (c) Calculated diffusion coefficient D_{Ag^+} of AgCrSe₂ under 0% and 2% tensile strain. The predicted D_{Ag^+} under 0% strain above 475 K matches the experimental data [117] very well. Under 2% tensile strain, D_{Ag^+} increases by an order of magnitude at room temperature. (d) MD simulations of Li₁₀GeP₂S₁₂ (top panel) show the presence of Li⁺ dimers (marked by blue circles), with an average interatomic distance of approximately 2.75 Å, which can be directly determined from the radial distribution function $g_{\text{Li}^+-\text{Li}^+}(r)$ (bottom panel).

Consequently, the shrinkage of the Ag⁺—Ag⁺ bond is indeed energetically favorable despite of the energy barriers imposed by the local CrSe₂ host lattice. In addition, after the formation of the Ag⁺ dimers and trimers, a substantial amount of “free volume” is created, thus further mitigating the energy barrier for diffusion and allowing subsequent migration of neighboring Ag⁺ ions. This successive diffusion through the fluctuating creation of free volume process is illustrated in Fig. 6(a) and demonstrated in Figs. 5(f) and 5(g). We remark that the same conclusion could also be made by the conventional nudged elastic band and potential of mean force methods (Supplemental Material Sec. 11 [26]). As shown in Figs. S14 and S15 of Supplemental Material [26], the formation of Ag dimers would drastically reduce the repulsion interactions between Ag ions and allows the migration from the α site to β site. Similarly, it is found that the potential of mean force

between two Ag⁺ ions is extremely shallow at 300 K, and its global minimum shifts to a Ag⁺—Ag⁺ length of approximately 3.00 Å (Fig. S16 [26]).

The reduction of local energy barriers together with the creation of excess free volume via the spontaneous formation of local contracted structures is not exclusive to AgCrSe₂ and has significant implications for other SICs as well. By introducing a lattice difference parameter $\eta = [(d_{\text{host}} - d_{\text{ion}})/d_{\text{host}}]$ (d_{host} , average lattice parameter of the mobile ions frozen in the host at low temperature; d_{ion} , bond length of mobile ions at high temperature) as a measurement of available free volume, we summarized in Fig. 6(b) a compilation of diffusion activation energies E_a versus η for a variety of Ag⁺-, Cu⁺-, Na⁺- and Li⁺-based SICs (see Supplemental Material Sec. 12 and Table SI for details [26]), in which a general inverse correlation between E_a and η could be found. This surprisingly simple but

ubiquitous relation can be fully exploited to optimize the ionic transport property of SICs by tuning the difference between d_{ion} and d_{host} either through internal “strain,” e.g. doping or alloying of the host lattice, or through external strain. As a direct demonstration, we performed MD simulations on AgCrSe_2 and compared the diffusion coefficient D_{Ag^+} under 0% strain and 2% tensile strain. Despite a discrepancy in T_C , the predicted D_{Ag^+} (0% strain) above 475 K is in excellent agreement with the experimental values [117] (Fig. 6(c)). Under 2% tensile strain, D_{Ag^+} can increase by an order of magnitude at room temperature, providing compelling evidence for the general applicability of the inverse correlation between E_a and η . Moreover, we also investigated the ubiquity of dimer and trimer structures through additional MD simulations on the well-known SIC $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS). As shown in Fig. 6(d) (top panel), a formation of Li^+ dimers (highlighted by the blue circles) can be found in LGPS as well. The average inter- Li^+ distance within the dimer is markedly reduced to approximately 2.75 Å, resulting in an η value of 0.14 and low E_a (approximately 0.25 eV). Similarly, tensile strain could give rise to a significant increase in the diffusion coefficient of Li^+ (see Supplemental Material Sec. 13 and Fig. S17 for details [26]). These findings provide further confirmation of the broad relevance of dimer and trimer structures and fast ion diffusion in SICs.

In principle, the present approach is not limited to materials with well-defined phase transitions and could be extended to systems lacking clear order-disorder boundaries by triggering ion diffusion with ultrafast heat pulses. Further advances in UED instrumentation, such as terahertz or far-infrared pumping sources, may further enable selective excitation of phonon modes and provide direct access to ultrafast ionic and sublattice dynamics in a wider range of materials. However, several practical challenges currently limit its application to Li-based superionic conductors, including the difficulty of growing sufficiently large single-crystalline samples for UED measurements, the strong electron-beam sensitivity of many Li-containing compounds, and their high reactivity toward air and moisture. Overcoming these challenges will require coordinated progress in materials synthesis, environmental control, and ultrafast instrumentation.

III. CONCLUSION

In conclusion, we directly tracked the dynamic evolution of local Ag^+ structures in AgCrSe_2 using UED and discovered unique Ag^+ dimers and trimers with a shortened $\text{Ag}^+ - \text{Ag}^+$ bond. Our work sheds light on a general and important ion transport mechanism in solids, where the dynamically contracted SRO structures simultaneously create a large free volume and reduce local energy barriers for diffusion. Such an intrinsic SRO structure can be fully

exploited and tuned by internal or external strain for the optimization of available free volume and the resultant ion-diffusion-related properties. Moreover, the UED technique used here is not exclusive to AgCrSe_2 . Its femtosecond-temporal resolution and atomic spatial resolution make it widely applicable for probing the spatiotemporal correlations of mobile ions, thereby opening new avenues to the future development of SICs.

IV. METHODS

A. MeV ultrafast electron diffraction

The structural dynamics were investigated by an MeV UED facility equipped with a double-bend achromat compressor [118]. An 800-nm laser with a pulse width of approximately 30 fs was used to pump the sample at a repetition rate of 100 Hz, and a 3-MeV electron beam was used to probe the structural dynamics. The electrons were produced in a photocathode radio-frequency gun and further compressed to a duration below 30 fs (FWHM) at the sample. The number of electrons per pulse was around 4000. The temporal resolution of the MeV UED was about 50 fs (FWHM) in this experiment. The electron-beam size at the sample was around 150 μm . The size of the pump pulse was 5 times larger than the electron beam, ensuring uniform excitation of the sample. An electron-multiplying CCD camera and a phosphor screen were used to measure the diffraction patterns. High-quality single-crystal AgCrSe_2 specimens with a thickness of 50 nm were prepared by ultramicrotomy (RMC-PT-3D). The temperature of the samples was controlled by an *in situ* cooling and heating holder. For the analysis of the diffraction data, the momentum coordinate is defined as $k = 2 \sin \theta / \lambda$, following the crystallographic convention.

The laser fluences and sample temperatures used in the UED experiments were chosen as a compromise of the reliable reversibility of the pump-probe process, optimized signal-to-noise ratio, and well-defined low-temperature-ordered and high-temperature-disordered phase. Laser fluences were first determined based on the sample’s damage threshold, which was approximately 200 μJ (25.30 mJ cm^{-2}). To ensure reversible dynamics and allow the sample to return to its ordered state, the maximum fluence was set below half of this threshold, i.e., 90 μJ (11.40 mJ cm^{-2}). Then, three fluences were selected to probe the sample’s response: 30 μJ (3.80 mJ cm^{-2}), 60 μJ (7.60 mJ cm^{-2}), and 90 μJ (11.40 mJ cm^{-2}) corresponding to low, medium, and high excitation levels, respectively. On the other hand, three sample temperatures, i.e., 100, 340, and 440 K were chosen. The latter two temperatures allow dynamics near T_C to be probed with good enough diffraction intensity differences while preserving sample integrity. The sample temperature of 100 K was selected as a control experiment to rule out the nonthermal process.

