Solid-state ion conductors (SSICs) are promising materials for replacing liquid ion conductors used in many important technological applications such as batteries, fuel cells, and supercapacitors, because they are typically non-flammable and could enable higher energy densities [1]. According to traditional ionic transport models (Fig. 1a), long-range ionic diffusion in SSICs involves thermally-activated site-to-site hopping of mobile ions in a host lattice of non-diffusing ions. Migration barriers are overcome when mobile ions obtain sufficient thermal energy. The hopping frequency of the mobile ion is estimated using a harmonic phonon description or included phenomenologically in traditional models [2-7]. Therefore, these models cannot capture the effects that arise when the mobile ion enters the saddle point region between local quasi-equilibrium geometries, which is an intrinsically anharmonic part of the potential energy surface (Fig. 1a) [2, 3, 5, 7]. It is in this region that vibrations of the mobile ion and host lattice may become coupled, changing the potential energy surface of the mobile ion, and potentially modifying significantly the migration barrier [2]. Accurately describing the atomic motions in SSICs therefore requires a departure from the harmonic phonon picture, the foundation of solid-state physics for explaining material properties at finite temperatures [2, 3, 5, 8, 9].

The importance of interactions between mobile ions and host lattice was discussed in recent computational and experimental work, indicating that the host lattice impacts ionic conductivities of SSICs in a way not yet captured by traditional theories [10-16]. Specifically, recent work has elucidated correlations between physical characteristics of the host lattice and ionic conductivity of SSICs e.g., with regards to its average vibrational frequencies, mechanical softness, polarizability, and coordination geometry [10-16]. However, major experimental and theoretical challenges have so far hindered direct observation and identification of anharmonic effects in the coupling of host lattice and mobile ions potentially present in SSICs. Since this coupling cannot be captured in harmonic approximations of ionic conductivity, sophisticated analyses of molecular dynamics (MD) computations are required to detect it [14, 15, 17]. Spectroscopic investigations of vibrational dynamics in SSICs must contend with the pronounced dynamic structural disorder that originates from hopping of mobile ions within a partially populated set of sites (Fig. 1b). In fast ion-conducting SSICs, this can result in the breakdown of phonon quasiparticles [9], and broad features are observed in the vibrational spectrum that are difficult to resolve and interpret because there is no analytical foundation for quantifying spectral properties of systems that show dynamically broken translational symmetry [9, 18-21]. Therefore, full interpretation of the vibrational spectrum of even α-AgI, the best-understood and longest-studied superionic SSIC, still remains unresolved, 40 years after first measurements were reported for this material [18-23]. Resolving these issues and providing a detailed account of vibrational coupling between mobile ion and host lattice is anticipated to provide major conceptual insights with regards to the role of significant anharmonicities in the ionic conductivity of SSICs.

In this letter, we demonstrate an approach to overcoming these challenges by combining cutting-edge THz frequency Raman polarization-orientation (PO) measurements and MD simulations. The approach is used to investigate the relationship between the dynamics of mobile ions and of the host lattice in the archetypal SSIC α-AgI (ionic conductivity of ∼1 S/cm at 443 K). We identify strongly anharmonic relaxational atomic motions in the iodine host lattice and establish that they are coupled...
FIG. 1. (a) Diagram of conventional ion transport mechanism and anharmonicity: a mobile ion (gray circle) hops (gray arrow) across barriers in the potential landscape due to the host lattice (blue circles) and surrounding mobile ions. (b) α-AgI crystal structure, with I atoms (purple) located at BCC positions and Ag atoms (dark grey) hopping (black dashed arrows) between empty tetrahedral sites (white).

As expected, all the Raman spectral features are found to exhibit clear periodicities in intensity as a function of orientation in both polarization configurations, which is very surprising since this establishes specific symmetries for these features and indicates clear structural order. This is in contrast to prior interpretations of the α-AgI Raman spectrum, which have primarily ascribed the spectrum to disorder-induced scattering or a liquid-like scattering response, both of which cannot show any periodicity with orientation (see Fig. S2 [34]) [20–23]. As such, our finding is striking since it signifies a high degree of order that must be reconciled with the high degree of dynamic structural disorder expected from the presence of highly mobile Ag⁺ ions.

The unique Raman intensity response in PO enabled us to discover the fundamental features of the α-AgI vibrational spectrum for the first time. To identify each feature, we individually fit each spectrum in the dataset (see SM for fit methodology [34]). Representative spectra and corresponding fits are shown in Fig. 2b, and the quantified PO Raman response of each feature is shown in Fig. 2c. The PO Raman response of α-AgI can be fully characterized by four spectral features with frequency and width that are consistent across all spectra in the dataset (Table S1 [34]), indicating that these features are the fundamental components of the spectrum. These features consist of one central component (fit by a Deybe relaxor) and three broad peaks (each fit with a damped Lorentz oscillator).

A fundamental tenet of solid-state physics is that the average crystal structure can be used to predict the number and symmetries of the normal modes of vibration [33]. However, the average Im3m space group of α-AgI under-predicts the number of Raman features we have observed and their symmetries because it cannot capture the lower symmetry real-time structure which Raman is sensitive to (Table S2, Table S3 [34]). In the other extreme, liquid-like or disorder-induced light scattering models, in which symmetry is completely lost, would predict no PO Raman dependence as can indeed be observed for liquids (Figure S2 [34]).

Instead, we find that a 'local tetrahedral oscillator' model of vibrations in α-AgI predicts the number of Raman features we have observed, their symmetry, and their PO response (Fig. 2c, see model details in SM, Table S3, and Figure S4 [34]). In our model, when an Ag⁺ ion hops to a tetrahedral site of the BCC lattice, a transient, orientationally-ordered, local AgI tetrahedral oscillator forms (Fig. 3a) whose symmetry is probed by our PO Raman measurements [38]. The critical innovation of our model is that the symmetry observed in the PO response is established locally through the AgI units, rather than through the long-range order of a phonon model of vibrations.

