

Not all H atoms contribute to low activation barrier diffusion in $\text{Ba}_{1.75}\text{LiH}_{2.7}\text{O}_{0.9}$

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Abstract

Superionic conductors have extremely high conductivity in some constituent ions even in the solid state, and many lose their superionicity below a critical temperature. The conductivity of K_2NiF_4 structure-based $\text{Ba}_{1.75}\text{LiH}_{2.7}\text{O}_{0.9}$ jumps over three orders of magnitude at ~ 573 K. This jump is not at a first-order structural phase transition temperature. Molecular dynamics (MD) simulations using a density functional theory (DFT) trained universal neural network potential (NNP) were conducted in this study. The Arrhenius plot of the tracer diffusion coefficient is a straight line between 455 and 741 K, which is inconsistent with the conductivity jump. The 3D activation barrier is ~ 0.3 eV, which is much lower than typical K_2NiF_4 structure-based oxyhydrides. The features in the radial distribution function are almost temperature independent. However, statistical inspection of the tracer diffusion coefficient for each atom, which is very difficult with DFT-MD but is feasible with NNP-MD, revealed the existence of effectively immobile H atoms over the entire studied temperature range. Most H do not engage in concerted migration, according to comparison with a universal curve for independent random walkers. These findings hold for all of β , γ , and δ phases, which have different distributions of Li, O, and H atoms in the same structural framework. Incorporating many vacancies, especially in ‘K’ sites of the K_2NiF_4 framework, could form a low activation barrier H diffusion network not available in conventional oxyhydrides with the same framework. Gaining access to such a percolating network above a certain temperature can explain the superionic transition at this temperature.

Keywords: Superionic conductivity, tracer diffusion coefficient, molecular dynamics, neural network potential, $\text{Ba}_{1.75}\text{LiH}_{2.7}\text{O}_{0.9}$

Impact statement

Neural network potential molecular dynamics show that the superionic transition in H⁻ conductor $\text{Ba}_{1.75}\text{LiH}_{2.7}\text{O}_{0.9}$ that does not accompany a structural transition is caused by

changes in non-migrating H with temperature.

1. Introduction

Superionic conductors are materials with very fast migration of some constituent atoms in the solid state. Faraday discovered this phenomenon in Ag_2S and PbF_2 . A comprehensive review of superionic conductors by Hull [1] discusses that AgI and PbF_2 are prototypical examples of most superionic conductors, with mobile cations and anions, respectively. The review states that ‘the superionic structure of the former is a bcc/fcc anion superlattice plus “liquid-like” cations, while the latter is a fluorite structure plus dynamic anion Frenkel defects’. In the review, however, site-deficient perovskites represented by the F^- conductor tysonite-structure LaF_3 are categorized as AgI -derivatives, while lithium ion superconductors (LISICON), such as $\text{Li}_{2+2x}\text{Zn}_{1-x}\text{GeO}_4$, are classified as a PbF_2 -based structure based on an hcp lattice. Recent intense competition to develop innovative batteries is motivating searching of new excellent Li^+ conductors. $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS), reported in 2011, is a 3D Li conductor based on a completely new framework structure [2]. Other excellent Li conductor examples are argyrodite structure $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) [3] and garnet structure $\text{Li}_{7-x}\text{La}_3(\text{Zr}_{2-x}, \text{Nb}_x)\text{O}_{12}$ [4].

The conductivity extrapolated from the Arrhenius plot at elevated temperatures often could not be sustained at lower temperatures. Boyce and Huberman categorized temperature-driven transitions between the superionic and non-superionic conducting phases into type I and II. Representative examples of the former and latter are AgI and PbF_2 , respectively. [5] The high temperature superionic phase of bcc-based $\alpha\text{-AgI}$ [6] transforms, when cooled below a transition temperature of 420 K [7], into a mixture of a poorly conductive wurtzite structure (space group $P6_3mc$) β phase [8] and a cubic γ phase [9]. The conductivity changes roughly 10^4 -fold at this temperature. The transition temperature decreases significantly to 313 K in a ~ 11 nm nanoparticle [10]. Crystalline $\alpha\text{-AgI}$ trapped in $0.78\text{AgI}\cdot 0.165\text{Ag}_2\text{O}\cdot 0.05\text{B}_2\text{O}_3$ glass does not undergo a phase transition upon cooling to 118 K because the change in volume that happens during the phase transition is not allowed by the surrounding glass [11]. On the other hand, cubic $\beta\text{-PbF}_2$ can exist from room temperature up to at least 1150 K, while an orthorhombic α phase is stable below 625 K. The conductivity of $\beta\text{-PbF}_2$ continuously changes and has four stages with different slopes on the Arrhenius plot. Samara [12] claims that the conductivities of PbF_2 in stage I (includes room temperature), II (up to ~ 550 K), and III (~ 500 -725 K) are dominated by extrinsic impurities, F vacancies, and F interstitials, respectively. In stage IV, the slope continuously changes, and the conductivity is nearly constant between ~ 850

and 1150K with no anomaly at the melting point of 1095 K.[13] A neutron powder diffraction study by Goff et al. finds that the onset of dynamic F⁻ disorder is at ~630 K. [14]

Ba_{1.75}LiH_{2.7}O_{0.9} (hereafter BLHO) [15] is a system with a type I transition. BLHO is a K₂NiF₄ structure based hydride (H⁻) ion conductor, joining other conductors in this family such as La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y} [16], (La,Pr,Nd)₂LiHO₃ [17], (La,Pr,Nd,Sm,Gd)SrLiH₂O₂ [18], Ba₂(Sc,Y)HO₃ [19,20], and Li(La,Ce,Pr,Nd,Sm)EuH_{2-x}O₂ and LiEu₂H₃O [21]. The conductivity of BLHO is about the same as Ba₂YHO₃ at less than 573 K. However, the conductivity jumps over three orders of magnitude at ~583 K and, above this temperature, the conductivity becomes roughly the same as fluorite-type LaH_{2.52}O_{0.24} [22] that belongs to another class of H⁻ conductors. The BLHO conductivity barely changes above the transition point, and even decreases slightly with increasing temperature above 603 K. [15].

Very interestingly, the conductivity jump temperature of BLHO, which is ~583 K, does not appear to coincide with β-γ and γ-δ structural phase transition temperatures of ~573 and ~623 K, respectively. The β, γ, and δ phases share the same framework, although how vacancies, H, and O distribute on the anion sites are slightly different. The conductivity is continuous at the structural transition temperatures, and the conductivity jump occurs within the γ phase [15]. This is very different from AgI, where superionic conduction happens only in the α-phase and is lost upon structural phase transition.

Molecular dynamics (MD) simulations based on density functional theory (DFT-MD), also called first principles or ab initio MD simulations, are commonly used to explicitly model migration of atoms. However, the largest reasonable supercell size in DFT-MD is approximately 100-200 atoms, and diverse local environments cannot be observed simultaneously in a partial occupancy system. A straight line on the Arrhenius plot of the logarithm of conductivity versus the reciprocal of temperature implies that the same diffusion mechanism is responsible for conduction. DFT-MD simulations are often conducted at very elevated temperatures to observe sufficient atom hops in a reasonable simulation duration.

The Arrhenius plots of some ionic conductors bend at temperatures too low for DFT-MD, such as ~470 K in ‘NASICON’-type Li conductor Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ [23], ~430 K in F conducting tysonite structure La_{0.95}Sr_{0.05}F_{2.95}[24], ~300 K in highly crystalline Li-

conducting Li_3YBr_6 [25], and ~ 350 K in H-conducting $\text{LaH}_{2.8}\text{O}_{0.1}$ [26]. The conduction mechanism below the transition temperature cannot be estimated from DFT-MD and results in systematic errors in the conductivity and diffusion coefficient well below the transition temperature. MD simulations using a potential fitted to DFT could be sufficiently fast to allow direct observation of the transition by calculating near the transition temperature. Arrhenius plot bending between 400 K and 500 K was detected by MD simulations using moment tensor potentials in Li-conducting “LLTO”-type $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$, Li_3YCl_6 , and $\text{Li}_7\text{P}_3\text{S}_{11}$ [27], and with the PreFerred Potential (PFP) [28], a universal neural network potential (NNP), in tysonite structure $\text{Ce}_{0.95}\text{Ca}_{0.05}\text{F}_{2.95}$ [29].

The PFP was also used to find a ~ 550 K transition in $\text{LaH}_{2.75}\text{O}_{0.125}$ [30]. The calculated Arrhenius plot of the tracer diffusion coefficient changes its slope at $1/T = 0.0018 \text{ K}^{-1}$. Migration of O happens at $1/T < 0.0018 \text{ K}^{-1}$, and the Arrhenius plot slope at low temperature is also found at very high temperatures and increased La and O mass. The change in the slope, which is the change in the dominating activation barrier, is attributed to the change in the effective activation barrier because of O moving away from the equilibrium position [30].

This study explored the origin of the H conductivity jump in BLHO. The PFP, which was trained on DFT and designed to model diverse systems, was used to perform MD simulations. The diffusion coefficient, radial distribution function (RDF), atom distribution, site occupancy, and atomic displacement parameters (ADP) of BLHO were obtained. The results were compared with those of α -AgI, which is a well-studied simpler system where there is only one type of diffusing atom, Ag, to identify the peculiarities of diffusion in BLHO.

2. Methods

2.1 Supercell model

2.1.1 α -AgI

The crystal structure of α -AgI (hereafter simply AgI) is shown in Fig. 1. The space group type is $Im\bar{3}m$ (number 229). The I atoms form a bcc framework, while Ag is distributed among $6b$, $12d$, and $24h$ sites represented by fractional coordinates $(0, 1/2, 1/2)$, $(1/4, 0, 1/2)$, and $(0, 3/8, 3/8)$, respectively. [31] The three sites are indicated by intersections of colored lines in Fig. 1, and possible paths for Ag migration between the nearest sites are the colored lines. Ag atoms were initially positioned in two $6b$ sites in a conventional cell, though Ag atoms are expected to migrate quickly and the choice of initial position among

the $6b$, $12d$, and $24h$ sites should not affect the MD results. The lattice parameter of $a = 5.1$ Å was used. Experimentally reported values range between 5.04 and 5.11 Å at ~ 420 and ~ 740 K, respectively [31], between 5.062 and 5.106 Å at 435 and 723 K, respectively [32], and between 5.05 ± 0.01 and 5.11 ± 0.01 Å at 420 ± 1 and 790 ± 1 K, respectively [33]. A $5 \times 5 \times 5$ supercell of this conventional cell was used, which contains 250 Ag and I atoms each.

2.2.2 BLHO

The crystal structures of β -, γ -, and δ -BLHO are shown in Fig. 2. The experimental lattice parameters in Takeiri et al. [15] were used. Supercells containing $6 \times 6 \times 2$ K_2NiF_4 units were used, which are described as $\text{Ba}_{252}\text{Li}_{144}\text{H}_{388}\text{O}_{130}$ or $\text{Ba}_{1.75}\text{LiH}_{2.694}\text{O}_{0.903}$. For comparison, Haruyama et al. used $4 \times 4 \times 1$ K_2NiF_4 unit supercells, with a total of ~ 210 atoms, in their recent DFT-MD simulations of BLHO [34].

The β phase has two symmetrically distinct Li sites and four Ba, equatorial anion, and axial anion sites each, all with Wyckoff position $2a$. The supercell is described as $\text{Ba}_{167}\text{Ba}_{259}\text{Ba}_{368}\text{Ba}_{458}$ Li_{144} $\text{Heq}_{151}\text{Heq}_{269}\text{Heq}_{359}\text{Heq}_{451}$ $\text{H}_{\text{ap}168}\text{O}_{\text{ap}14}\text{H}_{\text{ap}269}\text{O}_{\text{ap}23}\text{H}_{\text{ap}310}\text{O}_{\text{ap}362}\text{H}_{\text{ap}411}\text{O}_{\text{ap}461}$, where atom sites such as $\text{Ba}1$ and $\text{Heq}1$ are defined as in Ref. [15]. The two different Ba sites, two pairs of equatorial sites with very different H/vacancy ratios, and a pair of axial sites with very different H/O ratios are indicated with arrows in Fig. 2(a). The γ phase has one distinct Li site and two distinct Ba, equatorial anion, and axial anion sites each, all with Wyckoff position $4c$. The two axial sites have different H/O ratios, which are contrasted with the arrow in Fig. 2(b). The Ba sites have the same site occupancy and were not distinguished in the model generation. The δ phase (Fig. 2(c)) has only one distinct Ba, Li, equatorial anion, and axial anion site. The Wyckoff position is $4e$ except for the equatorial $4c$ site. The Li site is double-split, and one Li is placed arbitrarily in one of the sites. The supercells of the γ and δ phases are $\text{Ba}_{126}\text{Li}_{144}\text{Heq}_{230}\text{H}_{\text{ap}158}\text{O}_{\text{ap}130}$. The equatorial sites prefer low valence species, including vacancies, while high valence species favor apical sites.

Two supercells each, with different atom orderings, were considered for the three phases. The initial structures and MD trajectories are provided in the NIMS database for reproducibility. Diffusion coefficients and other results were averaged over the two supercells with the underlying assumption that the two supercells are two representative samples of a large particle.

2.2 MD procedure

MD simulations were conducted using the commercially available Matlantis package from Preferred Networks with their universal PFP [28] version 6.0.0, a NNP trained on VASP code [35,36] results based on Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) to DFT [37]. Diverse compounds consisting of any of 72 elements may be modeled using the same potential trained on 42 million training data. The PFP is available as a “take it or leave it” potential; the user cannot modify it. Fine-tuning potentials to specific systems is outside the scope of this work. The atom charge is not explicitly handled in the PFP, nor is the electron density. The projected electronic density of states (DOS) from a PBE calculation on a representative MD snapshot suggests that the H charge is -1 (see supplementary material). Bader charge analysis [38,39] showed Bader charges corresponding to $H^{-0.9}$ to $H^{-0.7}$. The exception is a H forming a very short bond with O. Although the DOS appears to clearly indicate that the charge is -1, the Bader volume of this H is zero and hence the Bader charge is H^+ . A similar H state is found in interstitial H of $BaTiO_3$. Defect formation energy analysis shows that the H defect must be H^+ , even though major peaks of interstitial H are found in the DOS at -6.5 and -19.4 eV from the Fermi level, and none above, in a +1 charged system with an interstitial H in $BaTiO_3$ [40]. The canonical, or constant number of atoms, volume, and temperature (NVT), ensemble was used with a Nosé–Hoover thermostat [41,42]. Further details on universal NNPs are discussed in Ref. [43].

MD simulations of AgI were conducted for 150,000 steps with 2 fs per step (0.3 ns in total). The first 30,000 steps (0.06 ns) were discarded as equilibrium steps. Atom positions were recorded every 100 steps, resulting in 1,200 relevant position recordings over 0.24 ns per run. The reciprocal of temperature ($1/T$) used in the runs was at 0.0001 K^{-1} intervals between 0.0010 and 0.0032 K^{-1} (1000 and 313 K, respectively) and 0.0002 K^{-1} intervals between 0.0032 and 0.0060 K^{-1} (313 and 167 K, respectively).

BLHO MD simulations were conducted for 2,100,000 steps with 1 fs per step (2.1 ns in total). The first 100,000 steps (0.1 ns) were discarded as equilibrium steps. Atom positions were recorded every 1,000 steps, resulting in 2,000 position recordings over 2 ns per run. A long simulation time was chosen to allow migrating atoms to move as much as possible. The $1/T$ used in the runs were between 0.00135 and 0.00220 K^{-1} (741 and 455 K, respectively) with 0.00005 K^{-1} intervals. The interval was halved to 0.000025 K^{-1} between 0.00160 and 0.00180 K^{-1} (625 and 556 K, respectively), which is near the experimental β to γ and γ to δ transition temperatures of approximately 573 and 623 K (0.00175 and

0.00161 K⁻¹, respectively) and the experimentally found jump in conductivity around 583 K (0.00172 K⁻¹).

NNP and PBE (DFT) energies of BLHO were compared using MD snapshots. The results are summarized in the supplementary material. A 1 eV energy difference in PBE corresponds to a 0.9 eV difference in NNP in MD simulations starting from the same atom positions.