As a summary, three laser fluences (30, 60, and 90 μJ) and three sample temperatures (100, 340, and 440 K) were selected, and eight UED datasets were collected (Supplemental Material Videos 1–8 [26]). The combination of 440 K and 90 μJ was neglected due to irreversible sample degradation. According to our results, experiments at 340 K with 60- and 90- μJ laser fluences result in optimal signal-to-noise ratio while assuring the sample's quality.

B. Sample preparation

Single-crystal AgCrSe_2 was grown by the chemical vapor transport method. The samples for the UED experiments were first sliced parallel to the a - b plane of the crystal using a diamond knife mounted on an Research and Manufacturing Company (RMC) ultramicrotome. The high-quality AgCrSe_2 thin-film samples with a thickness of 50 nm and lateral dimensions of approximately $300 \times 350 \mu\text{m}^2$ were then placed onto holey carbon-coated copper grids tailored for transmission electron microscopy. The specimen stage was then tilted and carefully aligned based on the diffraction pattern to ensure that the electron beam was directed precisely parallel to the crystallographic c axis during experiments.

C. rt-TDDFT calculations

rt-TDDFT calculations were carried out using the software package PWMAT [110,111]. Throughout the calculations, optimized norm-conserving Vanderbilt pseudopotentials with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional were used with the following valence electron configurations for Ag, Cr, and Se atoms: $4d^{10}5s^1$, $3d^54s^1$, and $4s^24p^6$, respectively. van der Waals correction was considered by the DFT-D3 method. Before the rt-TDDFT calculation, a $4 \times 4 \times 1$ supercell with 192 atoms was constructed from the hexagonal conventional cell with 12 atoms and conventional AIMD was carried out. In the AIMD calculation, a plane-wave energy cutoff of 45 Ry (approximately 612 eV), a Fermi-Dirac smearing of 0.03 eV, and single Γ -point mesh were employed. The supercell was equilibrated to 340 K in a Nose-Hoover ensemble for 30 ps with a time step of 2 fs.

After the AIMD calculation, an rt-TDDFT calculation was performed to simulate the dynamics of AgCrSe_2 under the irradiation of an ultrafast laser pulse. The laser pulse was modeled by an electric field $E(t) = E_0 \sin(\omega_0 t) \exp[-(t - t_0)^2/(2\sigma^2)]$ in the velocity gauge [119], where E_0 is the amplitude of the electric field, $t_0 = 47.09$ fs, a pulse width $2\sigma = 18.01$ fs corresponds to an FWHM of 30 fs, and the photon energy $\hbar\omega_0 = 1.55$ eV for an 800-nm laser. An E_0 of approximately $0.06\text{V}/\text{\AA}$ was chosen such that the energy transferred to the supercell (approximately 0.32 eV per primitive cell) was comparable to that absorbed by the specimen in experiments (approximately 0.34 eV per primitive cell for a laser fluence of 7.60 mJ cm^{-2}). The photoexcitation process was simulated

with the electric field shown in Fig. S18 in Supplemental Material [26] for 100 fs with a time step of 0.10 fs in a microcanonical (NVE) ensemble. Then, the hot carrier cooling effect, by which the photoexcited electrons relax to lower-energy states and also release energy to the lattice subsystem, was taken into consideration by including a Boltzmann factor in the simulation [119]. To accelerate the rt-TDDFT calculation, the hot carrier cooling calculation was performed for 3900 fs with a time step of 0.20 fs in an NVE ensemble. This photoexcitation (0–100 fs) hot carrier cooling (100–4000 fs) two-step process is clearly illustrated in Supplemental Material Fig. S19 [26], in which the time evolution of the energy change ΔE of the system's total, potential, and kinetic energy are plotted, respectively.

The nonadiabatic PES, or the average magnitude of microscopic forces exerted on each atomic species, before and after photoexcitation is investigated by calculating the mean forces on each atomic species $\langle |\vec{F}_{\mu,i}(t)| \rangle_i$. Here, $\vec{F}_{\mu,i}(t)$ is the force on the i th atom of atomic species μ at time t , and $\langle \cdots \rangle_i$ is the average over the atoms of the same species. Given this expression, we extracted forces from AIMD and rt-TDDFT calculations, and the distribution of $\langle |\vec{F}_{\mu,i}(t)| \rangle_i$ for Ag, Cr, and Se atoms are provided in Fig. S6 of Supplemental Material [26].

D. Density-functional-theory calculations

Spin-polarized DFT calculations were performed using the Vienna *ab initio* simulation package [120] based on the projected-augmented-wave method [121] and PBE exchange-correlation functional [122]. The electron configurations for the Ag, Cr, and Se elements were $4d^{10}5s^1$, $3p^63d^54s^1$, and $4s^24p^6$, respectively. A van der Waals correction was considered by the DFT-D3 method using the Becke-Johnson damping scheme [123]. A plane-wave energy cutoff of 500 eV and a Fermi-Dirac smearing of 0.03 eV were applied during preparation of the training and testing datasets for the neuroevolution potential by DFT calculations. A $15 \times 15 \times 15$ Monkhorst-Pack mesh was used for the ground-state calculations of the ferromagnetic primitive cell (four atoms). The electronic band structure and projected density of states are shown in Supplemental Material Fig. S4 [26]. A $2 \times 2 \times 2$ Monkhorst-Pack mesh was used for the calculation of the nondiagonal ferromagnetic supercells with 216 atoms.

Phonon dispersions with different electron temperatures were calculated on a $2 \times 2 \times 2$ diagonal supercell (32 atoms) via the finite displacement method using the PHONOPY software package [124]. The calculation was performed using a $5 \times 5 \times 5$ Monkhorst-Pack mesh. Electron smearing was set to 0.03, 0.25, 0.32, and 0.37 eV to simulate the Fermi-Dirac distribution of electrons at electron temperatures of 340, 2920, 3720, and 4315 K, respectively. The calculated phonon dispersions are shown in Supplemental Material Fig. S5 [26].

E. Training of the neuroevolution potential

The NEP was trained on a dataset containing 196 structures and validated on a testing dataset of 48 structures using GPUMDv3.9.2 [125]. An iterative active learning scheme was applied to construct the training and testing datasets. We first obtained a starting NEP by using 20 structures, and all structures were built from a nondiagonal ferromagnetic supercell (216 atoms) with random displacements and lattice deformations. Then, we successively carried out MD simulations of the supercell structure with 216 atoms at 100, 300, 500, and 700 K with running times of 100 ps, 1 ns, and 10 ns. For each running time at each temperature, 20 structures were evenly sampled and their energy, forces, and virials were validated against the DFT results. The well-predicted structures were placed into the testing dataset, while the poorly predicted results were added to the training dataset for future training. The input file `nep.in` and hyperparameters for the final training of NEP are provided in Table SII of Supplemental Material [26], where a total of 1.5×10^6 training steps were performed to achieve convergence. The final training loss function, and energy, force, and virial parity figures are provided in Fig. S20 of Supplemental Material Sec. 14 [26]. The root-mean-square error of energy, force, and virial of the training dataset were 0.47 meV/atom, 34.20 meV/Å, and 3.99 meV/atom, respectively.