The most interesting feature identified from the PO Raman response is the central component (Fig. 2), which is a categorical sign of anharmonic motion. Central components are a manifestation of relaxational motion (i.e.
motion that has no restoring force) in the frequency domain, characterized by a peak centered at 0 cm$^{-1}$ with a width that is determined by the characteristic relaxation time. In ion conductors, diffusive motion and the polarizability changes due to hopping of ions from one site to another are expected to give rise to a finite zero-frequency value in the vibrational density of states and a central peak in light scattering, respectively [39–41]. Theoretical work has predicted that the polarizability changes induced by ion hopping in $\alpha$-AgI are expected to generate a central peak of width $<5$ cm$^{-1}$ corresponding to the residence time of the ion, and prior Raman studies have indeed observed such a feature [5, 31, 39, 40, 42]. While our instrument prevented observation of the 5 cm$^{-1}$ central peak, our measurements clearly exhibit a second, wider ($\sim25$ cm$^{-1}$) central component (Table S1 [34]), that indicates a different, faster relaxation process. While this component was previously identified, its physical origin and significance were not understood [31].

Our quantification of the PO response of the central component (Fig. 2c) reveals that it is actually composed of two elements, one that is orientation-dependent, and the other being an orientation-independent background (Figure S5, Table S3 [34]). These components correspond to relaxational motions of differing physical origin. First, in regards to the polarization-independent feature, it appears as a background in both the parallel and perpendicular configurations that grows in prominence as temperature increases, but remains fully reversible and does not indicate, for instance, sample degradation effects. The PO response of this element is distinctly ‘liquid-like’, being depolarized and without orientation dependence (compare to central component of Figure S2 [34]), a behavior not previously observed in a solid, to our knowledge. The increasing dominance of this element with increasing temperature must indicate a continuous change toward a more fluid-like condition throughout the stability region of the $\alpha$-phase.

Second, the polarization-dependent element of the central component is identified by its symmetry as one of the fundamental vibrational modes of the tetrahedral oscillator model (Figure S5, Table S3 [34]). In a fully harmonic system, this element would present as a normal mode of finite frequency. However, our PO Raman measurements have clearly established that the atomic motions involved are relaxational in nature, and this must be reconciled with its identification as one of the fundamental modes of the tetrahedral oscillator. This can be explained by hypothesizing that this element arises from overdamping of the vibrational motion through direct coupling to Ag$^+$ hopping. We further hypothesize that the atomic motion of the mode involves the relaxation of iodine in response to Ag$^+$ hopping.

Stimulated by these interesting observations, we in-
FIG. 3. (a) Diagram of AgI$_4$ tetrahedral site of the BCC lattice, with the I-I-I bond angle $\theta$ analyzed in MD simulations indicated. Lines of the same texture have the same length. (b) Time series of $\theta$ for $\alpha$-AgI MD simulation at 500 K with all atomic motions allowed and (c) when Ag is fixed to zero velocity at tetrahedral sites. (d) Mean square displacement as a function of time for Ag, for the cases: all atomic motions allowed (black line), I fixed at BCC lattice positions (yellow), and I fixed in an instantaneous thermally populated distribution of positions (red), where ten different iodine distributions are shown.

Investigate via MD the relationship between iodine relaxational motion and Ag diffusion. Our force-field MD simulations at 500 K (see SM [34]) are qualitatively accurate in capturing the Ag$^+$ diffusion coefficient and vibrational density of states (Figure S6 [34]) [20, 43]. Our approach is to temporally and spatially resolve atomic motions in the AgI$_4$ tetrahedra of the local tetrahedral oscillator model. Specifically, we investigate dynamically changing tetrahedral geometries by computing trajectories of the I-I-I bond angle $\theta$ (Fig. 3a) in one selected AgI$_4$ tetrahedron. Any deviations of this bond angle from its expectation value, i.e. the 70.5$^\circ$ angle of the BCC lattice (see Fig. 1a), indicate distortions to the shape of the tetrahedron. Fig. 3b reports an MD trajectory of $\theta$, which shows very large angular fluctuations that seem to appear on short time scales. As discussed above, the most interesting aspect of the local tetrahedral oscillator model was the low-frequency relaxational motion giving rise to the central component in the PO Raman response. To probe the atomic motions associated with it, we obtain trajectories of $\theta$ retaining only the low frequency ($<5$ cm$^{-1}$) dynamics (see SM for further details [34]). This frequency regime exclusively contains relaxational components that are not present in purely harmonic systems. Fig. 3b demonstrates that $\theta$ undergoes fluctuations of up to $10^5$ from its expectation value in the low-frequency regime, over a period of up to 10 ps, indicating large, long-lived rearrangements of iodine tetrahedra that arise from anharmonic relaxation events.

A series of MD-enabled gedankenexperiments establishes the coupling between the iodine host lattice and Ag$^+$ motion. First, stipulating Ag to be fixed with zero velocity at tetrahedral sites, we find that the large amplitude oscillations of $\theta$ at low frequency disappear (Fig. 3c). This indicates that Ag motion (either vibrational and/or hopping) is causally connected with relaxational motion of the I lattice. Second, reversing the roles, we find that freezing I motion impedes Ag diffusion, as evidenced by the mean squared displacement of Ag vs. time (Fig. 3d), the slope of which is proportional to the diffusion constant. When I atoms are frozen at BCC lattice sites, Ag diffusion is completely stopped, indicating that I tetrahedral faces must expand to enable Ag hopping, consistent with prior findings [2, 3, 44–46]. When the MD simulation is first allowed to thermally equilibrate with full motion, and then I is frozen at instantaneous configurations obtained as snapshots of the MD simulations, Ag diffusion is hindered by a factor of $\sim$2 compared to the diffusion under full motion. These findings establish the strong interconnections between relaxational I host lattice motions and the dynamics of Ag.