BLHO diffusion coefficients less than an arbitrary cutoff of 10⁻⁸ cm²/s are regarded as unreliable in this study. A diffusion coefficient of 10⁻⁸ cm²/s corresponds to a displacement of only $\sqrt{1.2} \approx 1.1$ Å over the considered simulation time of 2 ns, which is much less than the distance between migrating atom sites.

3. Results and discussion

3.1 Diffusion coefficient and implied conductivity

Four important quantities appear in the section, which are discussed in Appendix A.1. The tracer diffusion coefficient (D^* , equation 4) is obtained directly from MD simulations. The conductivity based on the tracer diffusion coefficient and the Nernst-Einstein relation (σ^* , equation 10) is defined as the implied conductivity in this paper. The other two are the ionic conductivity (σ_{ion} , equation 5) and the diffusion coefficient derived from the ionic conductivity (D_{σ} , equations 6 and 7).

The tracer diffusion coefficient is readily obtained from MD simulations. In essence, the tracer diffusion coefficient is derived by averaging the slope of squared displacements versus temperature (mean squared displacement) multiplied by a constant (see Appendix A.2 for details). The symbols D_x , D_y , D_z , D_{xy} , and D are used in this study for calculated results; the generally used asterisk (*) is omitted here for brevity. The first three are the diffusion coefficient in the x , y , and z directions. D_{xy} is the sum of D_x and D_y , and D is the sum of D_x , D_y , and D_z , respectively. D_x , D_y , and D_z are, in principle, the same in an isotropic system, although there are slight differences when derived from simulation results.

The implied ion conductivity based on the tracer diffusion coefficient, σ , is defined using the Nernst-Einstein relation (equation 10); the asterisk (*) is omitted again for brevity. The charge and density of migrating species is necessary for the conversion from D to σ , where nominal charge and the assumption that all atoms of the migrating species

contribute to migration are generally used. This assumption turns out to be not valid in BLHO, which is discussed afterwards, but the validity is not questioned for now.

Figs. 3(a,b) show Arrhenius plots of $\log D$ and Nernst-Einstein relation-based implied $\log \sigma$, respectively, versus $1/T$ for AgI. A clear linear relation exists between $\log D$ and $1/T$, and the activation barrier is very low at 0.09 eV. Values from the literature are superimposed. The linear approximation of experimental D from Kvist and Tärneberg [44] is given in Fig. 3(a) together with MD simulations by Niu, Jing, Sun, and Aluru (NJSA) [45] using the potential by NJSA [45] or by Rahman, Vashishta and Parrinello (RVP) [46]. Experimental σ from the original paper on AgI conductivity by Tubandt and Lorenz [6], reproduced by Funke in Ref. [47], and from a recent experiment by Kumar et al. [48] are provided in Fig. 3(b) with RVP potential MD simulations and the Green-Kubo [49,50] or the Nernst-Einstein equation by Sato et al. [51] The D and σ values from NNP calculations in this study are smaller than the literature values, although by less than an order of magnitude.

In Sato et al, the conductivity derived using the Green-Kubo formalism is about three times larger than from the Nernst-Einstein equation and agrees better with the experimental results. [51] In concerted migration systems such as α -AgI, LGPS, and $\text{Na}_2\text{Ni}_2\text{TeO}_6$, the conductivity from a directed graph approach is almost the same as the Green-Kubo values. Here, the differences in position vectors of atoms (nodes) during a certain timeframe, namely 0.7 times the expected hopping time of a random model, were obtained. When the initial and final positions of two atoms are closer than a cutoff distance, the movements of two atoms were combined and treated as a movement of an atom. This treatment results in a larger mean square displacement of migrating species and therefore a larger conductivity than the Nernst-Einstein formalism.

Figs. 4 and 5 show plots of the mean square displacement (MSD) versus simulation time for select temperatures. The points reasonably lie along a straight line for all temperatures ($1/T$ between 0.0014 and 0.0020), all phases, and all directions.

Figs. 6 and 7 show tracer diffusion coefficients of BLHO. Fig. 6(a) gives Arrhenius plots of the 3D diffusion coefficient D . There is no prominent difference between the results of β , γ , and δ phases, as in most other analyses in this study, even though experimentally the δ phase has orders of magnitude higher conductivity than the β phase. The slopes for H and O are roughly the same. Very interestingly, there is no large jump in D , and all points

can be fitted by a straight line. The D of H could be better fitted by two lines, with very slightly different slopes, that cross at $\sim 0.0017 \text{ K}^{-1}$, but this fit is not discussed here. O diffusion is observed and its D is roughly one-tenth of H. The implied conductivity σ is shown in Fig. 6(b) together with the experimental conductivity in Takeiri et al.[15]. The underlying assumption used to derive the implied conductivity does not hold in BLHO because not all H contribute to H conduction, as is discussed in section 3.6. The values of D in Fig. 6 are consistent with recently reported DFT-MD results by Haruyama et al. [34]

The anisotropy of diffusion is explored next. Figs. 6(c,d) show Arrhenius plots of D_z and D_{xy} , respectively, and Fig. 6(e) is a scattering plot of D_z versus D_{xy} for all temperatures and phases. The line in Figs. 6(e,f) represents the isotropic situation of $D_x = D_y = D_z$. The points for H are mostly at the right of the line, meaning that H diffuses slightly faster in the x and y directions than the z direction. On the other hand, O diffusion is more isotropic. Fig. 6(f) plots D_x versus D_y . No substantial anisotropy is found in this plane even though there is very strong anisotropy in anion ordering in the β and γ phases.

Fig. 7(a) presents scattering plots of D of initially equatorial H (H_{eq}) and apical H (H_{ap}). The former is slightly larger than the latter, especially at small D . These values become almost the same at large D because more equatorial H migrates to apical sites, and vice versa, when the total displacement over the simulation time becomes larger, and distinguishing H based on the initial position loses its meaning. The D_{xy} of H_{eq} tends to be larger than H_{ap} (Fig. 7(b)), though the D_z of H_{eq} is almost the same as H_{ap} (Fig. 7(c)). H_{eq} diffuses faster in the x and y directions than in the z direction in all phases (Fig. 7(d)), while this anisotropy is found only in the β -phase in H_{ap} (Fig. 7(e)).

A very large anisotropy between D_{xy} and D_z was reported in $\text{Sr}_2\text{LiH}_3\text{O}$, another K_2NiF_4 structure-based H conductor, using DFT-MD calculations. Simulations at $\geq 1000 \text{ K}$ show that D_{xy} is more than one order of magnitude larger than D_z . The MD activation barrier for the c -direction, $0.93 \pm 0.13 \text{ eV}$, is comparable to the nudged elastic band (NEB) energy for hopping between equatorial and axial sites as well as between axial sites. The MD activation barrier in the ab -plane is about half of the c -direction at $0.43 \pm 0.08 \text{ eV}$ [52]. Haruyama et al. reports NEB activation barriers of up to 0.50 and 0.82 eV in the ab -plane and in the c -direction of δ -BLHO, respectively.[34] This type of anisotropy could be expected in other K_2NiF_4 -based ion conductors. However, BLHO is different from prototypical K_2NiF_4 -based ion conductors, such as $\text{Sr}_2\text{LiH}_3\text{O}$, because 1/8 of the Ba site (“K” site in K_2NiF_4) is intrinsically vacant in addition to some axial site vacancies. The

Ba/vacancy disorder with a large vacancy concentration makes NEB calculations very difficult because the coupling between local Ba/vacancy and O/H distribution would significantly change the nearby H diffusion paths and their barriers. From another point of view, incorporating many vacancies, especially in Ba sites, could form a network with low activation barriers, and thus enhance H conductivity, compared to conventional oxyhydrides with the same framework. Haruyama et al. identified NEB activation barriers of as low as 0.3 eV and 0.4 eV in the ab -plane and in the c -direction, respectively, in some hopping paths in δ -BLHO. [34] Diffusion could be significantly enhanced in BLHO compared to other K_2NiF_4 -based ion conductors if long-scale diffusion is possible using low activation barrier paths only.

3.2 RDF

The RDF (often called ‘pair distribution function’ by experimental researchers) is a measure of number of bonds as a function of interatomic distance. The RDF between atoms of two species, $s1$ and $s2$, is defined in this study as

$$g_{s1,s2}(r) = c \sum_{i \in s1, j \in s2} \frac{1}{4\pi r_{ij}^2} \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(r-r_{ij})^2}{2\sigma^2}\right). \quad (1)$$

This RDF is designed for use in periodic unit cells. The atom i is a species $s1$ atom in a unit cell, while atom j is any species $s2$ atom. The quantity r_{ij} is the distance between atoms i and j , and σ is a peak broadening factor. The RDF is generally calculated for r below a certain threshold, thus the number of relevant atoms j is quite limited for each atom i . The RDF is calculated for discrete r values, and the normalization factor c is arbitrarily chosen such that the maximum RDF over the calculated r is unity.

Fig. 8 shows the RDF for AgI at select temperatures. The bonds were counted over every 100 position recordings of each considered temperature. The Ag-I and I-I RDFs do not change much with temperature. However, in the Ag-Ag RDFs, increasing the temperature gradually flattens the peaks and valleys other than the first peak. The removal of long-range ordering is expected in a ‘melted sublattice’, but a ‘melting point’ where the RDF features change abruptly is not observed. Experimentally the α -AgI phase is only accessible between 420 K and 830 K. However, the α -AgI structure can be simulated at temperatures beyond this range because the supercell size, and thereby density, is constrained and transitioning to the β - or liquid phase is not possible.

RDFs of BLHO were also calculated for each element pair at select temperatures. Bond lengths from 20 position recordings each from the two initial models were used together in the derivation. RDFs for the initial models consistent with experimental refinement were also obtained. The Li-Li pair results are given in Fig. 9, and the other pairs are shown in Figs. S3-S5. The RDFs from MD simulations are almost the same regardless of the temperature and phase, and all RDFs of each element pair look very alike, suggesting no structural transition with temperature change. The MD simulation RDFs of the element pairs may be regarded as broadened RDFs of the refinement. However, in the Li-Li RDFs (Fig. 9), there is a broad peak at ~ 2.5 Å from the MD simulations that do not exist in the experimental refinement. This distance corresponds to $1/\sqrt{2}$ of the Li-Li nearest neighbor distance, which is approximately the nearest neighbor anion-anion distance. Interestingly, H-O bonds at ~ 1 Å are found at all $1/T$ in the β -phase, $1/T = 0.0014$ and 0.0015 K $^{-1}$ in the γ -phase, and $1/T = 0.0014$ K $^{-1}$ in the δ -phase, which are not expected from the refinement results [15]. The charge of such H is +1 (see supplementary material).

3.3 ADP

ADPs are often provided as part of crystallographic structural data and may represent atomic motion, possible static displacive disorder, and thermal vibration. ADPs are denoted with symbols $\mathbf{U}$, $\mathbf{U}^C$, $\mathbf{B}$, and $\boldsymbol{\beta}$ in the literature. [53] A direct lattice basis ($a^*\mathbf{a}$, $b^*\mathbf{b}$, $c^*\mathbf{c}$) is considered, where a^* , b^* , and c^* are the basis vector lengths of the reciprocal axes. When the displacement vector from the mean atom position vector has components $\Delta\zeta^1, \Delta\zeta^2, \Delta\zeta^3$, the ADPs are simply (co)variances of atom positions where

$$U^{ij} = \langle \Delta\zeta^i \Delta\zeta^j \rangle. \quad (2)$$

Therefore, direct derivation from MD simulations is possible without phonon calculations at 0 K. Diffusion coefficients are obtained by fitting the squared displacement versus simulation time, while ADPs are derived by fitting the (co)valences of the displacement regardless of simulation time. This approach was demonstrated [54] on MgO and three thermoelectric materials, Ag_8SnSe_6 [55], $\text{Na}_2\text{In}_2\text{Sn}_4$ [56], and $\text{BaCu}_{1.14}\text{In}_{0.86}\text{P}_2$ [57]. The time-averaged mean squared displacement from the experimentally derived sites was calculated in $\text{LaH}_{2.75}\text{O}_{0.125}$ [30], which is a very fast H $^-$ conductor [26], and tysonite structure CeF_3 [29]; these are not exactly ADPs because the actual average position of atoms may be slightly different than experimentally determined sites.

The atom position (co)valences should be, in principle, the same regardless of simulation

time when the atom is trapped near the equilibrium point. However, the atom position (co)valences of migrating atoms are not; note that the squared displacement of migrating atoms is expected to linearly increase with time and not bound within a certain value. Plotting the ADP versus T reveals whether atoms can migrate or not, even in cases where the diffusion distance is very short within the MD simulation duration and thus a reasonable diffusion coefficient cannot be obtained. The ADP is proportional to temperature when an atom is in a harmonic potential well (Einstein model) under classical dynamics, hence some information on the potential can be extracted too. Correcting for quantum effects, namely discrete energy levels and zero-point energy, to check consistency with experimental results is easily attained when the Einstein model is assumed. [54]

Fig. 10 shows the isotropic ADP, U_{iso} , for I in AgI. The U_{iso} , which is the arithmetic mean of U^{11} , U^{22} , and U^{33} , is roughly proportional to T for the entire calculated temperature range, indicating a harmonic potential (Fig. 10(a)). The U_{iso} versus T corrected for quantum mechanical effects based on a linear fit below 500 K is shown as the curve in Fig. 10(b). The deviation from classical dynamics is relevant only below ~ 50 K.

Fig. 11 shows the ADPs U^{11} , U^{33} , and U_{iso} for Ba, Li, and O in BLHO. The D of O exceeds 10^{-8} cm²/s at $1/T$ smaller than ~ 0.0018 K⁻¹, or T larger than ~ 556 K (Fig. 6(a)). All U values of O increase significantly with increasing temperature in this temperature range. U values are less than ~ 0.16 Å² at ~ 556 K (Fig. 11(c)). A variance of ~ 0.16 Å² corresponds to a standard deviation of 0.4 Å, and, assuming a normal distribution of the atom position, an atom is more than 1.2 Å away from the equilibrium position with a probability of 0.3 %. Interestingly, Li atoms are not fully bound to the equilibrium position at above ~ 550 K, and so are Ba atoms at above ~ 700 K. This is separate from the moving of atoms between different sites during the initial equilibration steps, such as movement of some Li to initially vacant Ba sites. The large movements of Li and Ba do not cause a large discontinuity or large change in the slope of D (Fig. 6), unlike in LaH_{2.75}O_{0.125} where movement of O visibly changes the slope of D of H. [30]

3.4 Site occupancy in BLHO

The site occupancies of equatorial and apical sites are important issues in BLHO. A refinement of synchrotron X-ray diffraction results assigned all H and O to equatorial and apical sites. The reported ADPs are on the order of $B=0.8$ Å² [15], or $U=0.01$ Å². The U is the (co)valence of atom positions, and $U=0.01$ Å² translates to a standard deviation of

0.1 Å. The largest experimental B in anion sites is 4.1 Å² [15], which is the H_{ap}/O_{ap}1 site of the γ phase at 587 K ($1/T=0.0017$ K⁻¹). This B corresponds to a standard deviation of 0.23 Å, thus atoms in this site should be in a sphere of radius 0.3 Å around the equilibrium position for ~80% of the time.

This is clearly inconsistent with MD simulation results shown in Fig. 12(a). Filled and empty symbols show the site occupancies of H and O, respectively, where a site is considered occupied when there is a H or O atom within 0.3 Å from the experimentally refined position. Circle and triangle symbols are those of equatorial and apical sites, respectively. The total (H+O) site occupancies of equatorial and apical sites are shown with solid and dashed lines, respectively. The site total occupancies of both sites are very low, decreasing from slightly less than 40% at 450 K to roughly 20% at 740 K.