The as-obtained NEP was also validated against the physical properties at low and medium temperatures, including heat capacity C_V , phonon dispersion, and lattice parameters. van der Waals corrections applied using the D3 Becke-Johnson damping method as a built-in function in GPUMD were included on top of the NEP model. To balance the efficiency and accuracy of the D3 method, we used a cutoff of 20 Å and coordination cutoff of 10 Å. Figure S9 in Supplemental Material [26] presents the heat capacity and phonon dispersion predicted by NEP + phonopy, which matched the DFT + phonopy results well. The lattice parameters at 300 K were determined by performing MD simulations using an N - P - T ensemble. The predicted lattice parameters $a = b = 3.68$ Å and $c = 21.11$ Å were in exact agreement with experimental values $a = b = 3.68$ Å and $c = 21.23$ Å [126]. As a final validation of the robustness and reliability of the trained NEP at high temperatures, we carried out extended 20-ns MD simulations at 700 K. The simulation successfully passed the validation without any unphysical structures or structural collapse.

F. Nonequilibrium pump-probe and equilibrium molecular dynamics simulations

The pump-probe process was simulated by nonequilibrium MD calculations based on NEP. The nonequilibrium steady state, which simulated the excitation by laser pumping, was achieved in LAMMPS [127] software by using a hot-spot thermostat based on the generalized

Langevin equation (GLE) [112,113]. The parameters for the thermostat were generated from the online GLE repository with parameters $\omega_0 = 7$ THz, $\Delta\omega = 2$ THz, $T_{\text{max}} = 1200$ K, $T_{\text{base}} = 120$ K, and $\gamma^{-1} = \gamma_{\text{base}}^{-1} = 0.20$ ps. MD simulations consisting of a supercell with 11 520 atoms and dimensions of $7.36 \times 7.65 \times 4.22$ nm were performed for 600 ps with a time step of 2 fs to ensure full equilibrium. The average kinetic temperatures of Ag and CrSe₂ were determined as approximately 340 and 700 K. Finally, the last atomic structure was used for simulation of the probe or the relaxation process in the NVE ensemble using GPUMD with a simulation time step of 2 fs. The atomic positions were recorded every 50 fs for later analysis and electron-diffraction simulations. The radial distribution functions (RDF) of Ag⁺-Ag⁺ $g_{\text{Ag}^+-\text{Ag}^+}(r)$ at various time delays were calculated and compared to rt-TDDFT calculations, which further validate the accuracy of our nonequilibrium MD simulations (Fig. S3 [26]).

The equilibrium MD simulations were similarly performed using GPUMD with a time step of 2 fs. We first carried out 1 ns calculation using the NPT ensemble to determine the lattice parameters at 100, 300, 340, 400, 500, 600 and 700 K. Then 200 ps NVT simulations were performed with the predicted lattice parameters. The atomic trajectories were recorded every 50 fs for later transport analysis and electron-diffraction simulations.

To explore the effects of tensile strain, additional MD simulations were performed on AgCrSe₂ with 2% tensile strain. In these simulations, the tensile strain was applied along all crystallographic axes, corresponding to a hydrostatic tensile strain. Specifically, the lattice parameters a and c were manually adjusted to $1.02a$ and $1.02c$, respectively, while all other simulation parameters were identical to those used in the equilibrium MD simulations.

G. Calculation of diffusion coefficients

D_{Ag^+} of Ag⁺ ions

The theoretical diffusion coefficients of Ag⁺ ions were directly calculated from the MD trajectories using the following expressions:

$$D_{\text{Ag}^+} = \frac{1}{2d} \lim_{t \rightarrow +\infty} \frac{d}{dt} \sum_{i=1}^N \langle |r_i(t_0 + t) - r_i(t_0)|^2 \rangle_{t_0}, \quad (1)$$

where $d = 2$ is the system dimension due to the quasi-2D transport of Ag⁺ ions, $r_i(t_0 + t)$ and $r_i(t_0)$ denote the positions of the i th Ag⁺ ion at times $t_0 + t$ and t_0 , and $\langle \dots \rangle$ is the ensemble average.

According to the Nernst-Einstein relation [115], the diffusion coefficient D_{Ag^+} can also be determined from experimental ionic conductivity σ as

$$\sigma = \frac{NQ^2}{k_B T V} D_{\text{Ag}^+}, \quad (2)$$

where N is the total number of Ag^+ ions in the simulation supercell, Q denotes the charge of the Ag^+ ion, k_B is the Boltzmann constant, T is the temperature, and V is the volume of the simulation supercell. From Eq. (2), we extracted the diffusion coefficients of Ag^+ ions from the literature, and the results are provided in both Fig. 6(c) and Supplemental Material Fig. S21 in Sec. 15 [26].

H. Simulation of MeV electron-diffraction patterns

The dynamical electron diffraction of the 3-MeV electrons were simulated based on the conventional multislice method using ABTEM [128] (further details can be found in Figs. S7 and S8 [26]). The atomic potentials were modeled by the Lobato parametrization [129] with a slice thickness of approximately 4.22 Å along the electron-beam direction and a real-space sampling of 0.03 Å/pixel. Thermal diffuse scattering due to phonon excitations or diffusion was naturally incorporated by the frozen-lattice approach [130], according to which the total scattering intensities consisted of an incoherent summation of snapshots from the scattering intensities of each structure.

ACKNOWLEDGMENTS

We give special thanks to Y. Xia for guidance on the sample preparation. L. X. would like to acknowledge Zihan Yan and Yizhou Zhu from Westlake University for sharing their machine-learning interatomic potentials and helpful discussions on lithium superionic conductors. We acknowledge the National Key Research and Development Program of China (Grant No. 2024YFB3813800), the National Natural Science Foundation of China (Grants No. 12434001, No. 52461160258, No. U25A20239), the Guangdong Provincial Key Laboratory of Advanced Thermoelectric Materials and Device Physics (Grant No. 2024B1212010001), the Outstanding Talents Training Fund in Shenzhen (Grant No. 202108), the Science, Technology and Innovation Commission of Shenzhen Municipality (Grant No. ZDSYS20141118160434515), and the Guangdong Provincial Program (2024JC08A027). J. Y. and M. B. kindly acknowledge support from the Ministry of Education, Singapore, under AcRF Tier 2 (Grant No. MOE-T2EP50122-0016). We thank the SUSTech Core Research Facilities for providing use of the TEM. The computational resources are supported by SongShan Lake HPC Center in Great Bay University. D. X. would like to acknowledge the support from the New Cornerstone Science Foundation through the Xplorer grant. The UED experiment was supported by the Shanghai soft x-ray free-electron laser facility.

L. X. and J. H. designed this work. L. X., D. X., M. B., and J. H. supervised the project. J. Y. prepared the samples. L. X. performed the calculations. J. Y. and L. X. conducted data analysis. Y. Q. and Z. C. performed the UED

experiments. J. L. performed the selected-area electron-diffraction experiments. M. H. and J. F. synthesized the sample, and B. J. conducted the transport property measurements. J. Y., L. X., D. X., and J. H. wrote the manuscript, with all authors contributing to the editing process.