Several other highly-conductive SSICs also show signs of a broad central component in their Raman response [19, 31, 47]. We suggest that a broad central component and corresponding relaxational motion of the host sublattice are indicators of a good ion conductor. Our indicator brings a physical understanding of microscopic dynamics to ionic conductor design that is not available in current rules of thumb [48, 49]. Moreover, this indicator explicitly includes information about the nature of the lattice dynamics, and specifically points out the need for anharmonic motion of the host lattice.

In conclusion, using PO Raman measurements and MD calculations, we developed a new understanding of the vibrational dynamics of $\alpha$-AgI. We introduced the local tetrahedral oscillator model in which the $\alpha$-AgI vibrational dynamics are localized to an AgI$_4$ tetrahedral configuration. The success of our model demonstrates the value of a local picture of vibrational dynamics in materials with dynamic structural disorder. Within that picture we have identified the presence of anharmonic relaxational motion in our Raman measurements and the
MD simulations, which demonstrated an anharmonic relaxational component in the iodine host lattice. Our MD computations indicate that iodine relaxation is causally connected to Ag motion, and vice versa Ag diffusion is strongly impacted by iodine vibrational motion. These results show that anharmonic motion of the host lattice is a critical component of the ion transport process in α-AgI. We hope our findings revitalize the efforts to understand the deep connection between vibrational dynamics and ionic conductivity, and thereby may lead to new SSIC design rules.

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See Supplemental Material [URL inserted by publisher] for supporting experimental and computational details.

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Peak 3 is not included in Fig. 2c as its intensity was fixed to a constant value in parallel and zero in perpendicular in the fits due to its symmetry – see Fig. S3 and fit methodology in SM.

'Orientational-order' denotes the limited tetrahedral orientations allowed by the BCC lattice. Related tetrahedral configurations, such as Ag₄I tetrahedra, could also explain our observations.

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Supplemental Materials: Anharmonic Host Lattice Dynamics Enable Fast Ion Conduction in Superionic AgI

Contents

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I. SUPPLEMENTARY FIGURES AND TABLES

FIG. S1. PO Raman measurements at temperatures of 443, 583, and 723 K. The top row gives measurements in the parallel (∥) polarization configuration, bottom row in perpendicular (⊥).

FIG. S2. PO Raman measurement of the tetrahedral (point group Td) molecule CCl₄, a liquid at room temperature. There is no dependence of any feature on orientation angle due to the random orientation of molecules. However, there are differences between the parallel and perpendicular analyzer configurations due to the symmetry of the internal molecular modes. There is a polarization-independent central peak at 0 cm⁻¹ that indicates stochastic relaxation processes with no order.
FIG. S3. Orientation dependence of the second shoulder of the Raman spectrum. (a) – (b) Intensity maps of the parallel (||) and perpendicular (⊥) polarization configurations showing the location of the linecut at 90 cm$^{-1}$, centered on the second shoulder in the Raman spectrum. (c) Linecuts of the || and ⊥ PO Raman data at 90 cm$^{-1}$, as a function of polarizer angle. This plot shows that this feature has a polarization dependence, that this dependence is different for parallel and perpendicular, and that there is a constant component in the || configuration that is not present in the ⊥ (blue dashed line). The constant component is modeled by Peak 3, and the polarization dependent component is captured by Peak 2 in the dynamic structural model in the main text. Both Peak 2 and Peak 3 have symmetries that are irreducible representations of the $D_{2d}$ point group.

TABLE S1. Fit position and width parameters from fits to the PO Raman data sets for each temperature measured. These parameters were held constant for all orientation angles and both polarization configurations. The intensity of Peak 3 was held constant in the parallel configuration and had intensity fixed to zero in perpendicular.

| Temperature (K) | Central Component Width (cm$^{-1}$) | Peak 1 Width (cm$^{-1}$) | Position (cm$^{-1}$) | Peak 2 Width (cm$^{-1}$) | Position (cm$^{-1}$) | Peak 3 Width (cm$^{-1}$) | Position (cm$^{-1}$) |
|-----------------|--------------------------------------|--------------------------|----------------------|--------------------------|----------------------|--------------------------|----------------------|
| 443             | 23.0                                 | 37.0                     | 101.3                | 93.3                     | 106.4                | 61.4                     |
| 583             | 24.3                                 | 37.7                     | 101.3                | 93.3                     | 108.4                | 64.1                     |
| 723             | 26.5                                 | 37.7                     | 101.3                | 93.3                     | 109.8                | 67.5                     |

TABLE S2. Irreducible representation of the optical vibrational modes for each of the models tested. Row 1 gives the model type and the point group used to generate the irreducible representation. For the space group model, both the Hermann-Mauguin and the Mulliken notation are given, to emphasize that the point group is $O_h$. The irreducible representation of each model is given in row 2. Row 3 shows only the Raman active modes. Row 4 gives the number of Raman active modes. The total number of features that need to be explained is 4. Only the lower symmetry tetrahedral models can account for all features, as shown in Table S3 below. Irreducible representations were determined employing the works of Rousseau et al. (crystal) and Nakamoto (molecules) [S1, S2].