The computational results are also given for cutoff radii of 0.6 and 0.9 Å in Fig. 12(b,c), respectively. The total occupancies at a very large cutoff of 0.9 Å ranges from approximately 90% to 80% and 80% to 70% in equatorial and apical sites, respectively. Therefore, many anions are located far away from the experimentally determined equatorial and apical sites.

For all cutoffs and phases, the anion occupying equatorial sites are mostly H but a very small amount of O is found, and the occupancy of apical sites is higher than equatorial sites. This is consistent with the experimental refinement where vacancies and O favor equatorial and apical sites, respectively.

3.5 Atom distribution

Examples of atom distribution during a MD simulation of γ -BLHO are shown in Fig. 13. The isosurface indicates a certain probability of an atom staying in that location, and does not indicate trajectories of migrating atoms. The distributions are projected along the a -axis, thus a plotted distribution appears in at least one of the six FU along the a -axis of the supercell and not necessarily in all of them.

Figs. 13(a-c) show Ba atom positions. Most Ba are at Ba sites; the positions of Ba sites along the c -axis are shown with blue wedges. Isosurfaces that connect some Ba sites are found in all temperatures, meaning that Ba could be found between the experimentally identified Ba sites at above a certain non-trivial probability. Figs. 13(d-f) illustrate Li atom positions. The Li sites are at orange wedges, and Li should only be there based on

the experimental refinement, but some Li are found at Ba sites in MD simulations. This result is reasonable considering that Ba^{2+} sites can prefer occupancy by a positively charged Li^+ instead of being vacant. Connected sites are found again. Figs. 13(g-i) show H atom positions. Connections over three or more sites are found at $T=556$ K and 625 K. Figs. 13(j-l) give O atom positions. Some O are at equatorial sites. Increasing T tends to increase connected sites. Similar trends are found in β - and δ -BLHO (Figs. S4 and S5, respectively).

The Ba vacancies cause some Ba to form a ‘split site’ connecting two experimentally determined Ba sites, and even move some Li to fill Ba vacancies. These changes in the cation positions perturb the anions, and the equilibrium position of each anion is slightly displaced from the refined position although the K_2NiF_4 framework is still sustained.

Large and long NNP-MD simulations unfortunately discourage some analysis methods used in DFT-MD. The large number of atoms, both diffusing and spectator, makes analysis of the atom trajectory difficult. Drawing the trajectories of all 388 H atoms in a $6\times6\times2$ supercell overlays too much information to gain insights.

3.6 Squared displacement distribution

The tracer diffusion coefficient is theoretically derived from the slope of mean of squared displacement versus simulation time, but how are the slopes of individual atoms distributed? The tracer diffusion coefficient of each atom can be obtained from its slope of squared displacement versus simulation time (Appendix A.2). The $\log D$ of each Ag atom in the AgI supercell was sorted and the distribution is shown in Fig. 14(a) for selected $1/T$. The curve has the shape of a slightly rotated tilde ($\sim$) symbol and has one inflection point. The $\log D$ values at each temperature is roughly within one order of magnitude, thus the slowest atom has a D of approximately 1/10 that of the fastest.

This distribution is very different from independent random walkers, which follow the universal curve in Fig. 14(b) (derivation in Appendix A.3) that covers more than four orders of magnitude. When the average diffusion coefficient of random walkers is D , the sort of individual diffusion coefficients D' follow the curve

$$\log(D'/D) = \log D' - \log D = \log(2\Xi^2), \quad (3)$$

where $\text{erf}(\Xi)$ is the fraction of random walkers with diffusion coefficients less than D' . Fig. 14(b) has labels “Individual $\log D'$ -Average $\log D$ ” versus “Atom (scaled)”, and the parameter Ξ does not explicitly appear. When an atom has the m -th smallest D' among n migrating atoms in the system, the scaled position of this atom in the horizontal direction is m/n . This m/n is $\text{erf}(\Xi)$, and the corresponding parameter Ξ is used to derive the vertical axis value of $\log(2\Xi^2)$.

Ag in AgI behave very differently from independent random walkers because Ag is subject to concerted migration, a topic discussed in detail in section 3.7. The universal curve cannot be stretched nor shrunk in the vertical direction, thus Fig. 14(a) cannot be fit with the universal curve.

A similar analysis for D_x , D_y , and D_z per atom in BLHO gives striking results (Figs. 15-17). The curves have three inflection points, with a jump of D at approximately $10^{-8} \text{ cm}^2/\text{s}$. Atoms with D larger and smaller than $10^{-8} \text{ cm}^2/\text{s}$ (shown with a dotted line in the figures) are categorized as mobile and immobile atoms, respectively, recalling that a D of $10^{-8} \text{ cm}^2/\text{s}$ corresponds to a displacement of $1.1 \text{ \AA}$ over the simulation time.

The MD-based activation barrier for H in $\text{Sr}_2\text{LiH}_3\text{O}$, which is based on the same K_2NiF_4 structure, is roughly 0.43 and 0.93 eV in the ab -plane and c -direction, respectively [52], and MD simulations at $\geq 1000\text{K}$ were necessary using DFT. Most H in BLHO would be subject to a similar activation barrier if there are no mechanisms to enhance H diffusion, and these atoms will be regarded as ‘immobile’ in a system where the activation barrier is $\sim 0.34 \text{ eV}$ (Fig. 6). In other words, atom diffusion is dominated by atoms that can access an enhanced diffusion mechanism. The breakaway from the activation barriers of typical K_2NiF_4 structure oxyhydrides is made possible by the large concentration of defects, especially Ba vacancies, thus incorporating many vacancies in the ‘K’ sites of the K_2NiF_4 structure would be a powerful mechanism to enhance H conductivity.

The distribution of H in the H conductor $\text{LaH}_{2.75}\text{O}_{0.125}$ from the author’s previous MD calculations [30] is given in Fig. 18. The simulation time excluding equilibrium steps is 1 ns. Two kinds of distributions exist with a boundary around $1/T = 0.0018 \text{ K}^{-1}$ (green line in Fig. 18, the calculated Arrhenius plot of D changes its slope at this temperature). In the high temperature regime, the distribution resembles those of AgI and the D of all H atoms are mobile above a cutoff of $10^{-8} \text{ cm}^2/\text{s}$. In contrast, the distribution at the low temperature

regime is similar to BLHO. A jump in distribution is found near 10^{-8} cm²/s, some H are immobile, and the amount of immobile atoms increase with decreasing temperature. Two universal curves are shown in Fig. 18, with parameters $(D_1, p_0) = (-5.5, 0)$ and $(-6.7, 0.05)$ defined in equations 28-29. The curves can be shifted vertically to obtain a fit, but not shrunk or stretched. The D curves from MD simulations are obviously gentler than the universal curve, and fitting is not possible for LaH_{2.75}O_{0.125} in all temperatures. Removing immobile atoms from consideration for large $1/T$ (low T), which means using a non-zero positive p_0 , steepens the universal curve and worsens the fit.

The slopes are gentler than the universal curve in concerted migration systems AgI and LaH_{2.75}O_{0.125} while the slope is steeper in H with very high D in BLHO. Therefore, the origin of very high D in some H in BLHO might not be concerted migration mechanisms as in AgI and LaH_{2.75}O_{0.125} but instead of proximity to fast diffusion paths with few diffusion inhibiting chokepoints. However, concerted migration cannot be ruled out in this study.

Existence of an unpercolated H diffusion network would result in an anomaly in the MSD versus time plot (Figs. 4,5), where the MSD cannot increase above a certain value. When there are two networks, an unpercolated low activation barrier diffusion network and a percolated high activation barrier percolated network, the plot would be steep when atoms move in the former and becomes gentle above a certain MSD where atom diffusion is forced to use the latter. Such anomalies are not found. Whether a network is percolated or not in BLHO is difficult to attain from Figs. 15-17. D of 10^{-6} , 10^{-7} , and 10^{-8} cm²/s correspond to displacements of 1.1, 3.5, and 11 Å, respectively, during the simulation. Atoms with $D > 10^{-6}$ cm²/s in one direction are less than 10% at $1/T = 0.0015$ K⁻¹, and roughly 30-40% of atoms have $D > 10^{-7}$ cm²/s (displacement of 3.5 Å) at $1/T = 0.0017$ K⁻¹, which is slightly above the experimentally observed superionic transition temperature of ~ 0.00172 K⁻¹. The unit cell size in the shortest direction is ~ 24 Å, thus the simulation time is too short to exclude confinement with a large cluster. Substantially increasing the simulation time to attain displacements comparable to the unit cell size is not realistic because the walltime of a simulation is already very long at about 3 days and increasing the displacement by 10 times requires increasing the simulation length by 100 times.

3.7 Simple detection of random walker behavior

The possibility of concerted migration is considered, where multiple atoms migrate in a

correlated manner. Concerted migration is often found in systems where migrating species occupy split sites in a broad sense. Atoms prefer to stay near positions with local energy minima. When such positions are too close, simultaneous occupancy of neighboring such sites is not allowed. One ‘atom site’ might therefore have two or more local minima but only one atom can occupy at the same time. Too close atom positions may be recognized as different sites though simultaneous occupancy could not be possible. In these situations, an attempt of atom A moving to a neighboring site occupied by atom B forces atom B to move to another site for the movement of atom A to succeed. Atoms A and B migrate in a concerted fashion in this case, and such chain of movements may involve more than two atoms.

Na-conducting ‘NASICON’-type $\text{NaZr}_2(\text{PO}_4)_3$ (space group $R\bar{3}c$) is a representative example. The NASICON structure has the general formula $\text{A}_x\text{M}_2(\text{XO}_4)_3$. There are Na1, Na2, and Na3 sites in $\text{NaZr}_2(\text{PO}_4)_3$. Na1 is the most stable site and is a split site that does not allow simultaneous occupancy. A Na2 atom attempt to migrate into a filled Na1 site can succeed when the Na2 atom, which is in an unfavorable position, enters the unoccupied well and displaces the Na1 atom in the occupied well into another Na2 site. [58] Garnet-type cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO, space group $Ia\bar{3}d$) has tetrahedral and octahedral Li sites. The Wyckoff position of tetrahedral Li is $24d$, while the bridging octahedral site is ideally $48g$ but split into two $96h$ sites that cannot be simultaneously occupied. An experimental study claims 56% and 88% occupancies in the tetrahedral and octahedral sites [59], respectively, which is consistent with computational studies that demonstrate concerted migration.[60,61] Concerted migration is expected in Li-stuffed $\text{Li}_x\text{A}_3\text{B}_2\text{O}_{12}$ garnet structure ($x=3+\delta$) and NASICON structures owing to their diffusion networks. [62] Locally low barriers and flat energy landscapes are preferable to activate low-barrier concerted migration. [63] Calculations of Li-excess $\text{Li}_{4+x}\text{P}_2\text{S}_6$ suggest that the excess Li in interstitial sites does not directly hop to an adjacent interstitial sites but instead displaces a neighboring Li that, in turn, moves to a neighboring interstitial. [64]

Concerted migration is reported in other systems. Topological data analysis using MD simulations confirmed the existence of concerted migration in $\alpha\text{-AgI}$ [65]. The Ag $6b$, $12d$, and $24h$ sites are very close to each other at 0.9 Å. The DFT-MD study by Haruyama et al. shows that BLHO undergoes concerted migration at $T \geq 900$ K when there is sublattice melting. About 1/3 of the hops are concerted at 700 K, while concerted migration barely happens at 500 K.[34] The experimental study on BLHO [15] measured the conductivity up to ~630 K only[15], and domination of concerted migration might not

be experimentally accessible. LGPS has split Li1 and Li3 sites in the primary Li conduction channel in the [001] direction, and Li conduction with a low energy barrier of ~ 0.3 eV is possible by concerted migration, according to DFT calculations [66]. The number of atoms that move in one step must be finite; a NEB simulation under periodic boundary conditions that forces all atoms in a channel to concertedly move at the same time has an activation barrier of infinity even though the barrier per supercell may be low. [63] A concerted mechanism for Cl migration in $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ (chlorapatite) was observed using MD simulations. Here, vacancies resulting from Frenkel pair formation makes Cl migration possible even in perfect stoichiometry supercells. There are pairs of local energy minima lattice sites for Cl in this system. [67]

Concerted migration in a broad sense is proposed in K_2NiF_4 -structure oxyhydride La_2LiHO_3 . The equatorial anion sites form a topologically square lattice where the O:H ratio is 1:1. When a H is replaced with a vacancy, the H and vacancy cannot switch positions, which is necessary for long-distance migration of that vacancy, unless O can hop between neighboring equatorial sites. [17]

The plot of D sorted by migrating atom cannot be fitted with the universal curve for independent random walkers (equations 28 and 29 in appendix A.3) when there is concerted migration. The converse is not always true, mechanisms other than concerted migration, such as correlated hopping behavior, may result in a scenario other than independent random walker diffusion. The curves for AgI (Fig. 14(a)) and $\text{LaH}_{2.75}\text{O}_{0.125}$ (Fig. 18) cannot be fitted by the universal curve. The fitting results for BLHO are shown in Figs. 15-17; surprisingly the universal curve assuming some immobile H provides a good fit for most H. The fraction of immobile atoms, p_0 , in the fits are plotted in Fig. 19, which shows that less H participates in diffusion along the c -axis compared to the ab -plane and that immobile H decreases with increasing temperature. The D_1 is tabulated in Table 1; there are no significant dependencies on the phase and direction and only the temperature matters.

There are immobile atoms even at the high temperature of 714 K (0.0014 K^{-1}), and the amount of immobile atoms increase with decreasing temperature. A too short MD simulation in an independent random walker scenario would result in fitting of the universal curve at D above a certain threshold that corresponds to a hop between sites during the simulation. The p_0 in this scenario should be 0, unlike the fits in Figs. 15-17. Atoms with large D typically have D that are consistently above the universal curve fit,

although the increase is not that large; a log D difference of 0.3 translates to difference by a factor of 2. Such atoms with D above the universal curve could have participated in some form of correlated hopping, including concerted migration, though the random walker scenario is the norm rather than the exception. DFT-MD results from Haruyama et al. show that correlated migration is not the main mode of H transport at 500 and 700 K. [34]

The Q-averaged total scattering intensity spectrum from quasi-elastic neutron scattering (QENS) is surprisingly almost the same between β -BLHO at 548 K and γ -BLHO at 588 K, which are on other sides of the conductivity jump temperature. The clear quasi-elastic signal indicates facilitation of H diffusion at 548 K. The QENS spectra can be better reproduced using two quasi-elastic components, suggesting that the dynamics include several different relaxations or types of motion. [15] This observation is consistent with Figs. 15-17, where H diffusion is activated in β -BLHO below the structural transition temperature and there are at least two modes of H migration, namely an independent random walker type hopping behavior in most mobile H and an accelerated diffusion mechanism found in $\sim 10\%$ of H.

3.8 Understanding the H diffusion mechanism in BLHO

The above investigations suggest the following H diffusion situation in BLHO. The β , γ , and δ phases show very similar diffusion characteristics even though the experimentally refined anion distribution and/or Ba/vacancy distributions may differ. The 3D activation barrier for H diffusion in the NNP-MD calculations is ~ 0.3 eV, which is much lower than what is expected for K_2NiF_4 structure oxyhydrides (~ 0.5 eV in the ab -plane, 0.8 eV along the c -axis). Only part of the H participates in this diffusion and less H diffuses along the c -axis compared to the ab -plane. Most of the H diffusion is not concerted and is based on random hopping, while migration of some very fast diffusing H may be concerted.

The temperature dependence of mobile H concentration implies that the enhanced diffusion network appears to change with temperature. A sudden jump in conductivity is possible when the enhanced diffusion network is available for long-distance migration only above a certain temperature, but this speculation cannot be confirmed nor rejected from the current simulations. Confirmation that the enhanced diffusion network does not percolate below the experimentally observed transition temperature ($T \sim 583$ K within the γ -phase) is not possible from the already long simulated time with NNP-MD. Extrapolation from high temperature simulations, for instance 900 of 1200 K, toward low

temperatures is not appropriate if the diffusion scenario is totally different, as is suggested by DFT-MD simulations by Haruyama where concerted migration dominates at 900 and 1200 K but does not happen at 500 K.[34]

4. Conclusions

NNP MD simulations of β -, γ -, and δ -BLHO were conducted and compared with those of α -AgI. There are no spontaneous structural transitions within the investigated $1/T$ range, which is between 0.001 and 0.006 K⁻¹ (1000 and 167 K, respectively) for AgI and 0.00135 and 0.0022 K⁻¹ (741 and 455 K, respectively) for BLHO, respectively, for all of these crystals. 3D diffusion of H happens in all BLHO phases, where the tracer diffusion coefficient is larger in the equatorial xy -plane. Noticeable diffusion of O happens above $\sim$ 600 K.