DATA AVAILABILITY

The data are not publicly available. The data are available from the authors upon reasonable request.

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- [1] A. J. E. Rettie, J. Ding, X. Zhou, M. J. Johnson, C. D. Malliakas, N. C. Osti, D. Y. Chung, R. Osborn, O. Delaire, S. Rosenkranz, and M. G. Kanatzidis, *A two-dimensional type I superionic conductor*, *Nat. Mater.* **20**, 1683 (2021).
 - [2] W. Zhang, J. Cui, S. Wang, H. Cao, A. Wu, Y. Xia, Q. Jiang, J. Guo, T. He, and P. Chen, *Deforming lanthanum trihydride for superionic conduction*, *Nature (London)* **616**, 73 (2023).
 - [3] J. Zhi, S. Zhao, M. Zhou, R. Wang, and F. Huang, *A zinc-conducting chalcogenide electrolyte*, *Sci. Adv.* **9**, eade2217 (2023).
 - [4] M. R. Lukatskaya, O. Mashtalir, C. E. Ren, Y. Dall'Agnesse, P. Rozier, P. L. Taberna, M. Naguib, P. Simon, M. W. Barsoum, and Y. Gogotsi, *Cation intercalation and high volumetric capacitance of two-dimensional titanium carbide*, *Science* **341**, 1502 (2013).
 - [5] K. Jun, Y. Chen, G. Wei, X. Yang, and G. Ceder, *Diffusion mechanisms of fast lithium-ion conductors*, *Nat. Rev. Mater.* **9**, 887 (2024).
 - [6] Y.-C. Yin *et al.*, *A LaCl_3 -based lithium superionic conductor compatible with lithium metal*, *Nature (London)* **616**, 77 (2023).
 - [7] Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba, and R. Kanno, *High-power all-solid-state batteries using sulfide superionic conductors*, *Nat. Energy* **1**, 16030 (2016).
 - [8] P. Boolchand and W. J. Bresser, *Mobile silver ions and glass formation in solid electrolytes*, *Nature (London)* **410**, 1070 (2001).
 - [9] H. Liu, X. Shi, F. Xu, L. Zhang, W. Zhang, L. Chen, Q. Li, C. Uher, T. Day, and G. J. Snyder, *Copper ion liquid-like thermoelectrics*, *Nat. Mater.* **11**, 422 (2012).
 - [10] K. Zhao, P. Qiu, X. Shi, and L. Chen, *Recent advances in liquid-like thermoelectric materials*, *Adv. Funct. Mater.* **30**, 1903867 (2020).
 - [11] D. J. Voneshen, H. C. Walker, K. Refson, and J. P. Goff, *Hopping time scales and the phonon-liquid electron-crystal picture in thermoelectric copper selenide*, *Phys. Rev. Lett.* **118**, 145901 (2017).
 - [12] J. L. Niedziela, D. Bansal, A. F. May, J. Ding, T. Lanigan-Atkins, G. Ehlers, D. L. Abernathy, A. Said, and O. Delaire, *Selective breakdown of phonon quasiparticles across superionic transition in CuCrSe_2* , *Nat. Phys.* **15**, 73 (2019).
 - [13] T. Famprikis, P. Canepa, J. A. Dawson, M. S. Islam, and C. Masquelier, *Fundamentals of inorganic solid-state electrolytes for batteries*, *Nat. Mater.* **18**, 1278 (2019).