| Model | Irreducible Representation of Optical Modes | AgI$_4$ $D_{2d}$ Tetrahedral Oscillator | AgI$_4$ $T_d$ Tetrahedral Oscillator |
|-------|--------------------------------------------|-----------------------------------------|-------------------------------------|
| Im$ar{3}$m ($O_h$) Space Group | $A_{2g} + E_g + T_{2u} + T_{2g} + 2T_{1u} + T_{1g}$ | $2A_1 + B_1 + 2B_2 + 2E$ | $A_1 + E + 2T_2$ |
| Number of Raman Active Modes | $E_g + T_{2g}$ | $2A_1 + B_1 + 2B_2 + 2E$ | $A_1 + E + 2T_2$ |
| 2 | 7 | 4 |
TABLE S3. Symmetry assignment of each fit component for each model tested. For the space group model, both the Hermann-Mauguin and the Mulliken notation are given, to emphasize that the point group is $O_h$. The symbols for the tetrahedral oscillator models are the Mulliken symbols labeling the irreducible representations of each point group. The peak frequency of each feature is provided.

*The number of Raman active modes in the $O_9^h$ model is insufficient to account for all features.
†The central component has two elements. The symmetry assignment here is only for the polarization-dependent element. The liquid-like background element has no symmetry to it.

| Fit Component | $Im3m$ ($O_9^h$) Space Group* | AgI$_4$ $D_{2d}$ Tetrahedral Oscillator | AgI$_4$ $T_d$ Tetrahedral Oscillator | Frequency (cm$^{-1}$) |
|---------------|-------------------------------|----------------------------------------|-----------------------------------|-----------------|
| Central Component† | $E$ | $A_1 + B_1$ | $E$ | 0 |
| Peak 1 | $T_2$ | $B_2 + E$ | $T_2$ | 37.7 |
| Peak 2 | — | $B_2 + E$ | $T_2$ | 101.3 |
| Peak 3 | — | $A_1$ | $A_1$ | 108 |
FIG. S4. Expected orientation dependence of the Raman mode symmetries in each of the models tested, for light incident normal to the (110) plane of the BCC unit cell. The details of these calculations are given in the methods section and the discussion of the local tetrahedral oscillator model below. Both the parallel (∥, blue) and perpendicular (⊥, orange) orientation dependences are given. Each plot is titled with the Mulliken symbol for the irreducible representation of the mode. First column: polarization dependence expected for the modes of the static, time-average model, namely the space group $Im3m (O^9_h)$. Second and third columns: polarization dependence expected for the modes of the local tetrahedral oscillator model. The second column shows the $D_{2d}$ model employed in the main text. While modes with symmetry $B_1$, $B_2$, and $E$ contain only one element in the Raman tensor, the $A_1$ mode contains two elements in its Raman tensor. Therefore, we have shown several possible ratios of the two tensor elements ($a:b$): dashed line $a = b$; solid line $b = 0.2a$; dotted line $b = 2a$. The third column shows the alternative $T_d$ model. The $T_d$ and $D_{2d}$ models are both tetrahedral models, where $D_{2d}$ is a lower-symmetry subgroup of the perfect tetrahedral point group $T_d$. Because of its lower symmetry, the modes of $D_{2d}$ have broken degeneracy. The correspondence between $D_{2d}$ and $T_d$ modes is shown by the arrows between columns two and three and in the table at the bottom of column three.
FIG. S5. Comparison of normalizations of the fitted intensity coefficients of the central component for all measured temperatures. (a) shows the intensity coefficients only normalized by their maximum for the parallel and perpendicular polarization configurations. (b) shows the intensity coefficients after baselining to zero and then normalizing. The baseline and normalize procedure demonstrates that the changes observed with temperature arise from an increasing orientation-independent background, while the actual orientation response does not change, and matches that predicted by our local tetrahedral oscillator model (gray dotted line).

FIG. S6. Velocity autocorrelation function (VACF) for the MD simulation of α-AgI at 500K. The total spectrum is divided into contributions from Ag and I. The total VACF has been multiplied by a factor of 2 for clear visibility. The intensity at 0 cm\(^{-1}\) (marked with a blue X) can be used to determine the diffusion coefficient, which provides a value of 1.8 \times 10^{-5} \text{ cm}^2/\text{s}, in close agreement with experimental data.
II. METHODS

Preparation of $\beta$-AgI Single Crystals

Crystals were prepared according to a published procedure [S3]. The following was performed under ambient atmosphere, in regular lab lighting conditions: 57 wt.% HI (unstabilized, 99.99%, Sigma Aldrich) was diluted with an equal volume of deionized H$_2$O. 2.5g of AgI powder (99.9%, Alfa Aesar) were dissolved in 20 mL of the diluted HI by gentle heating (0.125 g/mL). Glass vials containing 5 mL of solution were prepared, and 2.5 mL of methanol was added to each. The vials were kept with caps loosely placed on top. The vials were kept in an undisturbed area, in the dark for approx. 1 month while crystals precipitated. Upon removal, the crystals were rinsed with methanol and then soaked in methanol for several days to remove HI inclusions. Only crystals showing the expected hexagonal pyramid habit were used for measurement. The pyramid basal plane was determined to be (002) by x-ray diffraction pole figures, as expected from literature [S3].

Preparation of $\alpha$-AgI Crystals from $\beta$-AgI Single Crystals

$\alpha$-AgI crystals were prepared from $\beta$-AgI single crystals according to the procedure of Mills et al. [S4]. A hexagonal pyramid-shaped $\beta$-AgI single crystal was cleaved with a scalpel parallel to the base to form a flat clean surface. $\beta$-AgI readily cleaves along this plane (the (002) plane). The cleaved crystal was dropped onto a heated (523K) microscope stage (Linkam THMS600) with its base parallel to the stage. It is critical to drop the crystal onto its base, and not any other face, and to keep the crystal above 423K at all times. This procedure produces crystals oriented with the (110) plane parallel to the microscope stage, i.e. (002) → (110), as verified below (see section on self-consistent orientation determination) and expected from literature [S4].