The Arrhenius plot of the tracer diffusion coefficient lies on a straight line in both AgI and all BLHO phases within the calculated temperature range. As a result, there the activation barrier is expected to be the same, and so is the diffusion mechanism within the scope of the simulations in this study. The 3D activation barrier for H diffusion in BLHO is $\sim$ 0.3eV, which is much lower than what is expected for K₂NiF₄ structure oxyhydrides ($\sim$ 0.5 eV in the ab -plane, 0.8 eV along the c -axis). An enhanced H diffusion network is therefore found in BLHO, and the many vacancies, especially in Ba sites, could realize the enhanced H diffusion in BLHO.

The plot of sorted diffusion coefficient for each atom follows a universal curve, independent of the dimension, in a random walk scenario. In contrast to AgI, where all Ag contribute to diffusion, some H in BLHO is immobile, even at $\sim$ 700 K, and the amount of immobile atoms increases with decreasing temperature.

The experimentally observed jump in conductivity at $\sim$ 583 K in the γ -phase of BLHO, which does not accompany a structural phase transition, may be explained if the enhanced diffusion network can be used only above the transition temperature. However, the analysis in this study cannot support nor reject this hypothesis.

Supplementary Material

See supplementary material for discussion of PBE calculations of BLHO, comparison of PBE and NNP energies of BLHO, electronic DOS of BLHO, RDFs of BLHO and atom

position isosurfaces of β - and δ -BLHO.

Disclosure statement.

The authors report there are no competing interests to declare.

Data Availability Statement

The MD trajectories will be uploaded to the NIMS Materials Data Repository.

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Appendix. Mathematical details

A.1 Relations between tracer diffusion coefficient and conductivity

According to equations 6-10 in Ref. [69], the tracer, or self, diffusion coefficient is defined as

$$D^* = \lim_{t \rightarrow \infty} \frac{d}{dt} \left[\frac{1}{2dN} \sum_{i=1}^N \left(\Delta \vec{R}_i(t) \right)^2 \right], \quad (4)$$

where d is the dimensionality of the transport, $\Delta \vec{R}_i(t)$ is the time-dependent vector displacement of atom i , and N is the number of mobile atoms in the system. The diffusion coefficient in one direction in multi-dimensional systems is obtained by setting the displacement vectors to zero in the dimensions that are not considered. On the other hand, the (direct current) bulk ionic conductivity is given by

$$\sigma_{\text{ion}} = \lim_{t \rightarrow \infty} \frac{d}{dt} \left[\frac{(ze)^2}{Vk_B T 2d} \left(\sum_{i=1}^N \Delta \vec{R}_i(t) \right)^2 \right]. \quad (5)$$

Here, z , e , V , k_B , and T are the charge number of the ions, unit charge, sample volume, Boltzmann constant, and temperature, respectively.

Using the Nernst-Einstein equation, the conductivity diffusion coefficient D_σ is defined as

$$\sigma_{\text{ion}} = \frac{N_V (ze)^2}{k_B T} D_\sigma. \quad (6)$$

The $N_V = N/V$ is the number density of mobile species. Combining equations 5 and 6,

$$D_\sigma = \lim_{t \rightarrow \infty} \frac{d}{dt} \left[\frac{1}{2dN} \left(\sum_{i=1}^N \Delta \vec{R}_i(t) \right)^2 \right]. \quad (7)$$

The summation is taken over the square in equations 4 and 5, while the square of the summation is used in equation 7.

The activation barriers for tracer and conductivity diffusion coefficients are written in the Arrhenius equation form as

$$D^*(T) = D_0^* \exp \left(-\frac{E_D}{k_B T} \right) \quad (8)$$

and

$$D_\sigma(T) = D_{\sigma 0} \exp \left(-\frac{E_\sigma}{k_B T} \right), \quad (9)$$

respectively, under the assumption that prefactors D_0^* and $D_{\sigma 0}$ as well as E_D and E_σ are temperature-independent constants obtained by fitting of the relevant Arrhenius plot.

The implied conductivity based on the tracer diffusion coefficient is given by using the Nernst-Einstein equation as

$$\sigma^* = \frac{N_V (ze)^2}{k_B T} D^*. \quad (10)$$

Note that σ^* is not exactly a straight line in the Arrhenius plot because

$$\sigma^* = D_0^* \frac{N_V (ze)^2}{k_B T} \exp \left(-\frac{E_D}{k_B T} \right), \quad (11)$$

thus

$$\log \sigma^* = \log \left(D_0^* N_V (ze)^2 \right) - \log(k_B T) - \frac{\log(e) E_D}{k_B T}. \quad (12)$$

A.2. Using MD to obtain the diffusion coefficient and conductivity

A mathematical quantity easily derivable from MD calculations is the average slope of the squared displacement of an atom i in the x -direction, Δx_i^2 , as a function of simulation time t defined as

$$s_{x,i} = \lim_{t \rightarrow \infty} \frac{\Delta x_i^2}{t}. \quad (13)$$

This slope is obtained by a linear fit of Δx_i^2 versus t that passes through the origin. Counterparts for y and z directions, $s_{y,i}$ and $s_{z,i}$, respectively, are similarly obtained. A slope is converted into the tracer diffusion coefficient by

$$D_{x,i} = \frac{s_{x,i}}{2d}. \quad (14)$$

The dimensionality d is 3 in this study. Counterparts for y and z directions are denoted as $D_{y,i}$ and $D_{z,i}$, respectively. The diffusion coefficients in the xy -plane and in 3D are given by

$$D_{xy,i} = D_{x,i} + D_{y,i} \quad (15)$$

and

$$D_i = D_{x,i} + D_{y,i} + D_{z,i}, \quad (16)$$

respectively. The diffusion coefficients of the system D_x , D_y , D_z , D_{xy} , and D are simply the mean averages over each atom, such as

$$D_x = \frac{1}{N} \sum_i D_{x,i}. \quad (17)$$

where N is the number of atoms in the system.

A.3. Distribution of tracer diffusion coefficients among individual random walkers

The solution to a 3D anisotropic heat equation,

$$\frac{\partial f}{\partial t} = \sum_{i=1}^3 D_i \frac{\partial^2 f}{\partial x_i^2}, \quad (18)$$

is

$$f(x_1, x_2, x_3, t) = \prod_{i=1}^3 \frac{1}{\sqrt{4\pi D_i t}} \exp\left(-\frac{x_i^2}{4D_i t}\right) \quad (19)$$

when the initial condition for f at $t=0$ is a delta function at the origin. The variance in the x_1 -direction is

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} x_1^2 f dx_1 dx_2 dx_3 = 2D_1 t, \quad (20)$$

stating that the mean squared position of the function in the x_1 direction divided by time is $2D_1$.

The positions of independent anisotropic 3D random walkers are expected to follow this distribution f .

Let $P(X_1)$ be the probability that the x_1 -coordinate of a random walker is in the range $-X_1 < x_1 < X_1$. The function

$$g(x_1) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f dx_2 dx_3 = \frac{1}{\sqrt{4\pi D_1 t}} \exp\left(-\frac{x_1^2}{4D_1 t}\right), \quad (21)$$

is considered, which is a normalized Gaussian function (Fig. 20(a)). Using dimensionless variables

$$\xi = \frac{x_1}{\sqrt{4D_1 t}}, \quad (22)$$

and the constant

$$\Xi = \frac{X_1}{\sqrt{4D_1 t}}, \quad (23)$$

$$P(X_1) = 2 \int_0^{X_1} g(x_1) dx = \frac{2}{\sqrt{\pi}} \int_0^{\Xi} \exp(-\xi^2) d\xi = \text{erf}(\Xi). \quad (24)$$

(Fig. 20(b)).

The individual diffusion coefficient corresponding to an atom that moved X_1 during the diffusion duration time of t is (see Fig. 20(c))

$$D' = \frac{X_1^2}{2t} = 2D_1\Xi^2. \quad (25)$$

Fig. 20(d) plots the “universal curve” of $\log(D'/D_1) = \log(2\Xi^2)$ versus $\text{erf}(\Xi)$. The graph is also given in Fig. 14(b) for comparison with AgI MD results. The horizontal axis is denoted as “atom (scaled)” in Fig. 14(b) to not explicitly show $P(X_1)$ in the figure. The curve in Fig. 14(b) should be obtained under an ideal random walker situation and when the D of all atoms in a system are sorted in ascending order,. The value in the horizontal axis is scaled by the number of migrating atoms in the system. When an atom has the m -th smallest D' among n migrating atoms in the system, the scaled position of this atom in the horizontal direction is simply m/n . The distance that this atom has moved is X_1 , and $P(X_1)=m/n$ in the discussion concerning equations 21-25.

This relation universally holds for all independent random walkers regardless of the diffusion time and diffusion coefficient. The same result is obtained even when the dimension is different (maximum value of i in equation 18 is not 3).

Assume that the fraction of non-migrating atoms of a specific species is p_0 , the probability $p > p_0$ that the diffusion coefficient of an atom in the x_1 -direction is less than D' is implicitly given using Ξ as

$$\log D' = \log(2\Xi^2) - \log D_1 \quad (28)$$

and

$$p = (1 - p_0) \text{erf}(\Xi) + p_0. \quad (29)$$

The quantities D_1 and p_0 may be obtained by fitting to a D' versus p plot.

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Table 1. Value of $\log D_1$ (unit cm^2/s) of the fits, by phase and coordinates, in Figs. 15-17. The same number is used for D_{1x} and D_{1y} in δ -BLHO.

T (K)	β, x	β, y	β, z	γ, x	γ, y	γ, z	δ, xy	δ, z
714	6.3	6.2	6.45	6.35	6.25	6.35	6.2	6.25
667	6.55	6.45	6.6	6.5	6.55	6.55	6.45	6.4
625	6.65	6.6	6.7	6.6	6.75	6.55	6.6	6.55
588	6.7	6.7	6.8	6.75	6.85	6.85	6.95	6.9
556	7.0	6.8	6.9	6.9	6.9	6.85	7.1	7.05
500	7.1	7.0	6.9	7.05	6.9	7.1	7.1	7.0

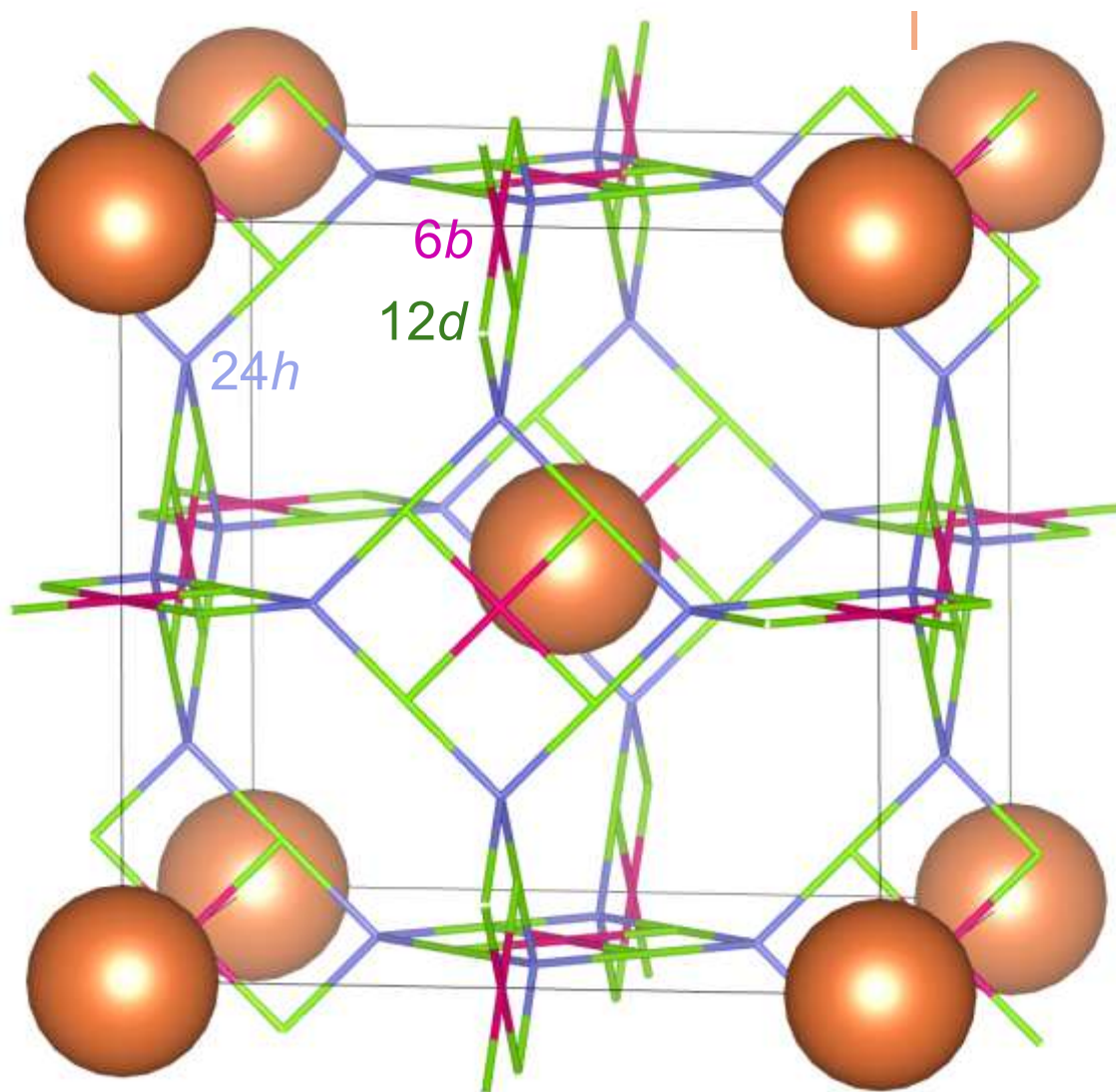


Fig. 1. Crystal structure of α -AgI. The Ag $6b$, $12d$, and $24h$ sites are the intersections of colored lines, and the colored lines indicate Ag diffusion paths between the Ag sites. The Ag sites are all partially occupied.

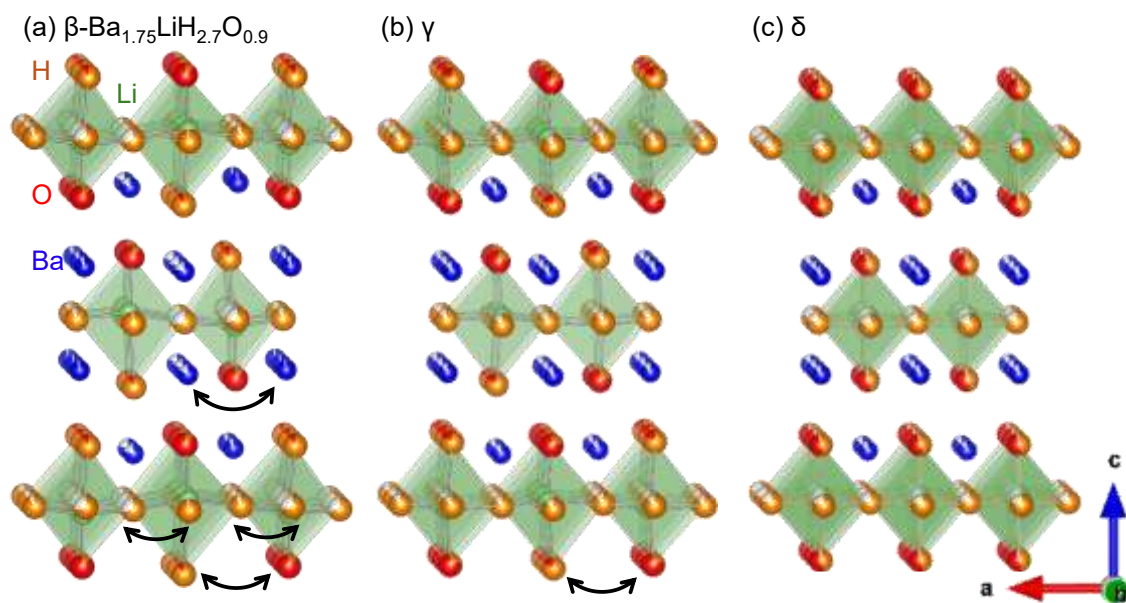


Fig. 2. Crystal structures of (a) β -, (b) γ -, and (c) δ - $\text{Ba}_{1.75}\text{LiH}_{2.7}\text{O}_{0.9}$. The curved arrows indicate differences in site occupancies of Ba/vacancy sites, equatorial anion sites, or axial anion sites (this order from top to bottom in (a)).