- [14] L. Wang, T. Liu, A. Dai, V. De Andrade, Y. Ren, W. Xu, S. Lee, Q. Zhang, L. Gu, S. Wang, T. Wu, H. Jin, and J. Lu, *Reaction inhomogeneity coupling with metal rearrangement triggers electrochemical degradation in lithium-rich layered cathode*, *Nat. Commun.* **12**, 5370 (2021).
- [15] X. He, Y. Zhu, and Y. Mo, *Origin of fast ion diffusion in super-ionic conductors*, *Nat. Commun.* **8**, 15893 (2017).
- [16] L. Xie, D. Wu, H. Yang, Y. Yu, Y. Wang, and J. He, *Direct atomic-scale observation of Ag^+ diffusion structure in the quasi-2D “Liquid-like” state of superionic thermoelectric AgCrSe_2* , *J. Mater. Chem. C* **7**, 9263 (2019).
- [17] M. A. Kraft, S. P. Culver, M. Calderon, F. Böcher, T. Krauskopf, A. Senyshyn, C. Dietrich, A. Zevalkink, J. Janek, and W. G. Zeier, *Influence of lattice polarizability on the ionic conductivity in the lithium superionic argyrodites $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)*, *J. Am. Chem. Soc.* **139**, 10909 (2017).
- [18] D. Voneshen, K. Refson, E. Borissenko, M. Krisch, A. Bosak, A. Piovano, E. Cerni, M. Enderle, M. Gutmann, M. Hoesch, M. Roger, L. Gannon, A. Boothroyd, S. Uthayakumar, D. Porter, and J. Goff, *Suppression of thermal conductivity by rattling modes in thermoelectric sodium cobaltate*, *Nat. Mater.* **12**, 1028 (2013).
- [19] A. D. Poletayev, M. C. Hoffmann, J. A. Dawson, S. W. Teitelbaum, M. Trigo, M. S. Islam, and A. M. Lindenberg, *The persistence of memory in ionic conduction probed by nonlinear optics*, *Nature (London)* **625**, 691 (2024).
- [20] Q. Ren, M. K. Gupta, M. Jin, J. Ding, J. Wu, Z. Chen, S. Lin, O. Fabelo, J. A. Rodríguez-Velamazán, M. Kofu, K. Nakajima, M. Wolf, F. Zhu, J. Wang, Z. Cheng, G. Wang, X. Tong, Y. Pei, O. Delaire, and J. Ma, *Extreme phonon anharmonicity underpins superionic diffusion and ultra-low thermal conductivity in argyrodite Ag_8SnSe_6* , *Nat. Mater.* **22**, 999 (2023).
- [21] J. Ding, J. Niedziela, D. Bansal, J. Wang, X. He, A. May, G. Ehlers, D. Abernathy, A. Said, A. Alatas, Y. Ren, G. Arya, and O. Delaire, *Anharmonic lattice dynamics and superionic transition in AgCrSe_2* , *Proc. Natl. Acad. Sci. U.S.A.* **117**, 3930 (2020).
- [22] J. Ding, M. K. Gupta, C. Rosenbach, H.-M. Lin, N. C. Osti, D. L. Abernathy, W. G. Zeier, and O. Delaire, *Liquid-like dynamics in a solid-state lithium electrolyte*, *Nat. Phys.* **21**, 118 (2025).
- [23] E. J. Sie *et al.*, *An ultrafast symmetry switch in a Weyl semimetal*, *Nature (London)* **565**, 61 (2019).
- [24] Y. Cheng, A. Zong, L. Wu, Q. Meng, W. Xia, F. Qi, P. Zhu, X. Zou, T. Jiang, Y. Guo, J. van Wezel, A. Kogar, M. W. Zuerch, J. Zhang, Y. Zhu, and D. Xiang, *Ultrafast formation of topological defects in a two-dimensional charge density wave*, *Nat. Phys.* **20**, 54 (2024).
- [25] B. Li, H. Wang, Y. Kawakita, Q. Zhang, M. Feyngenson, H. L. Yu, D. Wu, K. Ohara, T. Kikuchi, K. Shibata, T. Yamada, X. K. Ning, Y. Chen, J. Q. He, D. Vaknin, R. Q. Wu, K. Nakajima, and M. G. Kanatzidis, *Liquid-like thermal conduction in intercalated layered crystalline solids*, *Nat. Mater.* **17**, 226 (2018).
- [26] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/s6rh-7219> for detailed information on the experiment details, data analysis, as well as theoretical calculation approaches, which includes Refs. [27–105].
- [27] J. Li, Y. Qi, Q. Yang, L. Yue, C. Yao, Z. Chen, S. Meng, D. Xiang, and J. Cao, *Femtosecond electron diffraction reveals local disorder and local anharmonicity in thermoelectric SnSe* , *Adv. Mater.* **36**, 2313742 (2024).
- [28] J. Groefsema, X. Feng, C. Morice, Y. Huang, and E. Van Heumen, *Optical phonons and magneto-elastic coupling in the ionic conductor AgCrSe_2* , *Phys. Rev. Mater.* **6**, 115402 (2022).
- [29] A. Krishnamoorthy *et al.*, *Optical control of non-equilibrium phonon dynamics*, *Nano Lett.* **19**, 4981 (2019).
- [30] Z. Lin, L. V. Zhigilei, and V. Celli, *Electron-phonon coupling and electron heat capacity of metals under conditions of strong electron-phonon nonequilibrium*, *Phys. Rev. B* **77**, 075133 (2008).
- [31] Q. Zeng, B. Chen, S. Zhang, D. Kang, H. Wang, X. Yu, and J. Dai, *Full-scale ab initio simulations of laser-driven atomistic dynamics*, *npj Comput. Mater.* **9**, 213 (2023).
- [32] P. Srinivasan, D. Demuriya, B. Grabowski, and A. Shapeev, *Electronic moment tensor potentials include both electronic and vibrational degrees of freedom*, *npj Comput. Mater.* **10**, 41 (2024).
- [33] W.-H. Liu, J.-W. Luo, S.-S. Li, and L.-W. Wang, *Microscopic force driving the photoinduced ultrafast phase transition: Time-dependent density functional theory simulations of IrTe_2* , *Phys. Rev. B* **102**, 184308 (2020).
- [34] P. M. Zeiger and J. Ruzs, *Frequency-resolved frozen phonon multislice method and its application to vibrational electron energy loss spectroscopy using parallel illumination*, *Phys. Rev. B* **104**, 104301 (2021).
- [35] J. P. Langmore and M. F. Smith, *Quantitative energy-filtered electron microscopy of biological molecules in ice*, *Ultramicroscopy* **46**, 349 (1992).
- [36] R. F. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope* (Springer Science & Business Media, New York, 2011).
- [37] Y. Seto and M. Ohtsuka, *ReciPro: Free and open-source multipurpose crystallographic software integrating a crystal model database and viewer, diffraction and microscopy simulators, and diffraction data analysis tools*, *J. Appl. Crystallogr.* **55**, 397 (2022).
- [38] C. R. Hall and P. B. Hirsch, *Effect of thermal diffuse scattering on propagation of high energy electrons through crystals*, *Proc. R. Soc. A* **286**, 158 (1997).
- [39] A. Stukowski, *Visualization and analysis of atomistic simulation data with OVITO—the Open Visualization Tool*, *Model. Simul. Mater. Sci. Eng.* **18**, 015012 (2010).
- [40] D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications* (Elsevier, New York, 2023).
- [41] R. Wang, M. Guo, Y. Gao, X. Wang, Y. Zhang, B. Deng, X. Chen, M. Shi, L. Zhang, and Z. Zhong, *A pre-trained deep potential model for sulfide solid electrolytes with broad coverage and high accuracy*, *arXiv:2406.18263*.
- [42] N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, and A. Mitsui, *A lithium superionic conductor*, *Nat. Mater.* **10**, 682 (2011).