Temperature-Dependent Polarization-Orientation (PO) Raman Measurement

PO employs polarized light to probe the components of the Raman tensor in a single crystal, providing identification of mode symmetries [S5]. The measurements were performed on a Zeiss Axio Vario Scope.AI microscope with a 20x NIR objective in backscatter configuration with the excitation source impinging perpendicular to the (110) plane of $\alpha$-AgI (as verified self-consistently from the PO measurements, and expected from literature, see below) [S4]. The sample was enclosed in a Linkam THMS 600 microscope heating stage under N2 purge. The sample temperature was controlled via the Linkam. We note that care must be taken with PO Raman measurements of $\alpha$-AgI at high temperatures. We observed microscopic morphological changes in the sample over time at 723K that correlated to a drop in Raman intensity, without lineshape change (Figure S7), followed by stabilization. PO Raman could only be performed after this process completed. This may explain the drop in Raman intensity with increasing temperature reported in previous literature [S6].

The Raman crystallography measurement setup is shown in Figure S8. A 1064 nm laser (Coherent Mephisto) was used for the Raman excitation. This proved critical as shorter wavelength lasers caused a photographic effect during measurement, ruining the long-time scale measurements required for Raman crystallography. The laser was filtered for any amplified spontaneous emission (ASE) using volume holographic ASE filters (Ondax). The beam shape was optimized by a pinhole spatial filter. The laser was polarization filtered by a calcite polarizer (Thorlabs), and the polarization was rotated with respect to the sample with a monochromatic half-wave plate (Thorlabs). The polarized beam is directed into the microscope and to the sample via a 90/10 volume holographic beam splitter (Ondax). A 20x NIR objective (Zeiss) was used to focus the laser onto the sample. An excitation power of 5 mW was used, measured just before the objective. The backscattered Raman signal and Rayleigh reflection are collected by the objective and passed back to the beam splitter, where 90% of the Rayleigh is eliminated and the Raman signal is transmitted. An achromatic half-wave plate is used to rotate the signal polarization back to the polarization of the laser before the monochromatic half-wave plate (parallel configuration) or perpendicular to it (perpendicular configuration). Another polarizer (called the analyzer) filters the polarization of the signal. The remaining Rayleigh component of the signal is then attenuated by two volume holographic notch filters (Ondax). The signal is then directed to a one meter spectrometer (Horiba) and detected by a 1D InGaAs detector array (Horiba). Due to fixed-pattern dark noise in the InGaAs detector, a dark spectrum is subtracted from each spectrum. We found the system could achieve an extinction ratio ($I_\parallel/I_\perp$) between 0.001 and 0.01 depending on the orientation of the 1st 1/2-λ plate.

To accumulate a Raman crystallography dataset, we rotated the polarization orientation of the incident laser beam (of polarization $\vec{e}_i$, see Figure S8) stepwise from $\theta = 0 - 360^\circ$ in a plane parallel to the $\alpha$-AgI (110) crystal face. The backscattered Raman signal is then filtered for light polarized parallel ($\vec{e}_{s,\parallel}$) and perpendicular ($\vec{e}_{s,\perp}$) to the incident light. At each $\theta$ step, a Raman spectrum is collected for both $\vec{e}_{s,\parallel}$ and $\vec{e}_{s,\perp}$ analyzer configurations.

Fitting of PO Raman data

We fit each spectrum in the PO Raman dataset with a sum of damped Lorentz oscillators and a single Debye relaxor. The Debye relaxor is used to fit the central component, according to previous treatments [S7–S9]. A damped Lorentz oscillator was required to capture the extremely broad, low frequency features found in the spectra. The
FIG. S7. Time dependence of α-AgI single crystal morphology and Raman spectrum at 723 K. Top panel: The Raman intensity steadily drops over time, and then stabilizes. This process takes 6-8 hours. The microscope images show the crystal morphology changes that occur during annealing. The Raman intensity maps show the change in Raman intensity with time, measured in a single polarization/orientation configuration. The raw data shows the drop and subsequent stabilization of intensity. The normalized data demonstrate that the lineshape does not change during this intensity drop. We hypothesize that the drop in Raman intensity is due to morphological changes at the sample surface. After stabilization, the Raman crystallography measurement can be taken.

sum of oscillators was multiplied by the Bose-Einstein population factor \( c_{BE}(\nu, T) \) to account for the temperature dependence of the phonon populations. The fitted equation is:

\[
I(\nu, T) = c_{BE}(\nu, T) \left( \frac{c_0 \gamma_0 \nu}{\nu^2 + \gamma_0^2} + \sum_{i=1}^{n} \frac{c_i \gamma_i^3 \nu}{\nu^2 \gamma_i^2 + (\nu^2 - \nu_i^2)^2} \right)
\]

(S1)

where \( I \) is the Raman intensity, \( \nu \) is the Raman shift, the \( \nu_i \) are the resonance energies of the damped Lorentz oscillators, \( \gamma_0 \) and \( \gamma_i \) are the damping coefficients of the Debye relaxor and Lorentz oscillators, \( c_0 \) and \( c_i \) are the intensity coefficients of the Debye relaxor and Lorentz oscillators, and \( T \) is the temperature. Due to instrumental artifacts affecting the Stokes/Anti-Stokes ratio, we fit only the Stokes data with the temperature fixed to the sample temperature.