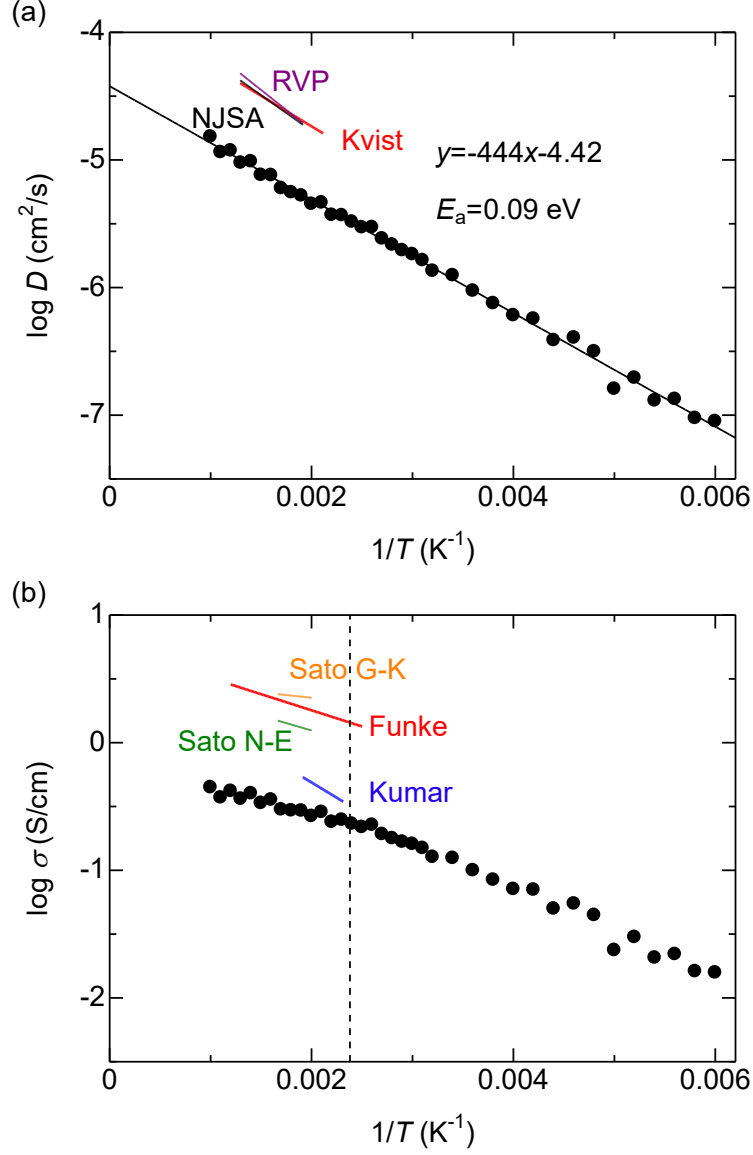


Fig. 3. Arrhenius plot of AgI of (a) the 3D tracer diffusion coefficient D and (b) conductivity derived using the Nernst-Einstein equation (N-E, equation 10). Data from the literature are also shown: experimental relation from Kvist and Tärneberg [44] (Kvist), MD simulations shown in Fig. 9 in NJSA [45] using the NJSA [45] or RVP [46] potential, dc conductivities from Funke (data read from Fig. 3 in ref. [47], which were originally published in Refs. [6,70]) and Fig. 3 in Kumar et al. [48] (Kumar), and conductivities from RVP MD simulations by Sato et al. [51] and the Green-Kubo (Sato G-K) or the N-E (Sato N-E) equation. The vertical line corresponds to the phase transition point of $T=420 \text{ K}$. The Kvist, RVP, and NJSA lines almost overlap in (a).

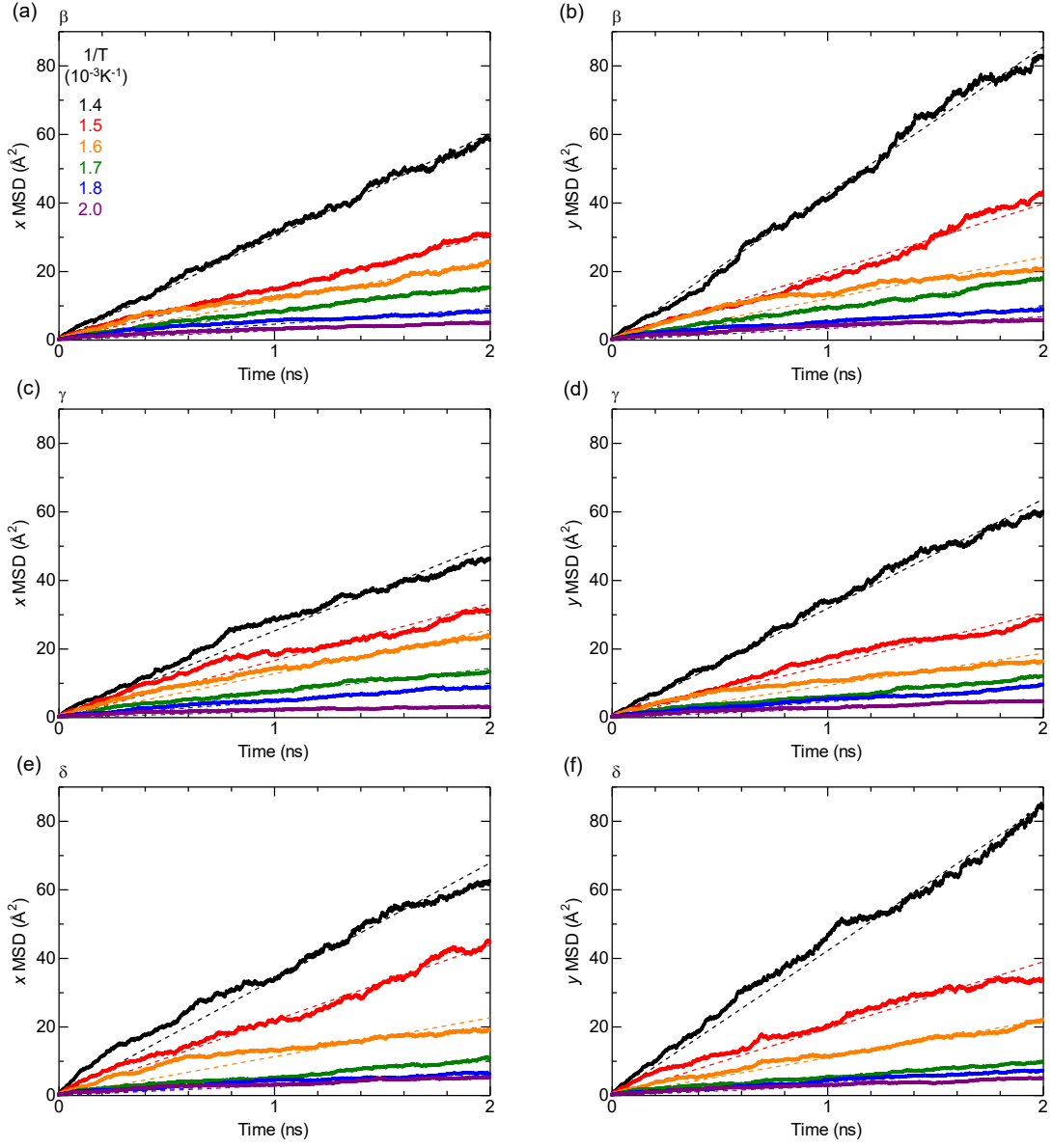


Fig. 4. MSD versus simulation time plots, for select temperatures, in the (a,c,e) x and (b,d,f) y directions in (a,b) β -, (c,d) γ -, and (e,f) δ -BLHO.

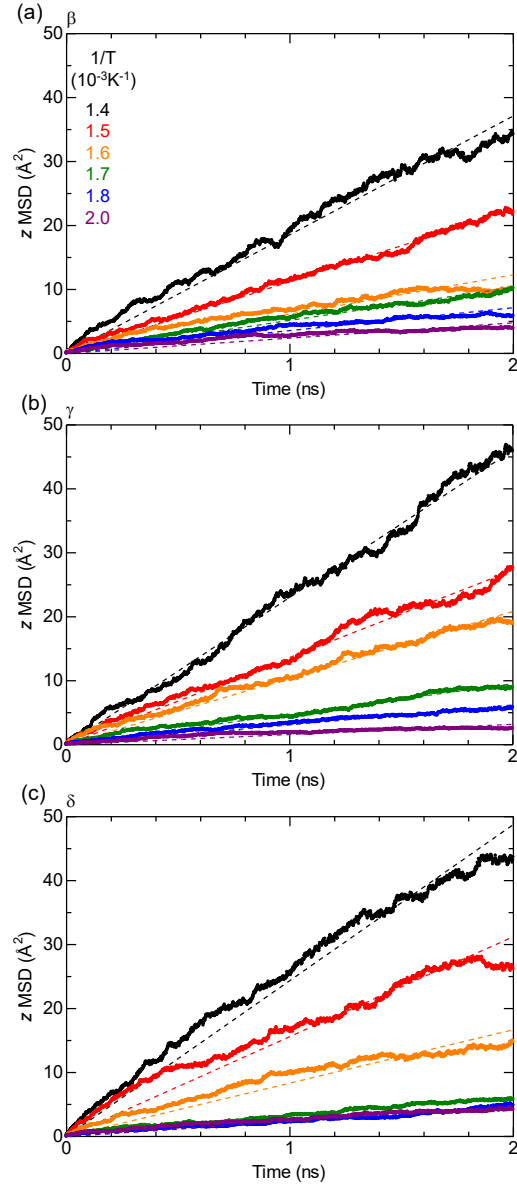


Fig. 5. MSD versus simulation time plots, for select temperatures, in the z direction in (a) β -, (b) γ -, and (c) δ -BLHO.

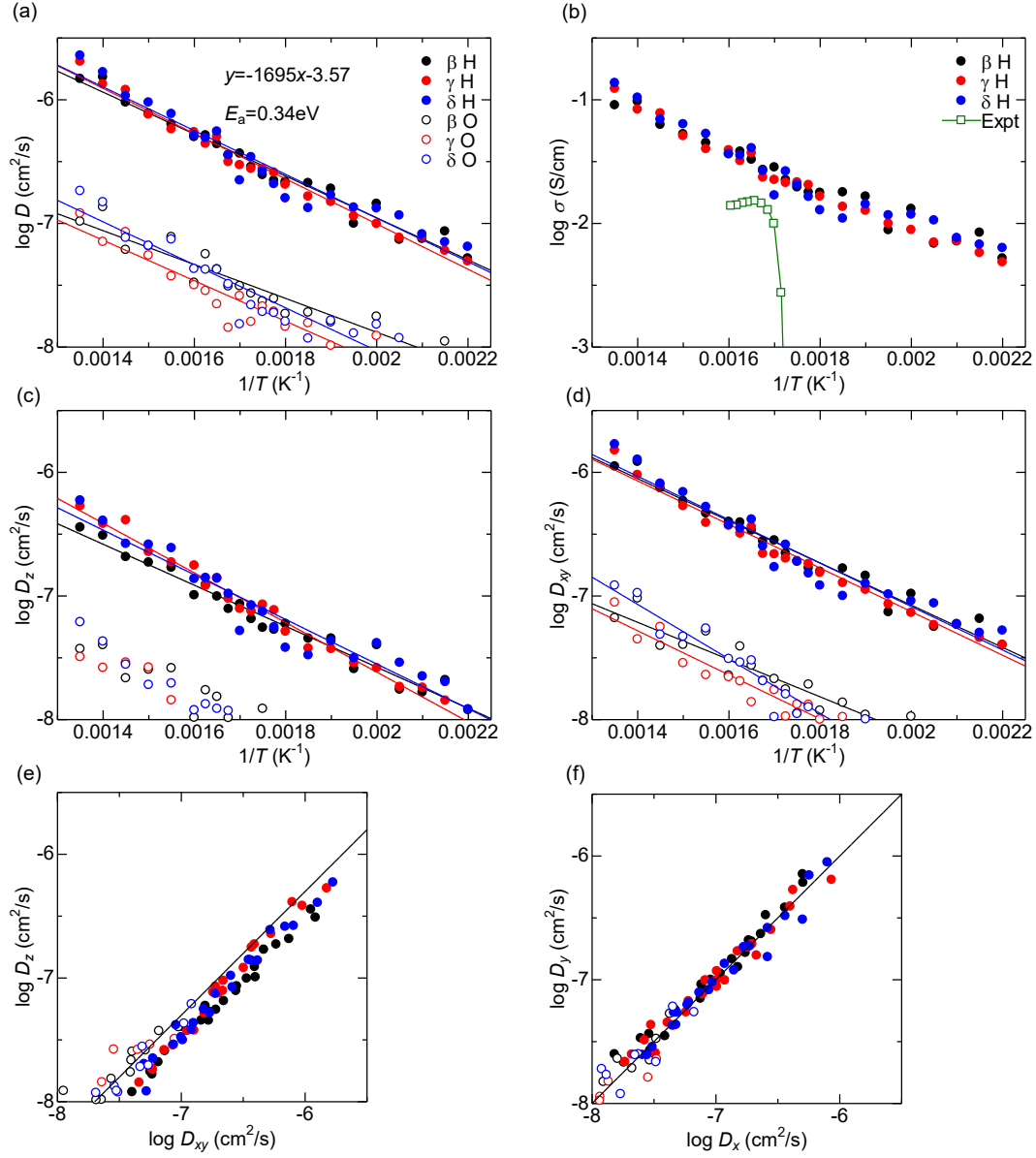


Fig. 6. Arrhenius plots of (a) the 3D tracer diffusion coefficient D , (b) implied conductivity derived using equation 10 as well as experimental values in Ref. [15] (the line for experimental results are solely to guide the eye), (c) tracer diffusion coefficient in the axial direction D_z , and (d) the 2D tracer diffusion coefficient in the equatorial plane D_{xy} of BLHO. Scattering plots, for BLHO, of (e) D_z versus D_{xy} and (f) tracer diffusion coordinates along the a and b axes, D_x and D_y , respectively. The regression equation and the activation barrier E_a is given for H in the β phase in (a). The lines in (a-d) are respective linear fits of H and O in β , γ , and δ phases, while the lines in (e,f) show the correlations in the isotropic case of $D_x = D_y = D_z$.