- [43] M. Baenitz *et al.*, *Planar triangular $S = 3/2$ magnet AgCrSe_2 : Magnetic frustration, short range correlations, and field-tuned anisotropic cycloidal magnetic order*, *Phys. Rev. B* **104**, 134410 (2021).
- [44] Y. Mo, S. P. Ong, and G. Ceder, *First principles study of the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ lithium super ionic conductor material*, *Chem. Mater.* **24**, 15 (2012).
- [45] A. Kuhn, V. Duppel, and B. V. Lotsch, *Tetragonal $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ and Li_7GePS_8 —exploring the Li ion dynamics in LGPS Li electrolytes*, *Energy Environ. Sci.* **6**, 3548 (2013).
- [46] D. W. Murphy, H. S. Chen, and B. Tell, *Superionic conduction in AgCrS_2 and AgCrSe_2* , *J. Electrochem. Soc.* **124**, 1268 (1977).
- [47] V. Antropov, V. Konev, V. Pleshchev, and N. Rogal', *Ionic conductivity of AgCrSe_2 in the region of phase transition*, *Phys. Solid State* **26**, 2545 (1984), [https://sciedata.urfu.ru/portal/en/publications/ionicconductivity-of-agcrse2-in-the-region-of-phasetransition\(e577f504-8908-4aa5-b8f9-bb33cca4a201\).html](https://sciedata.urfu.ru/portal/en/publications/ionicconductivity-of-agcrse2-in-the-region-of-phasetransition(e577f504-8908-4aa5-b8f9-bb33cca4a201).html).
- [48] J. Peng, Y. Liu, Y. Pan, J. Wu, Y. Su, Y. Guo, X. Wu, C. Wu, and Y. Xie, *Fast lithium ion conductivity in layered (Li-Ag) CrS_2* , *J. Am. Chem. Soc.* **142**, 18645 (2020).
- [49] T. Hibma, *The mixed conductor properties of AgCrS_2* , *Solid State Commun.* **33**, 445 (1980).
- [50] F. Shimojo, T. Inoue, M. Aniya, T. Sugahara, and Y. Miyata, *Ab initio molecular-dynamics study of static structure and bonding properties of molten AgI* , *J. Phys. Soc. Jpn.* **75**, 114602 (2006).
- [51] K. Shahi, *Transport studies on superionic conductors*, *Phys. Status Solidi A* **41**, 11 (1977).
- [52] Tallon, *Molecular-dynamics simulation of the phase behavior of AgI* , *Phys. Rev. Lett.* **57**, 2427 (1986).
- [53] Y. Tsuchiya, S. Tamaki, Y. Waseda, and J. M. Toguri, *The structure of $\alpha\text{-Ag}_2\text{S}$* , *J. Phys. C* **11**, 651 (1978).
- [54] O. Alekperov, O. Samedov, R. Paucar, N. Abdulzade, E. Nakhmedov, A. Nadjafov, K. Wakita, and N. Mamedov, *Impedance spectroscopy study of phase transitions to ionic and superionic conductivity states in Ag_2S and Ag_2Se* , *Phys. Status Solidi C* **12**, 610 (2015).
- [55] H. Okazaki, *Deviation from the Einstein relation in average crystals self-diffusion of Ag^+ ions in $\alpha\text{-Ag}_2\text{S}$ and $\alpha\text{-Ag}_2\text{Se}$* , *J. Phys. Soc. Jpn.* **23**, 355 (1967).
- [56] P. Simonnin, M. Sassi, B. Gilbert, L. Charlet, and K. M. Rosso, *Phase transition and liquid-like superionic conduction in Ag_2S* , *J. Phys. Chem. C* **124**, 10150 (2020).
- [57] A. Smith, R. Ravelo, and N. Pingitore, *Mobility of Ag atoms in the binary system $\text{Ag}_2\text{Se-Ag}_2\text{S}$: A molecular dynamics study*, *MRS Online Proc. Libr.* **481**, 279 (1997).
- [58] S. Fukushima, M. Misawa, A. Koura, and F. Shimojo, *GGA + U molecular dynamics study of structural and dynamic properties of superionic conductor Ag_2Se* , *J. Phys. Soc. Jpn.* **88**, 115002 (2019).
- [59] S.-y. Miyatani, *Ionic conductivity in silver chalcogenides*, *J. Phys. Soc. Jpn.* **50**, 3415 (1981).
- [60] J. E. Enderby and A. C. Barnes, *Liquid semiconductors*, *Rep. Prog. Phys.* **53**, 85 (1990).
- [61] H. Okazaki, *Deviation from the Einstein relation in average crystals. II. Self-diffusion of Ag^+ ions in $\alpha\text{-Ag}_2\text{Te}$* , *J. Phys. Soc. Jpn.* **43**, 213 (1977).
- [62] M. Kobayashi, K. Ishikawa, F. Tachibana, and H. Okazaki, *Diffusion path and Haven's ratio of mobile ions in $\alpha\text{-Ag}_2\text{Te}$* , *Phys. Rev. B* **38**, 3050 (1988).
- [63] R. Hoeven, *Modelling and Simulation of Thermoelectric Materials with a Superionic Phase Transition Using on-the-Fly Machine Learning Force Fields* (University of Twente, 2022), https://essay.utwente.nl/filesare/file/92459/vanderHoeven_BA_EEMCS_TNW.pdf.
- [64] H. Kim, S. Ballikaya, H. Chi, J.-P. Ahn, K. Ahn, C. Uher, and M. Kaviani, *Ultralow thermal conductivity of $\beta\text{-Cu}_2\text{Se}$ by atomic fluidity and structure distortion*, *Acta Mater.* **86**, 247 (2015).
- [65] T. Kanashiro, T. Ohno, M. Satoh, K. Okamoto, A. Kojima, and F. Akao, *Nuclear magnetic resonance and electrical conduction of copper chalcogenides*, *Solid State Ionics* **3-4**, 327 (1981).
- [66] M. K. Balapanov, R. A. Yakshibaev, and U. K. Mukhamed'yanov, *Ion transfer in solid solutions of Cu_2Se and Ag_2Se superionic conductors*, *Phys. Solid State* **45**, 634 (2003).
- [67] S. Kumar, M. K. Gupta, P. Goel, R. Mittal, O. Delaire, A. Thamizhavel, S. Rols, and S. L. Chaplot, *Solidlike to liquidlike behavior of Cu diffusion in superionic Cu_2X ($\text{X} = \text{S}, \text{Se}$): An inelastic neutron scattering and ab initio molecular dynamics investigation*, *Phys. Rev. Mater.* **6**, 055403 (2022).
- [68] S. M. K. Nazrul Islam, P. Mayank, Y. Ouyang, J. Chen, A. K. Sagotra, M. Li, M. B. Cortie, R. Mole, C. Cazorla, D. Yu, X. Wang, R. A. Robinson, and D. L. Cortie, *Copper diffusion rates and hopping pathways in superionic Cu_2Se* , *Acta Mater.* **215**, 117026 (2021).
- [69] K. Tsumuraya, T. Ohtsuka, H. Oshihara, H. Tomono, and M. Tsumuraya, *Dynamic Correlation between Superionic Coppers in $\alpha\text{-CuI}$* , *J. Phys. Soc. Jpn.* **81**, 044603 (2012).
- [70] J. B. Boyce and B. A. Huberman, *Dynamical evidence for sublattice melting in a superionic conductor: NMR on CuI* , *Solid State Commun.* **21**, 31 (1977).
- [71] B. K. Verma, V. Pratap, and H. B. Lal, *Transport studies of copper iodide*, *Jpn. J. Appl. Phys.* **20**, 1665 (1981).
- [72] Y. Yang, Z. Xu, C. Guan, R. Ouyang, H. Jing, and H. Zhu, *Activating the paddle-wheel effect towards lower temperature in a new sodium-ion solid electrolyte, $\text{Na}_{3.5}\text{Si}_{0.5}\text{P}_{0.5}\text{Se}_4$* , *J. Mater. Chem. A* **11**, 9555 (2023).
- [73] F. Kamm, F. Pielnhöfer, M. Schlosser, and A. Pfitzner, *Synthesis and characterization of $\text{Na}_4\text{Si}_2\text{Se}_6\text{-tP}_{24}$ and $\text{Na}_4\text{Si}_2\text{Se}_6\text{-oP}_{48}$, two polymorphs with different anionic structures*, *Inorg. Chem.* **62**, 11064 (2023).
- [74] H. Tang, Z. Deng, Z. Lin, Z. Wang, I.-H. Chu, C. Chen, Z. Zhu, C. Zheng, and S. P. Ong, *Probing solid-solid interfacial reactions in all-solid-state sodium-ion batteries with first-principles calculations*, *Chem. Mater.* **30**, 163 (2018).
- [75] T. Shibata, W. Kobayashi, and Y. Moritomo, *Sodium ion diffusion in layered Na_xCoO_2* , *Appl. Phys. Express* **6**, 9 (2013).
- [76] N. Gómez-Garduño, D. G. Araiza, C. A. Celaya, J. Muñiz, and H. Pfeiffer, *Unveiling the different physicochemical properties of M-doped $\beta\text{-NaFeO}_2$ (where $\text{M} = \text{Ni}$ or Cu) materials evaluated as CO_2 sorbents: A combined experimental and theoretical analysis*, *J. Mater. Chem. A* **11**, 10938 (2023).