Because all spectra in a Raman crystallography data set are taken under the same conditions of temperature, pressure, laser power, etc., we assume that all spectra reflect the same fundamental set of features whose widths and positions are fixed with respect to polarization filtering and polarization orientation. We used the symmetry-filtering effects of the polarized light to obtain accurate information about particular features by performing several pre-fits.
FIG. S8. Schematic for PO Raman measurement in backscatter configuration. 1064 nm laser light is polarized and directed at normal incidence ($\vec{k}_i$) to the (110) plane of an $\alpha$-AgI crystal, with its electric field polarized with an angle $\theta$ relative to the x-axis ($\vec{e}_i$). The x-y plane is equivalent to the (110) plane. Backscattered light ($\vec{k}_{s,\parallel}, \vec{k}_{s,\perp}$) is polarization-filtered by another polarizer (analyzer) for polarizations parallel ($\vec{e}_{s,\parallel}$) and perpendicular ($\vec{e}_{s,\perp}$) to the incident polarization, $\vec{e}_i$. During a PO Raman experiment, the polarization angle $\theta$ of $\vec{e}_i$ is rotated stepwise through 360° and spectra are recorded in the parallel (∥) and perpendicular (⊥) analyzer configurations for each step.

As mentioned in the main text, there are three major features clearly visible in the spectra: a central component, a shoulder near 40 cm$^{-1}$ (Peak 1), and a shoulder near 100 cm$^{-1}$ (Peak 3). We determined that the shoulder near 100 cm$^{-1}$ is actually composed of two peaks (Peaks 2 and 3, see Figure S3) during our fitting procedure. For all temperatures, in the parallel configuration at angles of 120° and 300°, the shoulder at 40 cm$^{-1}$ is completely absent, and the shoulder near 100 cm$^{-1}$ is minimized (see Figure Figure S3). These angles allowed the determination of the width of the central component and width and position of Peak 3. A major component of the feature at 100 cm$^{-1}$ is clearly constant in parallel and not present in perpendicular, while a component of lower intensity shows clear periodicity (Figure S3). By performing several pre-fits on the parallel and perpendicular data with the widths and positions of the central component and Peak 3 fixed, we iteratively determined the best widths and positions of the shoulder at 40 cm$^{-1}$ (Peak 1) and the second, orientation-dependent component near 100 cm$^{-1}$ (Peak 2). We also determined that Peak 2 has a different position and width than Peak 3 (Table S1), and that Peak 3 has nearly constant intensity in the parallel polarization configuration and nearly zero in perpendicular. Because Peaks 1 and 2 could not be isolated by polarization filtering, it was more challenging to determine their exact positions and widths, and we place less confidence in their exact determination. However, the polarization/orientation dependencies and symmetries reported in the main text are obtained regardless of the exact positions and widths of these modes, within a reasonable window.

In the final step, we fixed all widths and positions (see Table S1) and fixed the intensity of peak 3 to a constant value in parallel and zero in perpendicular. We then fit the spectra iteratively, beginning with $0^\circ$, and using the intensity parameters from the fit of the preceding spectrum as an initial guess for the current spectrum. The parallel and perpendicular data sets are fit separately, but with the same set of widths and positions. We extracted from these fits the intensity coefficients of each component as a function of polarization angle as reported in Figure 2c of the main text.

Theory of PO Raman Symmetry Determination

The intensity of a Raman mode $i$ ($S_i$) can vary with polarization orientation angle $\theta$ (see Figure S8 above) as well as with the polarization configuration (∥ or ⊥) according to the Raman tensor ($R_{i,j}$) of that mode. The Raman tensors
TABLE S4. Raman tensors for each of the point groups used for the quantitative modeling of the Raman spectra presented in Figure S4 and Figure 2 of the main text [S10]. The $O_h$ point group applies to the space group model, and the $T_d$ and $D_{2d}$ point groups apply to the local tetrahedral oscillator model, discussed below.

| Point Group | Raman Tensors for Each Irreducible Representation ($R_{i,j}$) | $A_{1g}/A_1$ | $E_g/E$ | $T_{2g}/T_2$ |
|-------------|-------------------------------------------------------------|---------------|----------|---------------|
| $O_h/T_d$   |                                                             | $a 0 0$       | $b 0 0$  | $0 d 0$       |
| Irreducible Representation | $0 a 0$                                                                 | $0 b 0$       | $0 \sqrt{3b} 0$ | $0 d 0$       |
|             | $0 0 a$                                                                 | $0 0 \sqrt{3b}$ | $0 0 d$       | $0 0 0$       |
|             | $0 0 -2b$                                                                | $0 0 0$       | $0 0 d$       | $0 0 0$       |

for all point groups employed in our modeling of the Raman are given in Table S4 [S10]. For the || and ⊥ polarization configurations, respectively, the Raman intensity will be proportional to:

$$S_{i,||} = \sum_j \left( \vec{e}_{s,||} \cdot R_{i,j} \cdot \vec{e}_i \right)^2$$

$$S_{i,\perp} = \sum_j \left( \vec{e}_{s,\perp} \cdot R_{i,j} \cdot \vec{e}_i \right)^2$$

where the sum over $j$ represents the degeneracy of the mode, and $\vec{e}_i$, $\vec{e}_{s,||}$, and $\vec{e}_{s,\perp}$ are the incident and scattered light (selected for parallel and perpendicular polarization configurations), respectively, as indicated in Figure S8 [S5].