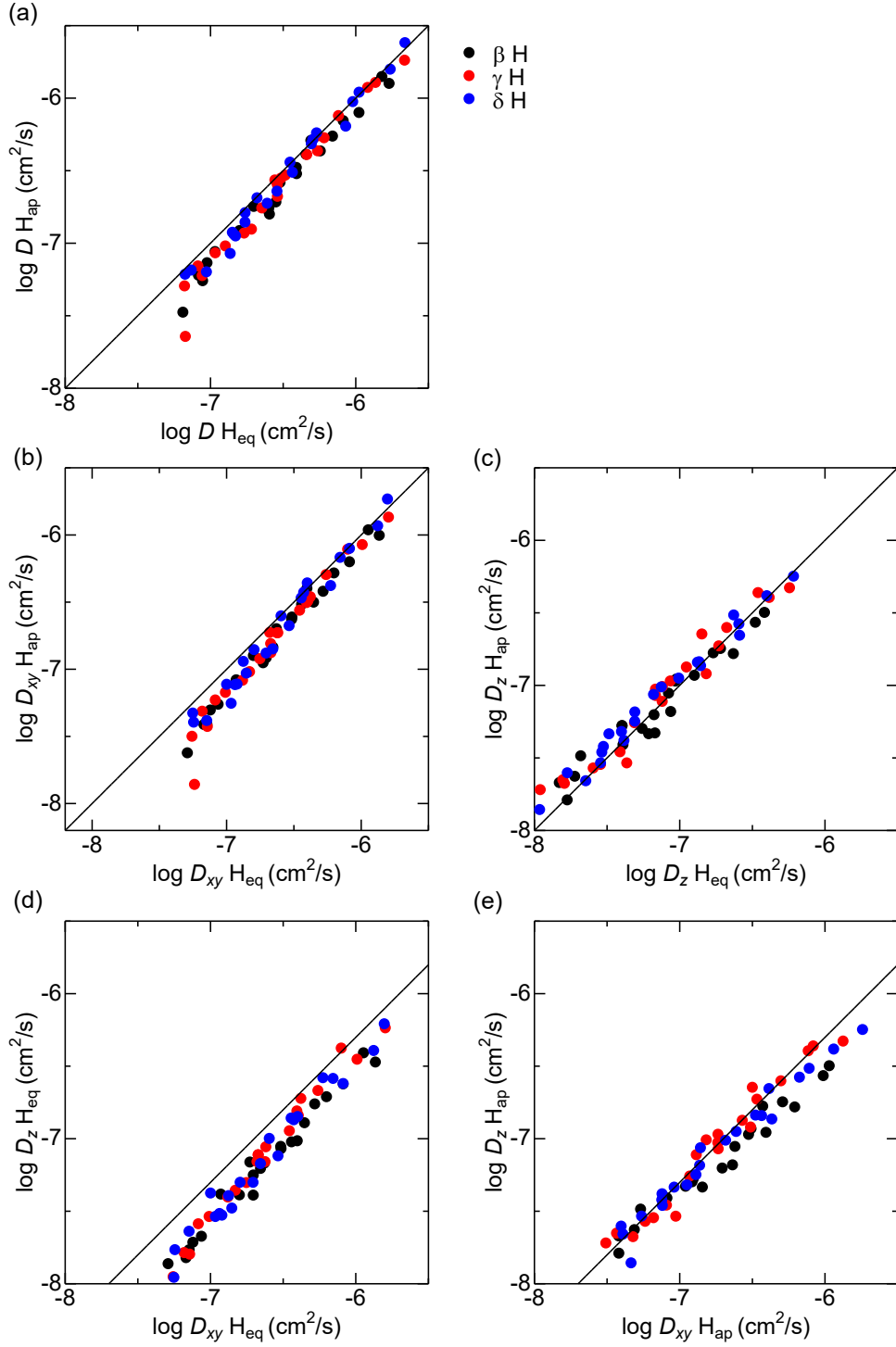


Fig. 7. Scattering plots of (a) D , (b) D_{xy} , and (c) D_z of apical H and equatorial H, respectively. D_z versus D_{xy} for (d) equatorial and (e) apical H, respectively, of BLHO. The lines in (a-c) are the case of same D between equatorial and apical H, and in (d,e) the isotropic situation of $D_x = D_y = D_z$.

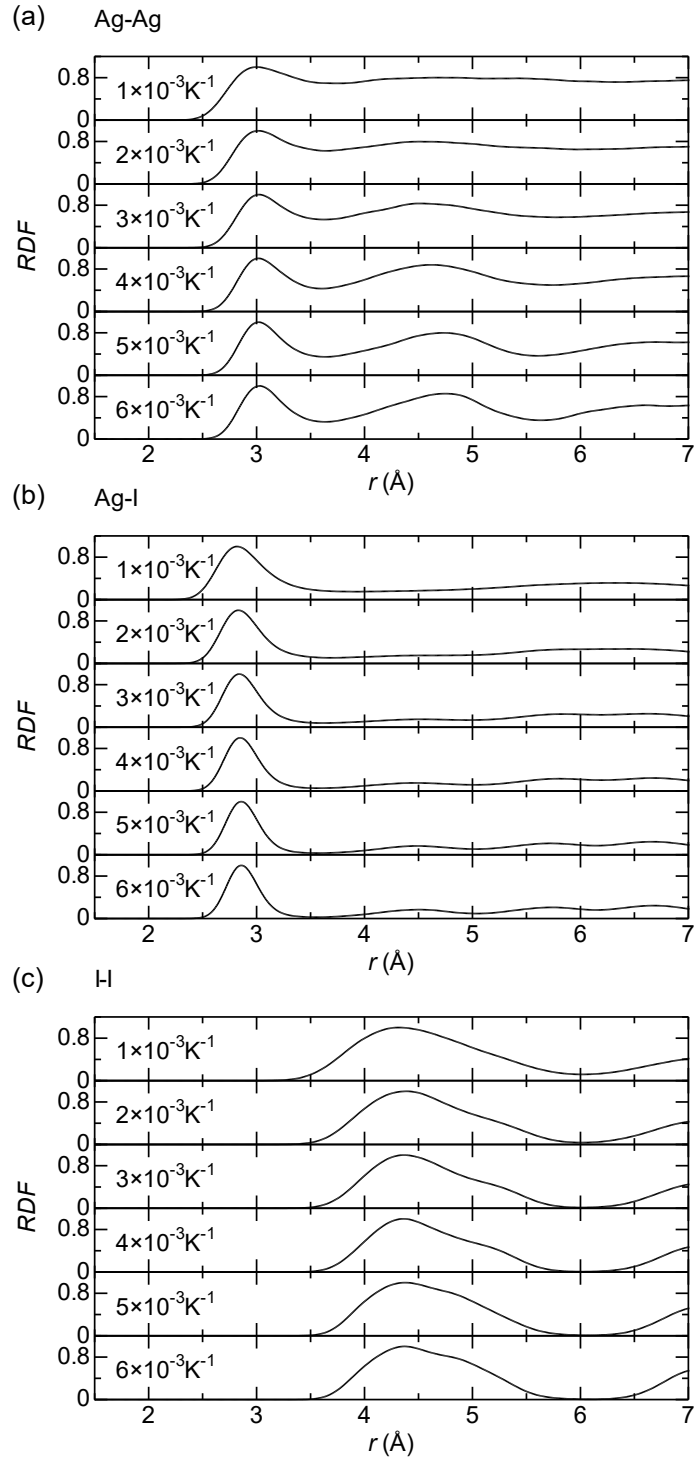


Fig. 8. (a) Ag-Ag, (b) Ag-I, and (c) I-I RDFs of AgI for various reciprocal temperatures.

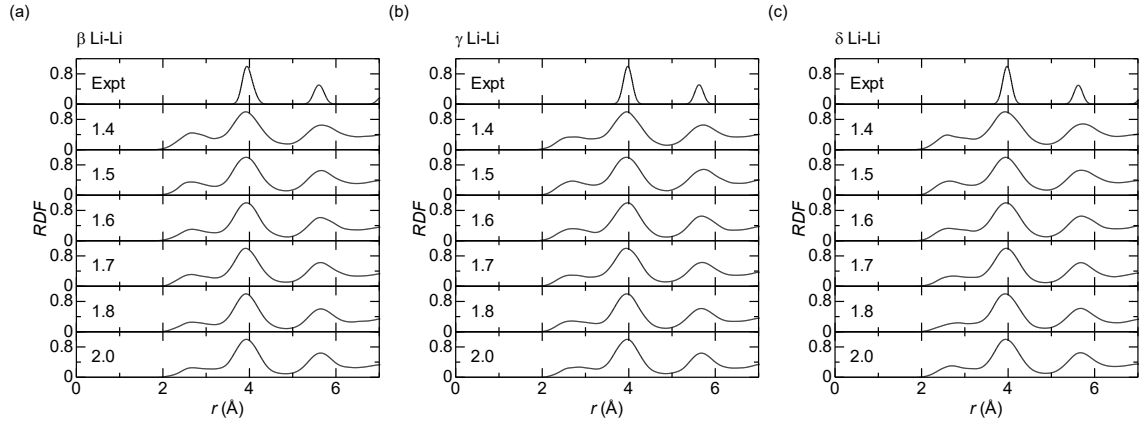


Fig. 9. Li-Li RDFs of (a) β -, (b) γ -, and (c) δ -BLHO. “Expt” is the RDF derived from refinements of experimental synchrotron X-ray diffraction results [15]. Numbers from 1.4 to 2.0 are the reciprocal temperature in units of 10^{-3} K^{-1} .

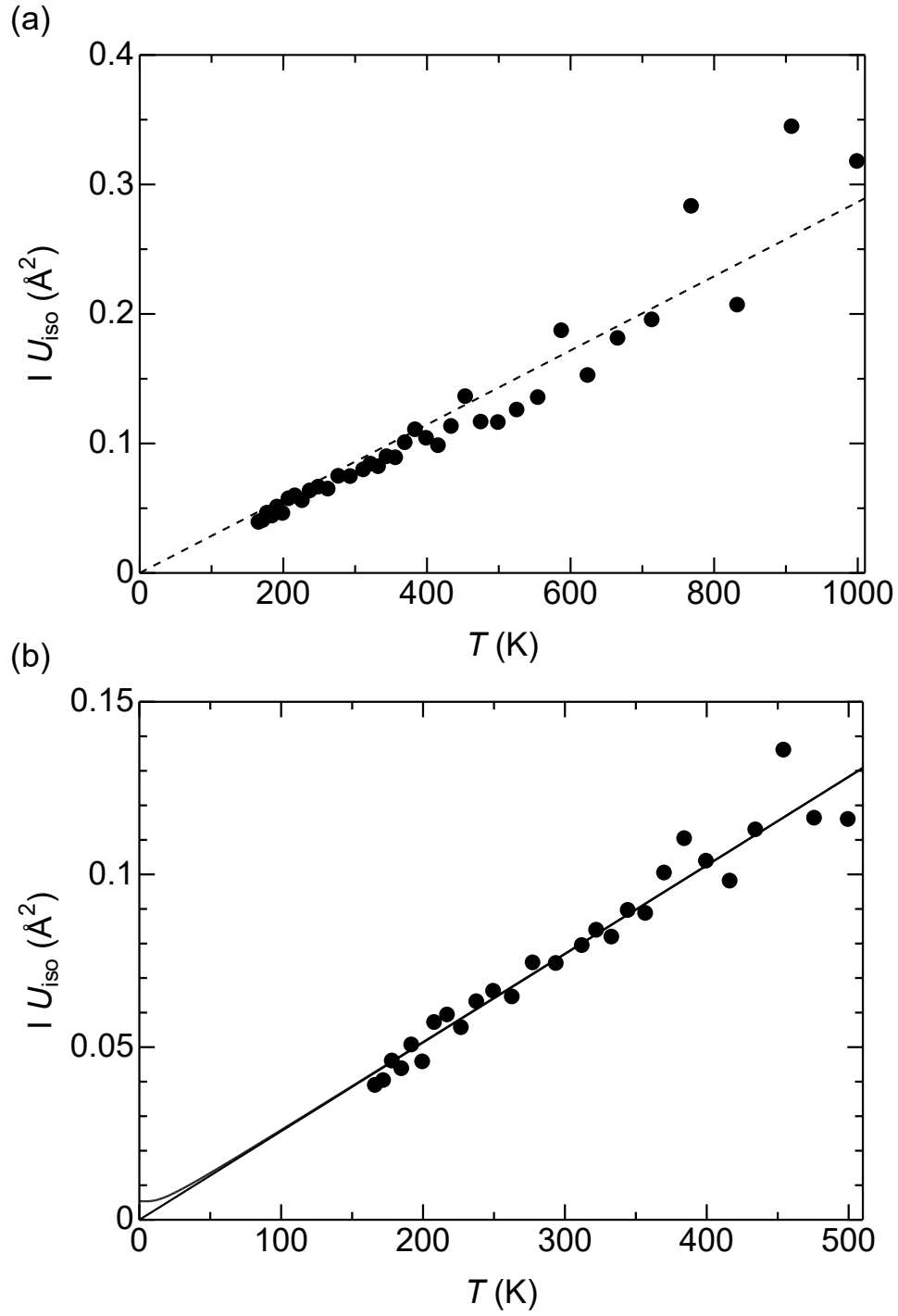


Fig. 10. The ADP U_{iso} of I in AgI for (a) all calculations and (b) calculations at $T \leq 500$ K. The straight lines are linear fits passing through the origin, while the curved line in (b) considers zero-point motion using the Einstein model.

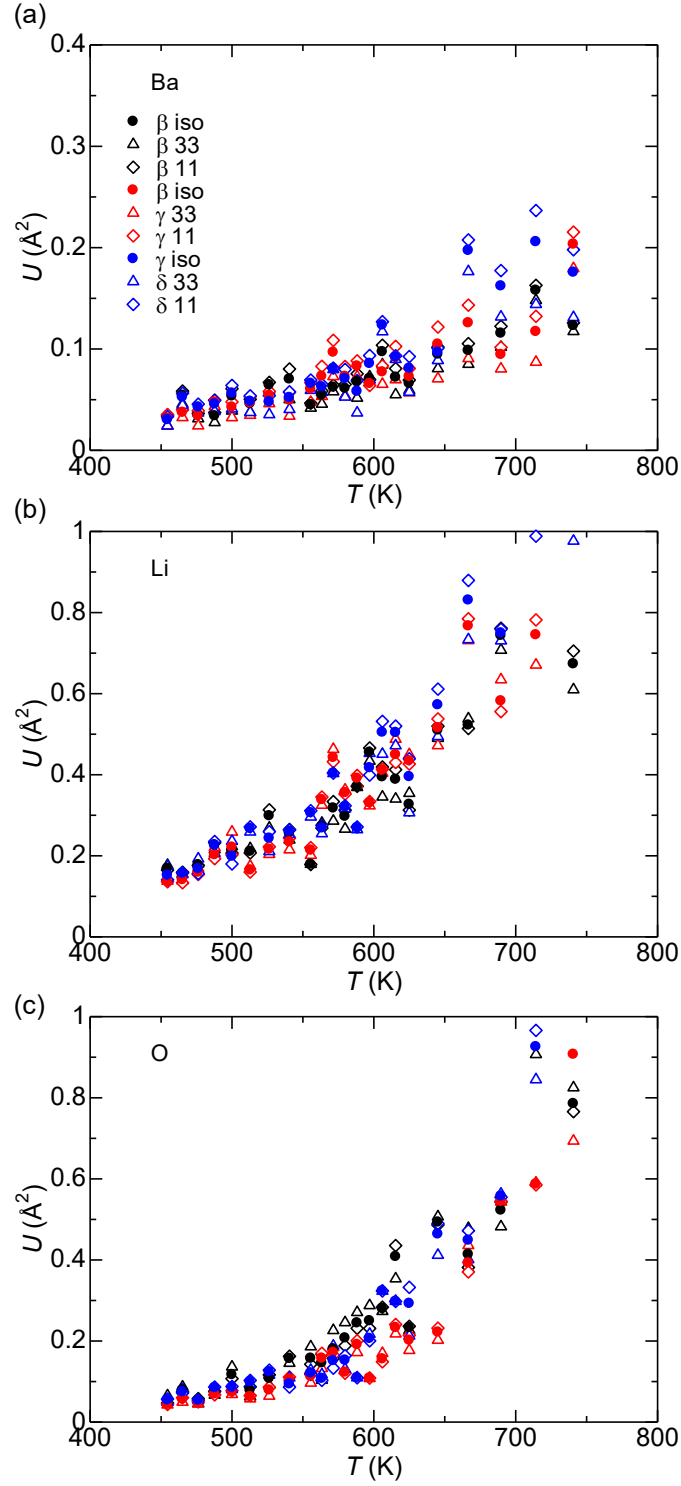


Fig. 11. ADP U^{11} , U^{33} , and U^{iso} values for (a) Ba, (b) Li, and (c) O calculated from MD simulations. Note that these ADP values do not reflect experimental values when atoms can migrate from their equilibrium positions.