- [77] N. V. Proskurnina, V. I. Voronin, G. S. Shekhtman, and N. A. Kabanova, *Crystal structure of NaFeO₂ and NaAlO₂ and their correlation with ionic conductivity*, *Ionics* **26**, 2917 (2020).
- [78] T. Miyagawa, N. Krishnan, M. Grumet, C. R. Baecker, W. Kaiser, and D. A. Egger, *Accurate description of ion migration in solid-state ion conductors from machine-learning molecular dynamics*, *J. Mater. Chem. A* **12**, 11344 (2024).
- [79] O. Maus, M. T. Agne, T. Fuchs, P. S. Till, B. Wankmiller, J. M. Gerdes, R. Sharma, M. Heere, N. Jalarvo, O. Yaffe, M. R. Hansen, and W. G. Zeier, *On the discrepancy between local and average structure in the fast Na⁺ ionic conductor Na_{2.9}Sb_{0.9}W_{0.1}S₄*, *J. Am. Chem. Soc.* **145**, 7147 (2023).
- [80] D. Zhang, X. Cao, D. Xu, N. Wang, C. Yu, W. Hu, X. Yan, J. Mi, B. Wen, L.-M. Wang, and L. Zhang, *Synthesis of cubic Na₃SbS₄ solid electrolyte with enhanced ion transport for all-solid-state sodium-ion batteries*, *Electrochim. Acta* **259**, 100 (2018).
- [81] Q. Zhang, C. Zhang, Z. D. Hood, M. Chi, C. Liang, N. H. Jalarvo, M. Yu, and H. Wang, *Abnormally low activation energy in cubic Na₃SbS₄ superionic conductors*, *Chem. Mater.* **32**, 2264 (2020).
- [82] J. A. Dawson, P. Canepa, M. J. Clarke, T. Famprikis, D. Ghosh, and M. S. Islam, *Toward understanding the different influences of grain boundaries on ion transport in sulfide and oxide solid electrolytes*, *Chem. Mater.* **31**, 5296 (2019).
- [83] C. Yu, S. Ganapathy, N. J. J. de Klerk, E. R. H. van Eck, and M. Wagemaker, *Na-ion dynamics in tetragonal and cubic Na₃PS₄, a Na-ion conductor for solid state Na-ion batteries*, *J. Mater. Chem. A* **4**, 15095 (2016).
- [84] A. Hayashi, K. Noi, A. Sakuda, and M. Tatsumisago, *Superionic glass-ceramic electrolytes for room-temperature rechargeable sodium batteries*, *Nat. Commun.* **3**, 856 (2012).
- [85] N. J. J. de Klerk and M. Wagemaker, *Diffusion mechanism of the sodium-ion solid electrolyte Na₃PS₄ and potential improvements of halogen doping*, *Chem. Mater.* **28**, 3122 (2016).
- [86] M. Kassem, T. Bounazef, A. Sokolov, M. Bokova, D. Fontanari, A. C. Hannon, I. Alekseev, and E. Bychkov, *Deciphering fast ion transport in glasses: A case study of sodium and silver vitreous sulfides*, *Inorg. Chem.* **61**, 12870 (2022).
- [87] M. Ribes, B. Barrau, and J. L. Souquet, *Sulfide glasses: Glass forming region, structure and ionic conduction of glasses in Na₂S-XS₂ (X = Si; Ge), Na₂S-P₂S₅ and Li₂S-GeS₂ systems*, *J. Non-Cryst. Solids* **38–39**, 271 (1980).
- [88] Z. Zhang, H. Li, K. Kaup, L. Zhou, P.-N. Roy, and L. F. Nazar, *Targeting superionic conductivity by turning on anion rotation at room temperature in fast ion conductors*, *Matter Radiat. Extremes* **2**, 1667 (2020).
- [89] H. Stöfler, T. Zinkevich, M. Yavuz, A. Senyshyn, J. Kulisch, P. Hartmann, T. Adermann, S. Randau, F. H. Richter, J. Janek, S. Indris, and H. Ehrenberg, *Li⁺-ion dynamics in β-Li₃PS₄ observed by NMR: Local hopping and long-range transport*, *J. Phys. Chem. C* **122**, 15954 (2018).
- [90] M. Tachez, J.-P. Malugani, R. Mercier, and G. Robert, *Ionic conductivity of and phase transition in lithium thiophosphate Li₃PS₄*, *Solid State Ionics* **14**, 181 (1984).
- [91] S. Teragawa, K. Aso, K. Tadanaga, A. Hayashi, and M. Tatsumisago, *Liquid-phase synthesis of a Li₃PS₄ solid electrolyte using N-methylformamide for all-solid-state lithium batteries*, *J. Mater. Chem. A* **2**, 5095 (2014).
- [92] N. H. H. Phuc, M. Totani, K. Morikawa, H. Muto, and A. Matsuda, *Preparation of Li₃PS₄ solid electrolyte using ethyl acetate as synthetic medium*, *Solid State Ionics* **288**, 240 (2016).
- [93] L. Gigli, D. Tisi, F. Grasselli, and M. Ceriotti, *Mechanism of charge transport in lithium thiophosphate*, *Chem. Mater.* **36**, 1482 (2024).
- [94] F. Forrester and J. Quirk, *Disentangling cation and anion dynamics in Li₃PS₄ solid electrolytes*, *Chem. Mater.* **34**, 10561 (2022).
- [95] N. J. J. de Klerk, E. van der Maas, and M. Wagemaker, *Analysis of diffusion in solid-state electrolytes through MD simulations, Improvement of the Li-ion conductivity in β-Li₃PS₄ as an example*, *ACS Appl. Energy Mater.* **1**, 3230 (2018).
- [96] J.-H. Chung, T. Proffen, S. Shamoto, A. M. Ghorayeb, L. Croguennec, W. Tian, B. C. Sales, R. Jin, D. Mandrus, and T. Egami, *Local structure of LiNiO₂ studied by neutron diffraction*, *Phys. Rev. B* **71**, 064410 (2005).
- [97] K. Nakamura, H. Ohno, K. Okamura, Y. Michihiro, I. Nakabayashi, and T. Kanashiro, *On the diffusion of Li⁺ defects in LiCoO₂ and LiNiO₂*, *Solid State Ionics* **135**, 143 (2000).
- [98] Y. Zhang and C. Wang, *Cycle-life characterization of automotive lithium-ion batteries with LiNiO₂ Cathode*, *J. Electrochem. Soc.* **156**, A527 (2009).
- [99] G. Luo, J. Zhao, X. Ke, P. Zhang, H. Sun, and B. Wang, *Structure, electrode voltage and activation energy of LiMn_xCo_yNi_{1-x-y}O₂ solid solutions as cathode materials for Li batteries from first-principles*, *J. Electrochem. Soc.* **159**, A1203 (2012).
- [100] K. Kang, Y. S. Meng, J. Bréger, C. P. Grey, and G. Ceder, *Electrodes with high power and high capacity for rechargeable lithium batteries*, *Science* **311**, 977 (2006).
- [101] D. Adipranoto, M. Yonemura, Y. Ishikawa, A. Hoshikawa, T. Ishigaki, K. Takashi, Y. Uchimoto, and Z. Ogumi, *Crystal-local structure analyses for cathode LIBs LiNi_{1-x}Co_xO₂ (0 ≤ x ≤ 1) by neutron diffraction*, *J. Phys. Soc. Jpn. Conf. Proc.* **8**, 031017 (2015).
- [102] D. Zeng, J. Cabana, J. Bréger, W.-S. Yoon, and C. Grey, *Cation ordering in Li[Ni_xMn_xCo_(1-2x)]O₂ Layered cathode materials: A nuclear magnetic resonance (NMR), pair distribution function, X-ray absorption spectroscopy, and electrochemical study*, *Chem. Mater.* **19**, 6289 (2007).
- [103] R. Amin and Y.-M. Chiang, *Characterization of electronic and ionic transport in Li_{1-x}Ni_{0.33}Mn_{0.33}Co_{0.33}O₂ (NMC₃₃₃) and Li_{1-x}Ni_{0.5}Mn_{0.20}Co_{0.30}O₂ (NMC₅₂₃) as a function of Li content*, *J. Electrochem. Soc.* **163**, A1512 (2016).
- [104] X. Liang, Y. Jiang, W. Cai, S. Wu, L. Wang, Z. Lei, J. Chen, Y. Lei, L. Yang, and J. Feng, *New Li₁₀GeP₂S₁₂ structure ordering and Li-ion dynamics unveiled in Li₄GeS₄ – Li₃PS₄ superionic conductors: A solid-state*