The symmetry of a particular mode can be identified from the periodicities in its intensity response ($S_i$), making Raman crystallography a powerful tool in the identification of modes. Additionally, the crystal orientation can be determined from Raman crystallography. Two other features of $S_{i,||}(\theta)$ and $S_{i,\perp}(\theta)$ can serve to confirm mode assignment. First, all modes share the same phase in $\theta$, meaning if a particular mode requires a phase shift $\Delta$ (i.e. $S_{i,||}(\theta + \Delta)$, $S_{i,\perp}(\theta + \Delta)$) compared to the other modes to fit the data, then the mode has been incorrectly identified. Second, the ratio $S_{i,\perp}(\theta)/S_{i,||}(\theta)$ must also agree with the theoretical calculation, meaning the intensity in the perpendicular must be at the proper ratio compared to the parallel. This serves as a check on both mode identification and the quality of the optical alignment. Both the phase and intensity checks have been confirmed for the mode assignment presented in this manuscript.

**Self-Consistent Determination of α-AgI (110) Orientation**

Using equation S2 and equation S3, the configuration of Figure S8, and the $T_d$ point group from the model discussed in the main text and in detail below, we have calculated the expected intensity response as a function of polarization angle for the three possible Raman mode symmetries for the three possible high symmetry orientations of the crystal, namely the {100}, {110}, and {111} classes of planes. We have used here the $T_d$ point group rather than $D_{2d}$ for ease of calculation and demonstration, but the same results apply to $D_{2d}$. The results are shown in Figure S9. In all cases, the $A_1$ symmetry shows the same response. The $E$ and $T_2$ symmetries show a differing response depending on the orientation. We consider only the $E$ and $T_2$ modes. The {111} planes show no polarization dependence for these modes. The {100} planes show only 90° periodicity. The {110} planes show a combination of 180° and 90° periodicity in the parallel configuration, while the perpendicular configuration only shows 90° periodicity. Only the {110} planes resemble the experimental findings in the main text, and in fact provide the best choice of facet to explain the experimental results.

**Molecular Dynamics Simulations**

Molecular dynamics (MD) simulations were performed using the LAMMPS package [S11]. The force field for AgI used parameters given in refs. [S12, S13], and as a timestep in solving the classical equations of motions we applied 1 fs. A canonical (NVT) ensemble with 128 atoms in a unit cell of volume of ~4736 Å³ was simulated at 500K: the system was first equilibrated for 10ps, followed by a 500 ps production run during which snapshots were taken each 10 fs. Data from the first 100 ps of the production run are shown in Figure 3 of the main text. The mean squared displacement, $MSD$, was calculated as implemented in the LAMMPS package. From it the diffusion constant can be obtained via: $MSD(t) = 6Dt$. To calculate the tetrahedral angles ($\Theta_i$), first the I atoms forming one AgI₄ tetrahedron were identified. Then, we calculated atomic distances $\vec{d}_{ij}(t) = \vec{R}_i(t) - \vec{R}_j(t)$ from the trajectories $\vec{R}_i(t)$, where the
FIG. S9. Intensity response as a function of polarization orientation for the three possible Raman mode symmetries of the $T_d$ point group, for the three high symmetry directions of the cubic unit cell. The parallel (∥, blue) and perpendicular (⊥, yellow) responses are plotted together.

indices $i$ and $j$ address the I atoms of the tetrahedron. Finally, from the atomic distances, the angles have been calculated as:

$$\Theta_i = \arccos \left( \frac{\vec{d}_{ij} \cdot \vec{d}_{ik}}{|\vec{d}_{ij}| |\vec{d}_{ik}|} \right) \quad (S4)$$

where $i$, $j$ and $k$ address I atoms of the tetrahedron. From the 12 possible angles, we selected one representative case and showed it in the main text, since the qualitative behavior of all angles was similar (see Figure S10).

For the gedanken-experiments discussed in the main text, either the I or Ag atoms were frozen by setting their velocities and forces acting upon them to zero. After this freezing, the system was equilibrated again for 10 ps. The thermostat for the frozen systems was set such that the temperature associated with the available degrees of freedom was set to 500 K. For the cases in which Ag atoms were selected from MD snapshots, 10 instantaneous Ag configurations, separated by 1 ps along the trajectory, were chosen from the MD run.

In our analysis, we have Fourier-filtered the nuclear trajectories according to

$$R_{filtered}(t) = F^{-1} [\Theta(\omega) \Theta(\omega_{max} - \omega) F[R(t)]] \quad (S5)$$

where $F$ denotes the Fourier transform and $\Theta$ the Heaviside step function. The upper limit in the frequency, $\omega_{max}$, was set to 4 cm$^{-1}$.

The frequency dependent velocity autocorrelation function (see Figure S6), $VACF(\omega)$, was calculated as:

$$VACF(\omega) = F [\langle \nu(\tau + t) \cdot \nu(\tau) \rangle] \quad (S6)$$
FIG. S10. Note: two page figure. All 12 I-I-I tetrahedral angles for the selected tetrahedron analyzed in the molecular dynamics simulation. Left column: Full Ag motion. Right column: frozen Ag simulation.
where \( \langle \ldots \rangle \) denotes the average over atoms and initial time, \( \tau \). From this, the diffusion constant, \( D \), can be determined as:

\[
D = \frac{VACF(\omega = 0)}{6} \tag{S7}
\]

The thusly obtained value for \( D \) was found to be \( 1.8 \times 10^{-5} \text{ cm}^2/\text{s} \) in good agreement with our data in Figure S6.

### III. THE ‘LOCAL TETRAHEDRAL OSCILLATOR’ MODEL

Our model is motivated by an analysis of whether a phonon picture of vibrations can extend to the vibrations of mobile Ag in \( \alpha \)-AgI. To propagate a phonon in this system, a stable ordered state of atoms is required, and a correlation length for the phonon is established by the residence time of Ag (\( \tau \approx 2 - 3 \text{ ps} \)) [S14–S17]. The decay time for Ag ordering at the unit cell level, assuming four Ag atoms in the unit cell that hop independently, is \( \tau \approx 500 \text{ fs} \). Ordering beyond the unit cell has an even shorter decay time. While correlated Ag motion may increase this value somewhat, it is clear from this estimate that crystallographic order does not exist in this material on the time scales required for substantial phonon propagation. A phonon-like picture of vibrations is therefore unlikely to be useful, and a local view is more appropriate.