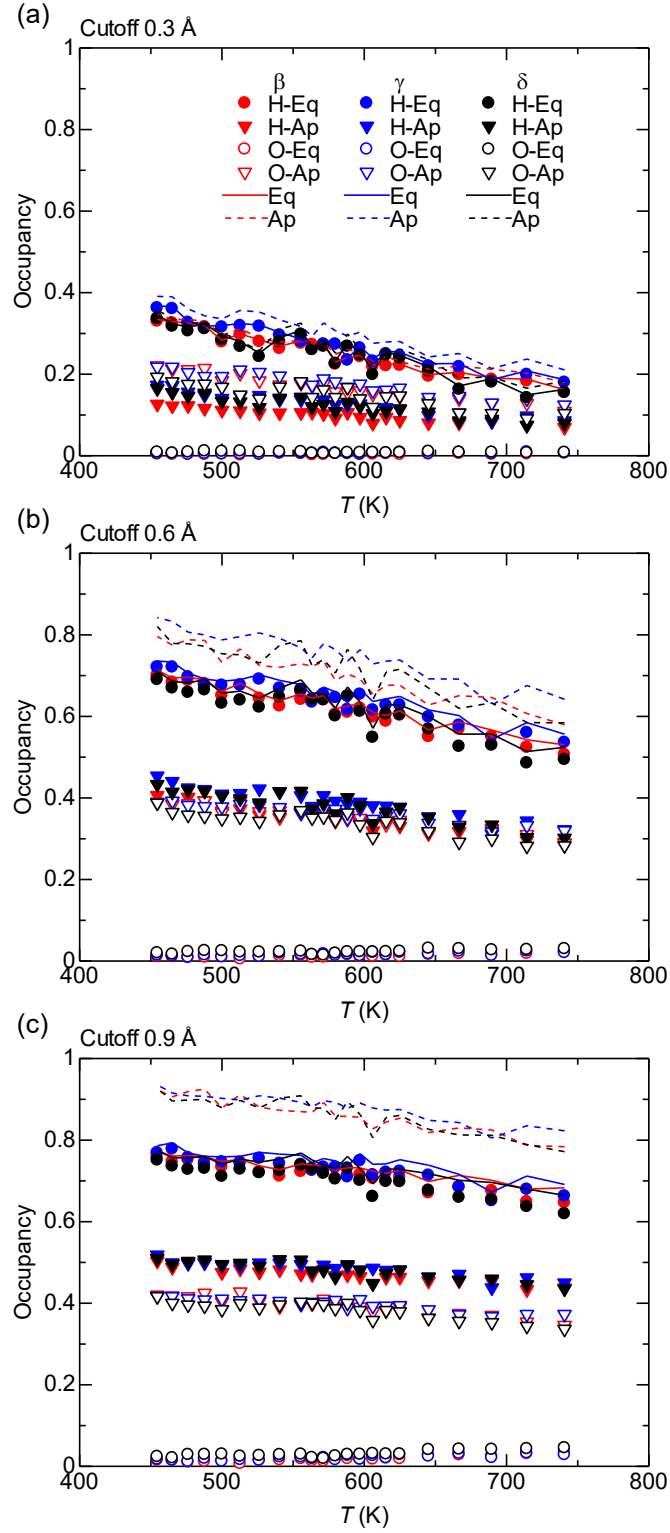


Fig. 12. (a-c) Site occupancies of O and H within a cutoff radius from the experimentally determined position. The lines indicate the occupancies of O and H combined.

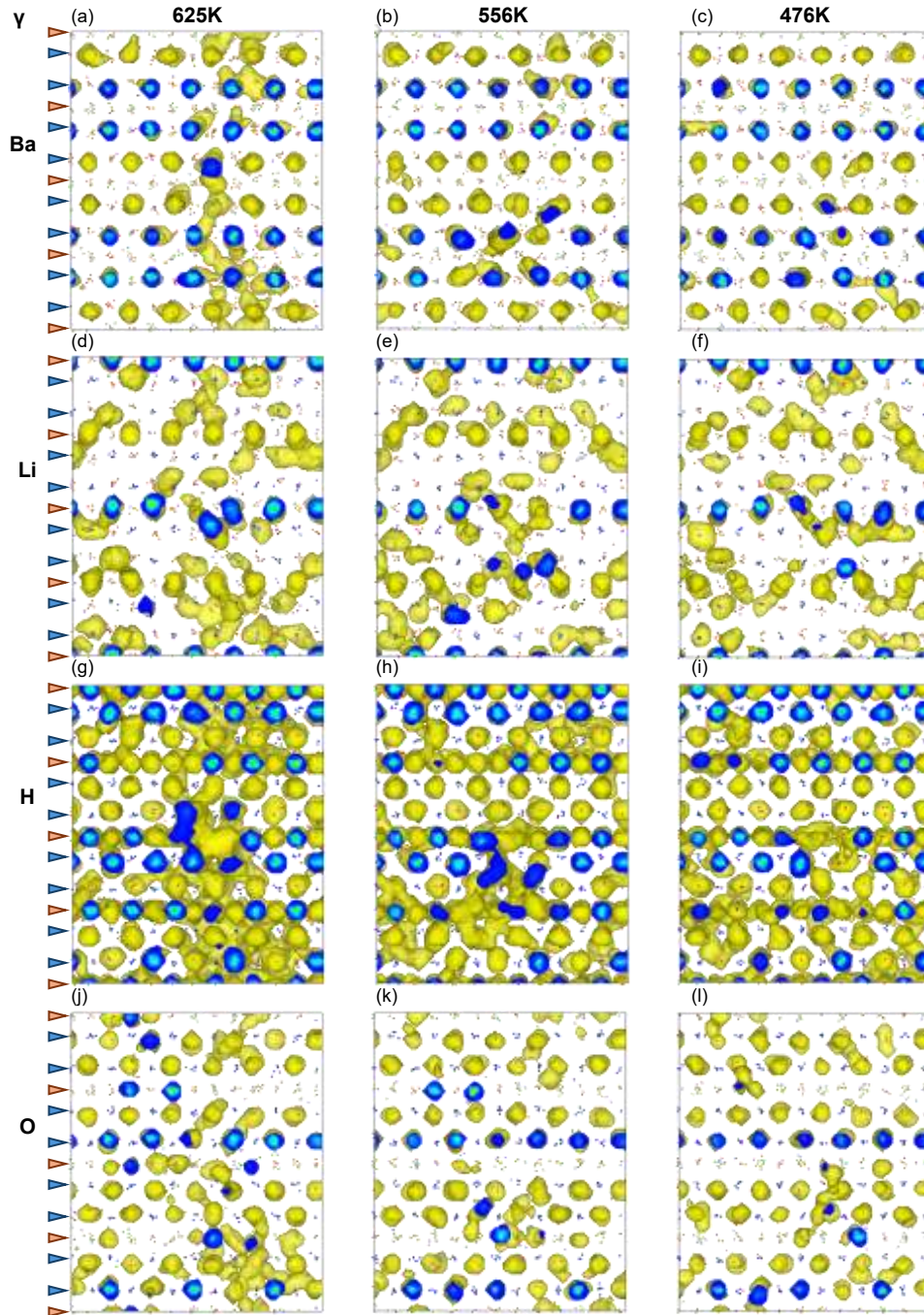


Fig. 13. (a-l) Isosurface plots showing the distribution of atom positions in γ -BLHO. The plots are projected normal to the a axis. The threshold is 0.001 based on the “isosurface” utility in the pfcc-extras package of Matlantis. Atom positions of a snapshot are given using very small blue, green, orange, and red dots for Ba, Li, H, and O, respectively. Blue wedges at the left indicate Li and equatorial H positions and the orange wedges are Ba and axial O/H positions.

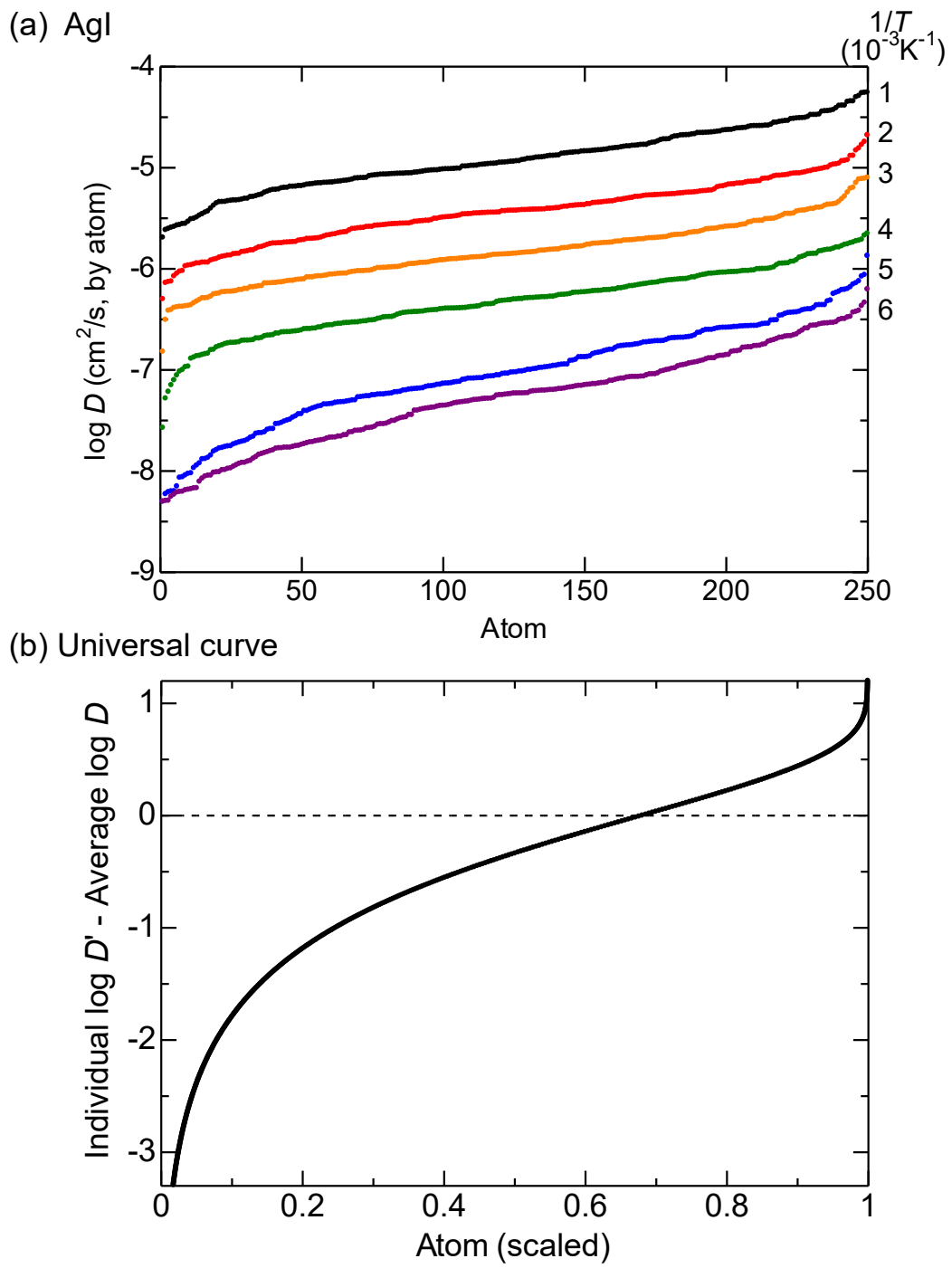


Fig. 14. (a) Sorted D values of each Ag atom for various temperatures in AgI. (b) The universal curve in the case of independent random walkers.

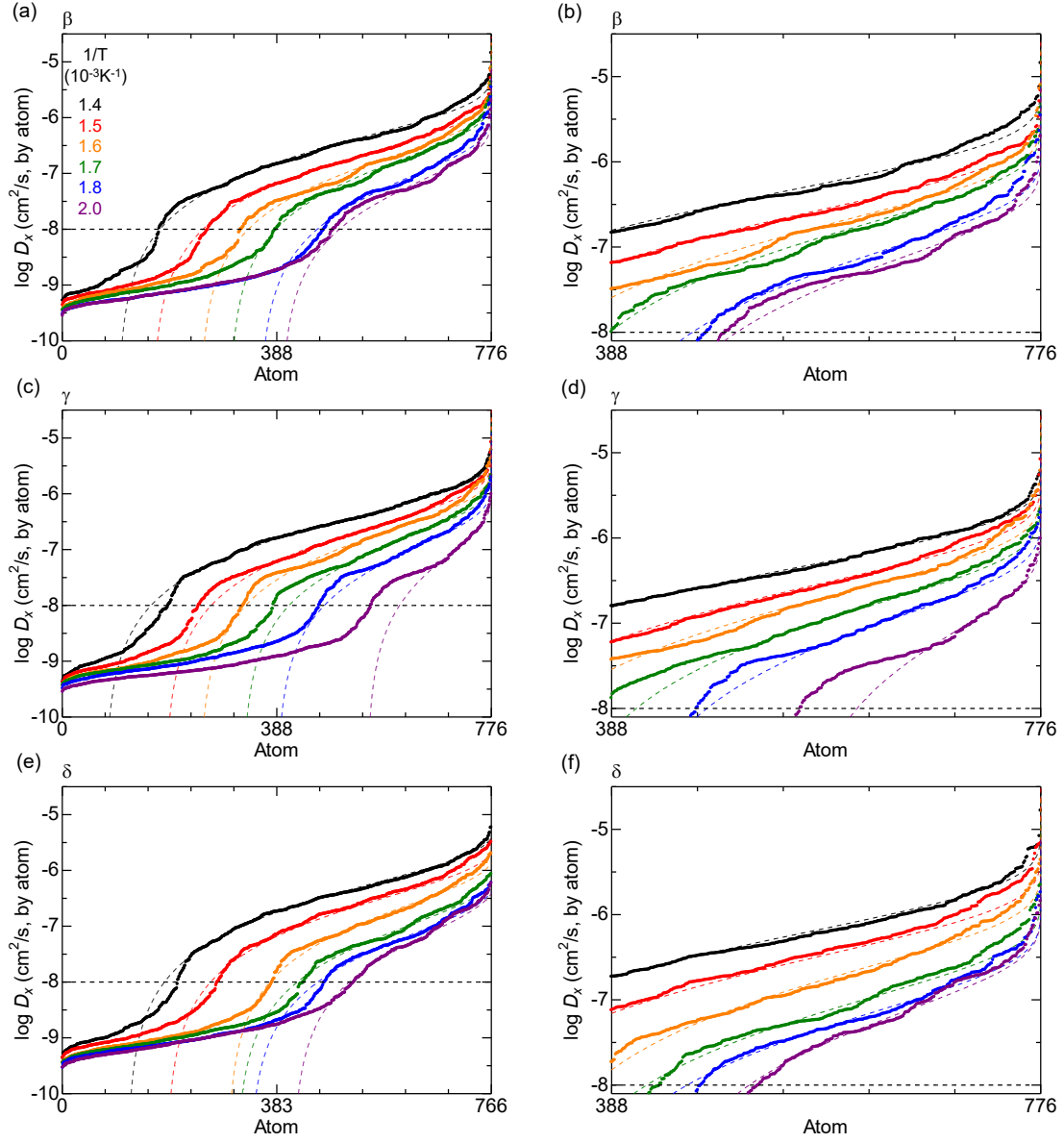


Fig. 15. Sorted D_x by atom for (a,b) β -, (c,d) γ -, and (e,f) δ -BLHO for various temperatures. Fits using the universal curve based on equations 28 and 29 are shown in dashed lines. (b,d,f) are enlargements of the top right portion of (a,c,e), respectively.