- nuclear magnetic resonance study, *ACS Appl. Mater. Interfaces* **12**, 27029 (2020).
- [105] Z.-H. Fu, X. Chen, N. Yao, X. Shen, X.-X. Ma, S. Feng, S. Wang, R. Zhang, L. Zhang, and Q. Zhang, *The chemical origin of temperature-dependent lithium-ion concerted diffusion in sulfide solid electrolyte Li₁₀GeP₂S₁₂*, *J. Energy Chem.* **70**, 59 (2022).
- [106] T. Hibma, *Diffuse x-ray scattering of the two-dimensional solid ionic conductor AgCrS₂*, *Phys. Rev. B* **28**, 568 (1983).
- [107] J.D. Fan, O.A. Karim, G. Reiter, and S.C. Moss, *Molecular-dynamics study of the temperature-dependent two-dimensional Rb liquid in graphite*, *Phys. Rev. B* **39**, 6111 (1989).
- [108] I. Hamley, *Diffuse scattering from lamellar structures*, *Soft Matter* **18**, 711 (2022).
- [109] M.J. Krogstad, S. Rosenkranz, J.M. Wozniak, G. Jennings, J.P.C. Ruff, J.T. Vaughey, and R. Osborn, *Reciprocal space imaging of ionic correlations in intercalation compounds*, *Nat. Mater.* **19**, 63 (2020).
- [110] W. Liu, H. Liu, Z. Wang, S. Li, L. Wang, and J. Luo, *Inverse design of light manipulating structural phase transition in solids*, *J. Phys. Chem. Lett.* **14**, 6647 (2023).
- [111] Z. Wang, S.-S. Li, and L.-W. Wang, *Efficient real-time time-dependent density functional theory method and its application to a collision of an ion with a 2D material*, *Phys. Rev. Lett.* **114**, 063004 (2015).
- [112] R. Dettori, M. Ceriotti, J. Hunger, C. Melis, L. Colombo, and D. Donadio, *Simulating energy relaxation in pump-probe vibrational spectroscopy of hydrogen-bonded liquids*, *J. Chem. Theory Comput.* **13**, 1284 (2017).
- [113] R. Dettori, M. Ceriotti, J. Hunger, L. Colombo, and D. Donadio, *Energy relaxation and thermal diffusion in infrared pump-probe spectroscopy of hydrogen-bonded liquids*, *J. Phys. Chem. Lett.* **10**, 3447 (2019).
- [114] F. Damay, S. Petit, S. Rols, M. Braendlein, R. Daou, E. Elkaïm, F. Fauth, F. Gascoin, C. Martin, and A. Maignan, *Localised Ag⁺ vibrations at the origin of ultralow thermal conductivity in layered thermoelectric AgCrSe₂*, *Sci. Rep.* **6**, 23415 (2016).
- [115] J. Wang, J. Ding, O. Delaire, and G. Arya, *Atomistic mechanisms underlying non-Arrhenius ion transport in superionic conductor AgCrSe₂*, *ACS Appl. Energy Mater.* **4**, 7157 (2021).
- [116] X. Shen, M. M. Koza, Y.-H. Tung, N. Ouyang, C.-C. Yang, C. Wang, Y. Chen, K. Willa, R. Heid, X. Zhou, and F. Weber, *Soft phonon mode triggering fast Ag diffusion in superionic argyrodite Ag₈GeSe₆*, *Small* **19**, 2305048 (2023).
- [117] B. A. Boukamp and G. A. Wieggers, *Ionic and electronic processes in AgCrSe₂*, *Solid State Ionics* **9–10**, 1193 (1983).
- [118] F. Qi, Z. Ma, L. Zhao, Y. Cheng, W. Jiang, C. Lu, T. Jiang, D. Qian, Z. Wang, W. Zhang, P. Zhu, X. Zou, W. Wan, D. Xiang, and J. Zhang, *Breaking 50 femtosecond resolution barrier in MeV ultrafast electron diffraction with a double bend achromat compressor*, *Phys. Rev. Lett.* **124**, 134803 (2020).
- [119] W.-H. Liu, J.-W. Luo, S.-S. Li, and L.-W. Wang, *The critical role of hot carrier cooling in optically excited structural transitions*, *npj Comput. Mater.* **7**, 117 (2021).
- [120] G. Kresse and J. Hafner, *Ab initio molecular dynamics for liquid metals*, *Phys. Rev. B* **47**, 558 (1993).
- [121] G. Kresse and D. Joubert, *From ultrasoft pseudopotentials to the projector augmented-wave method*, *Phys. Rev. B* **59**, 1758 (1999).
- [122] J.P. Perdew, K. Burke, and M. Ernzerhof, *Generalized gradient approximation made simple*, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [123] S. Grimme, S. Ehrlich, and L. Goerigk, *Effect of the damping function in dispersion corrected density functional theory*, *J. Comput. Chem.* **32**, 1456 (2011).
- [124] A. Togo, L. Chaput, T. Tadano, and I. Tanaka, *Implementation strategies in PHONOPY and PHONO3PY*, *J. Phys. Condens. Matter* **35**, 353001 (2023).
- [125] Z. Fan, W. Chen, V. Vierimaa, and A. Harju, *Efficient molecular dynamics simulations with many-body potentials on graphics processing units*, *Comput. Phys. Commun.* **218**, 10 (2017).
- [126] A. Van Der Lee and G. A. Wieggers, *Anharmonic thermal motion of Ag in AgCrSe₂: A high-temperature single-crystal X-ray diffraction study*, *J. Solid State Chem.* **82**, 216 (1989).
- [127] A.P. Thompson, H.M. Aktulga, R. Berger, D.S. Bolintineanu, W.M. Brown, P.S. Crozier, P.J. in 't Veld, A. Kohlmeyer, S.G. Moore, T.D. Nguyen, R. Shan, M.J. Stevens, J. Tranchida, C. Trott, and S.J. Plimpton, *LAMMPS—a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales*, *Comput. Phys. Commun.* **271**, 108171 (2022).
- [128] J. Madsen and T. Susi, *The ABTEM code: Transmission electron microscopy from first principles*, *Open Res. Eur.* **1**, 24 (2021).
- [129] I. Lobato and D. Van Dyck, *An accurate parameterization for scattering factors, electron densities and electrostatic potentials for neutral atoms that obey all physical constraints*, *Acta Crystallogr. Sect. A* **70**, 636 (2014).
- [130] B. D. Forbes, A. V. Martin, S. D. Findlay, A. J. D'Alfonso, and L. J. Allen, *Quantum mechanical model for phonon excitation in electron diffraction and imaging using a Born-Oppenheimer approximation*, *Phys. Rev. B* **82**, 104103 (2010).