Considering the above, we propose the vibrational dynamics to be localized to a sub-unit cell structure. As the Ag are tetrahedrally coordinated, it is natural to consider a tetrahedral model for the vibrational dynamics. As stated in the main text, we propose the fundamental unit of vibration is the orientationally ordered AgI tetrahedron. When Ag\(^+\) hops, one unit is lost followed by the formation of a new unit at the new site. We assume these tetrahedra vibrate independently, being localized by the strong dynamic structural disorder. A similar tetrahedral model was proposed to explain the Raman spectrum of RbAg\(_4\)I\(_5\), but the large number of tetrahedral orientations prevented a full assignment of mode symmetries [S18]. We now derive the Raman response presented in Figure 2c of the main text, Table S2, Table S3, and Figure S4 from this conceptual model.

In our local tetrahedral oscillator model, \( \alpha \)-AgI does not possess a space group because of the lack of translational symmetry of Ag discussed above. However, the symmetries observed in optical vibrations depend only on the point group, which does not include translational symmetries. Only a preservation of orientational symmetry is required to detect point group symmetries in our PO measurement, and this is preserved by the iodine sublattice. Therefore, we employ a point group model for the Raman mode symmetries. Tetrahedral configurations in a BCC lattice have \( D_{2d} \) point group symmetry. This symmetry is not cubic and is the point group for certain tetragonal space groups. The tetrahedron is distorted from the ideal, isotropic \( T_d \) tetrahedral point group. We have confirmed from our MD simulations (Fig. 3b in the main text) that the time-average structure retains the \( D_{2d} \) symmetry and we therefore employ this point group in our model. We note that a perfect tetrahedral \( T_d \) point group fits the data equally well (Figure S4), but we did not detect a structure of this symmetry within the MD simulations.

To accommodate the tetragonal \( D_{2d} \) symmetry to the cubic BCC structure, we first calculate the PO response for the \( D_{2d} \) point group using the Raman tensors for each of the irreducible representations (Table S4) [S10], as presented in Equations S2 and S3, for each of the possible orientations of the tetrahedron in the BCC structure. Symmetry considerations reduce the number of required calculations: there are only 3 inequivalent orientations within the BCC structure, as shown in Figure S11. We then sum the response over all orientations in the BCC unit cell, with equal weight on each orientation. The resulting response is:

\[
S^{D_{2d}}_{k||} = \sum_{k} \sum_{j} \left( \vec{e}_{s,||} \cdot \Phi_{k}^{T} \cdot R_{i,j} \cdot \Phi_{k} \cdot \vec{e}_{i} \right)^{2} \tag{S8}
\]

\[
S^{D_{2d}}_{k\perp} = \sum_{k} \sum_{j} \left( \vec{e}_{s,\perp} \cdot \Phi_{k}^{T} \cdot R_{i,j} \cdot \Phi_{k} \cdot \vec{e}_{i} \right)^{2} \tag{S9}
\]

where \( R_{i,j} \) is the Raman tensor (given in Table S4) of the \( j \)th degenerate component of the mode \( i \) in Equations S2 and S3 above, \( k = 1 - 3 \) is an index representing the 3 inequivalent orientations, and \( \Phi_{k} \) is a rotation matrix that rotates \( R_{i,j} \) to the \( k \)th inequivalent orientation. The \( S^{D_{2d}}_{k} \) were calculated for the experimental setup shown in Figure S8, with \( \vec{e}_{i} \), \( \vec{e}_{s,||} \), and \( \vec{e}_{s,\perp} \) all rotating in the \((110)\) plane of the BCC unit cell. The principal axis of the \( D_{2d} \) tetrahedron aligns with the BCC c-axis in the unrotated configuration, while the remaining axes align with the a- and b- axes in the conventional Raman tensor. The results are presented in Figure S4.

We performed similar calculations for the isotropic \( T_d \) point group. By comparing the polarization dependence of the \( D_{2d} \) and \( T_d \) models in Figure S4, it can be seen that the averaging process generates a polarization dependence that is very similar to \( T_d \) so that modes that had distinguishable symmetries no longer do (such as \( B_2 \) and \( E \)). These
FIG. S11. Inequivalent tetrahedral orientations in the BCC unit cell. Each triangle on the face of the cube represents a $D_{2d}$ tetrahedral site. There are 24 in total within the BCC unit cell. There are only 3 inequivalent sets when considering the Raman response. These three sets are colored with different colors (orange, green, and blue) on the surface of the cube. Each type appears with equal frequency. The opposite (non-visible) sides of the cube have the same color pattern as their corresponding visible side.

modes, while having the same effective symmetry, are still expected to be non-degenerate and should have different energies. However, we did not detect this in our measurements, and this lead us to the assignment in Table S3 of two non-degenerate irreducible representations to one feature. One reason that these modes cannot be distinguished by energy may be the tetrahedral relaxational motions observed in Figure 3 in the main text, which generate long-lived deviations from the perfect $D_{2d}$ structure. These distortions may smear out the oscillation frequencies of each mode, leading to overlap of energies and the overall broad features we see.

Another indeterminate aspect of our $D_{2d}$ model is the $A_1$ symmetry mode (Peak 3) where there is a possibility for orientation dependence. Unfortunately we cannot resolve this mode accurately enough to detect a polarization dependence.

Table S2 was prepared according to the works of Rousseau et al. (crystals) and Nakamoto (molecules) [S1, S2].

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