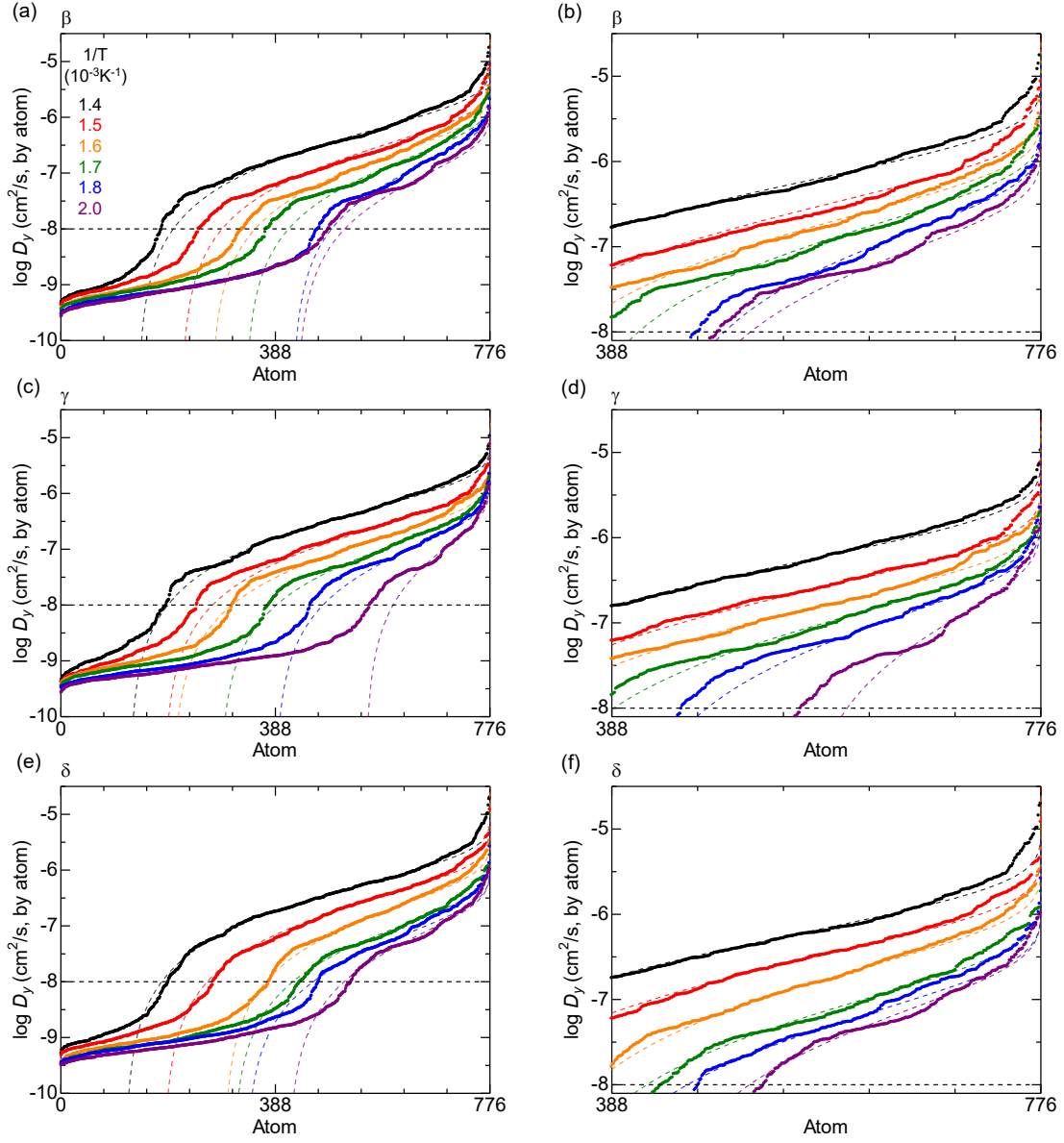


Fig. 16. Sorted D_γ by atom for (a,b) β -, (c,d) γ -, and (e,f) δ -BLHO for various temperatures. Fits using the universal curve based on equations 28 and 29 are shown in dashed lines. (b,d,f) are enlargements of the top right portion of (a,c,e), respectively.

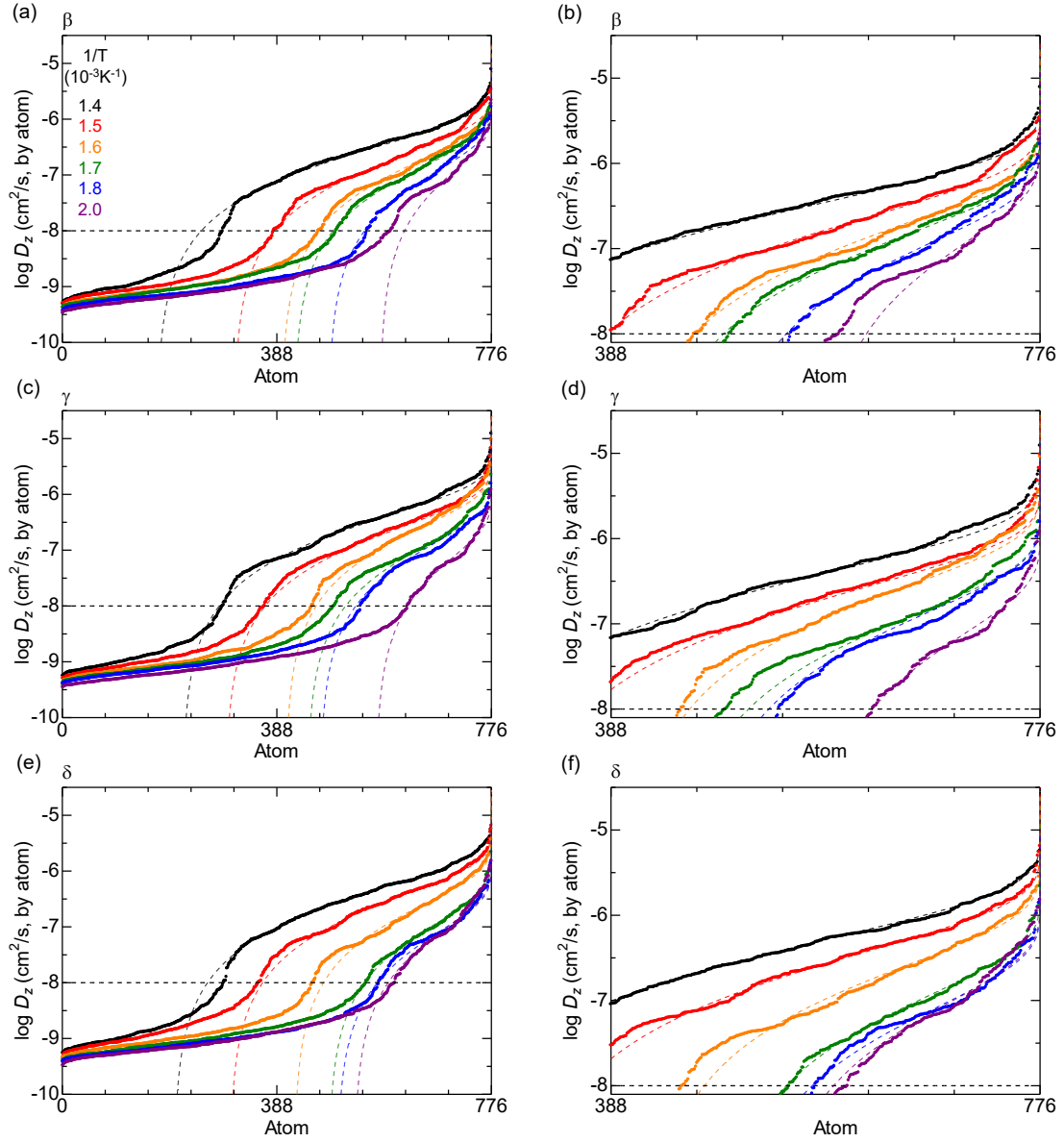


Fig. 17. Sorted D_z by atom for (a,b) β -, (c,d) γ -, and (e,f) δ -BLHO for various temperatures. Fits using the universal curve based on equations 28 and 29 are shown in dashed lines. (b,d,f) are enlargements of the top right portion of (a,c,e), respectively.

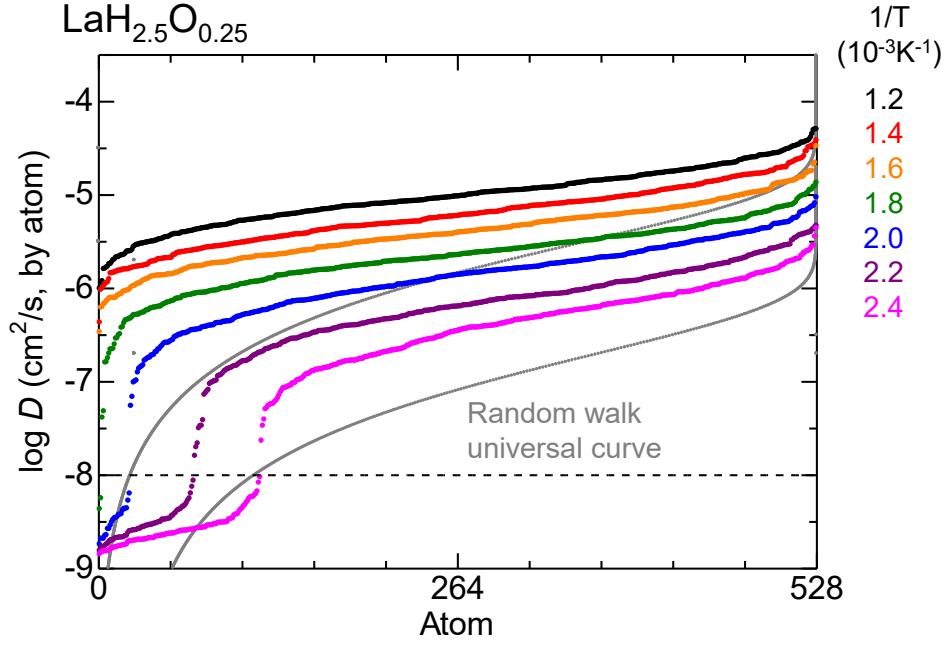


Fig. 18. Sorted D by atom for $\text{LaH}_{2.75}\text{O}_{0.125}$ based on MD simulations used in Ref. [30]. The random walk universal curve, which can be shifted vertically, is additionally shown. Their parameters in equations 28-29 are $(D_1, p_0) = (-5.5, 0)$ and $(-6.7, 0.05)$.

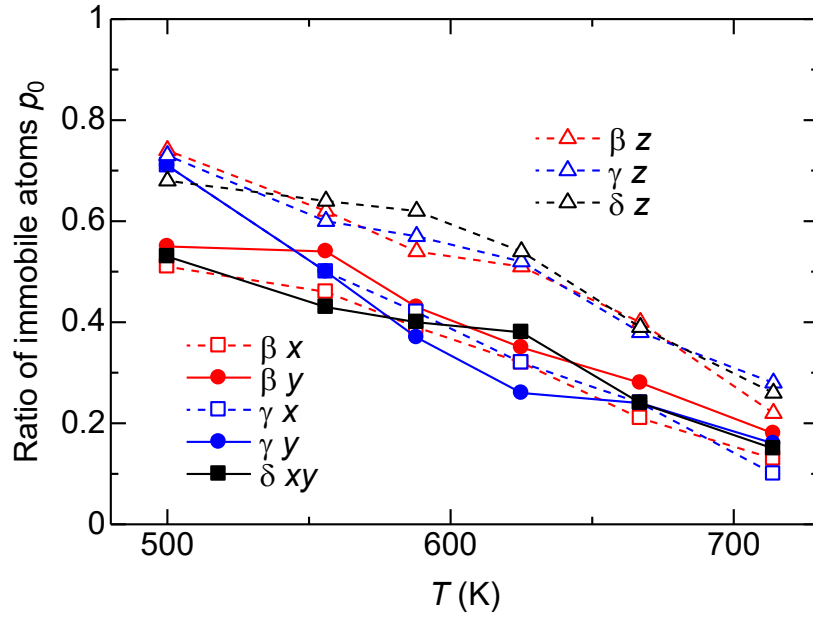


Fig. 19. The ratio of immobile atoms p_0 from the universal curve fits in Figs. 15-17. The lines are solely to guide the eye.

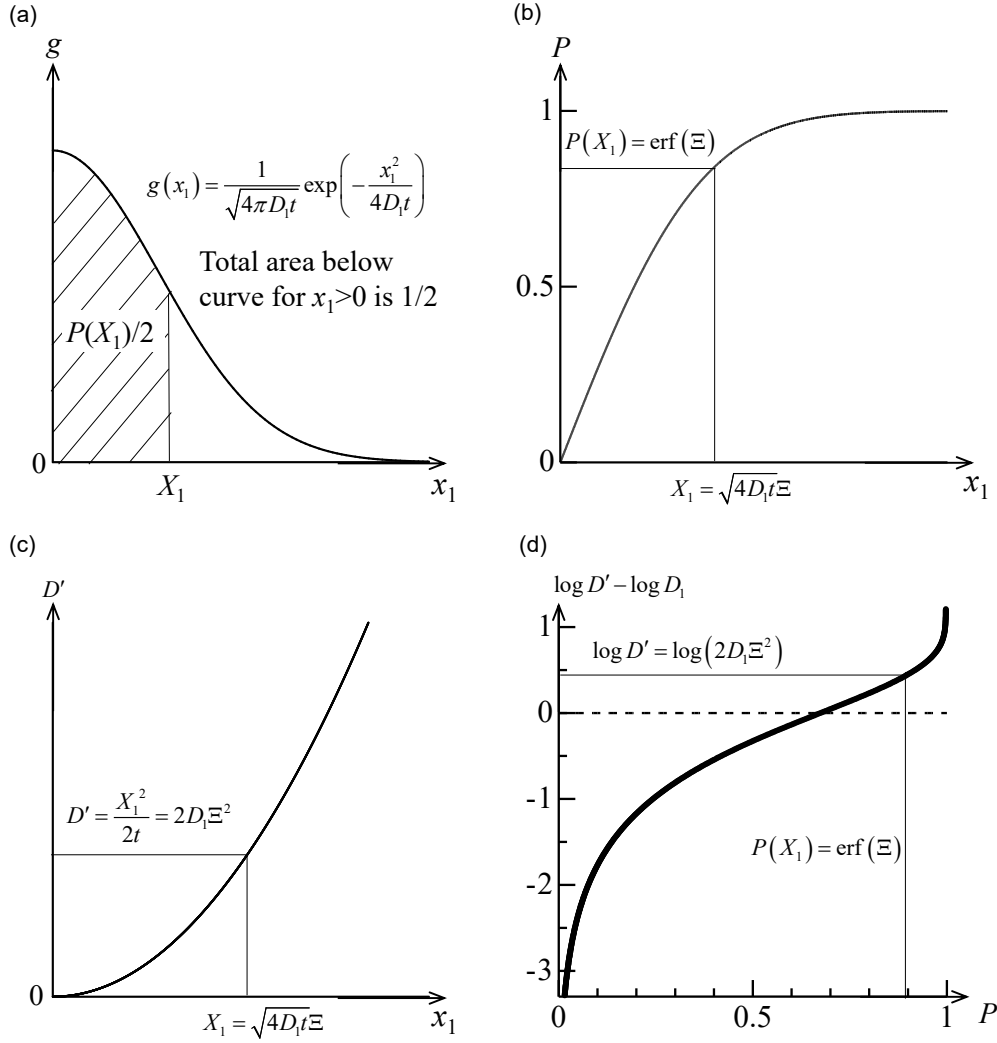


Fig. 20. Relations between various variables and functions used in derivation of the universal curve. (a-c) show equations 21, 24, and 25, respectively, and (d) combines results of equations 24 and 25.