

Article pubs.acs.org/cm

Structural, Chemical, and Dynamical Frustration: Origins of Superionic Conductivity in *closo*-Borate Solid Electrolytes

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Supporting Information

ABSTRACT: Li₂B₁₂H₁₂, Na₂B₁₂H₁₂, and their *closo*-borate relatives exhibit unusually high ionic conductivity, making them attractive as a new class of candidate electrolytes in solid-state Li- and Na-ion batteries. However, further optimization of these materials requires a deeper understanding of the fundamental mechanisms underlying ultrafast ion conduction. To this end, we use ab initio molecular dynamics simulations and density-functional calculations to explore the motivations for cation diffusion. We find that superionic behavior in $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ results from a combination of key structural, chemical, and dynamical factors that introduce intrinsic frustration and disorder. A statistical metric is used to show that the structures



exhibit a high density of accessible interstitial sites and site types, which correlates with the flatness of the energy landscape and the observed cation mobility. Furthermore, cations are found to dock to specific anion sites, leading to a competition between the geometric symmetry of the anion and the symmetry of the lattice itself, which can facilitate cation hopping. Finally, facile anion reorientations and other low-frequency thermal vibrations lead to fluctuations in the local potential that enhance cation mobility by creating a local driving force for hopping. We discuss the relevance of each factor for developing new ionic conductivity descriptors that can be used for discovery and optimization of *closo*-borate solid electrolytes, as well as superionic conductors more generally.

INTRODUCTION

All-solid-state batteries have gained significant attention as attractive replacements for current ion battery technologies based on liquid and polymer-gel electrolytes.¹ The replacement of an organic liquid electrolyte with an inorganic solid in these devices promises superior safety as well as mechanical and thermal stability. Properly chosen solid electrolyte materials would also enable the use of higher-voltage cathodes and metal anodes that could dramatically enhance the energy density of the battery. Although many candidates exist, none has achieved the combination of high conductivity, electrochemical stability, and low interfacial resistance necessary for widescale commercial deployment.²

Very recently, polyborate salts based on closo-borate $B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$, $CB_9H_{10}^{-}$, and $CB_{11}H_{12}^{-}$ anions have emerged as a new class of solid electrolytes with extraordinary ionic conductivity exceeding 10^{-1} S cm^{-1,3-10} In accordance with Wade's Rules,^{11,12} the *closo*-borate anions within these salts have (n + 1) skeletal electron pairs, where *n* represents the number of vertices. This electronic structure leads to an aromatic-like class of borohydrides that can be considered analogous to organic aromatic compounds, with similarly broad chemical tunability. The pseudoaromaticity of the closo-borate anions also ensures high chemical and thermal stability, with high electrochemical stability also expected. Although the superionic transition temperature in many of the pure polyborate materials is above the desired operating range, significant advances have been made in processing and chemical synthesis that have reduced operating temperatures and improved their viability for commercial all-solid-state batteries.^{6,13–20}

Aspects of the mechanism of ionic conductivity in polyborates were recently investigated in the context of $Na_2B_{10}H_{10}$, in which the apparent connection between anion dynamics and cation diffusion was specifically highlighted.²¹ Similar conclusions were reached in our previous study spanning all closo-borate and carbo-borate candidates using comprehensive ab initio molecular dynamics simulations (AIMD), in which we showed that explicitly constraining anion motion led to at least 3 orders of magnitude reduction in

Received: July 11, 2017 Revised: October 5, 2017 Published: October 11, 2017



Figure 1. Crystal structures of superionic $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$. Cubic unit cells are extracted from AIMD snapshots of superionic (a) fcc- $Li_2B_{12}H_{12}$ and (b) bcc- $Na_2B_{12}H_{12}$, demonstrating anion orientational disorder. Cations are omitted for clarity. Center inset shows an expanded view of the icosahedral $B_{12}H_{12}^{2-}$ anion, highlighting the B triad described in the text.

diffusivity.²² The importance of anion rotation for ionic conductivity was further suggested by nuclear magnetic resonance and quasielastic neutron scattering measurements of $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ showing that the superionic transition is accompanied by the facilitation of fast anion reorientations that are even faster than cation diffusion.^{10,23,24}

This influence of anion dynamics on cation mobility strongly suggests that cation motion is not dictated exclusively by the static structural characteristics of the crystal. Along these lines, several studies have pointed to the influence of soft-mode vibrations and rotations on atomic diffusion in fast ion conductors. ${}^{52,53,55-60}$ Others have shown that there can be a more specific interaction between the anion and the cation that transcends conventional Coulomb attraction and couples the anion and cation dynamics to one another. Indeed, the role of local chemical interactions beyond the Coulombic point-charge limit has long been proposed as important in superionic solids. Aniya et al. identified fluctuations in the nature of the anioncation chemistry as the key factor enabling diffusion in the superionic archetype AgI, and suggested that the phenomenon may be applied more broadly to a wide range of superionic materials.²³ ²⁷ Wood and Marzari further explored this concept using detailed electronic structure analysis to confirm that the bond fluctuations create intrinsic frustration that prevents cation ordering in AgI.²⁸ Recently, Adelstein and Wood performed a similar analysis on the halide-based solid electrolyte candidate Li₃InBr₆ and proposed that the same general physicochemical phenomenon plays a key role in enabling superionic conduction.²⁹ These factors are expected to be equally important for polyborate-based salts, and may be related to the proposed "paddlewheel" mechanism, whereby Li⁺ and Na⁺ cations in these systems can "dock" and "undock" with closo-borate anions as they rotate.4,5

Inspired by broad similarities among many superionic conductors and building on our previous investigation of trends in ionic conductivity in various polyborate salts,²² this paper focuses on a detailed analysis of intrinsic structural, chemical, and dynamical properties of these materials. We find that the density of accessible interstitial sites, the nature of the local bonding, and the soft anion dynamics all play a role in generating intrinsic disorder. We propose that the combination of multiple physical motivations creates a frustrated energy landscape that can fluctuate locally in space and time, which leads to an inability of the system to find a well-ordered and stable ground state. Instead, the cations continue exploring the complex energy landscape as they diffuse. We suggest how our

results can be used to devise descriptors for optimizing *closo*borate solid electrolytes, as well as to improve fundamental understanding of superionic conductivity.

METHODS

AIMD simulations were performed using the Quantum Espresso code³⁰ using the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional.³¹ Our calculations adopted a plane-wave cutoff of 30 Ry, sampling of the Brillouin zone at the Γ point, and ultrasoft Rappe-Rabe-Kaxiras-Joannopoulos (rrkjus) pseudopotentials³² downloaded from the Quantum Espresso Web site as part of the standard pseudopotential library.³⁰ The simulations employed the Car-Parrinello (CP) method³³ with a time step of $\Delta t = 6$ au (0.145 fs) and an effective electron mass of 400 au. The mass of hydrogen was set to that of deuterium. All AIMD simulations were performed at constant pressure within a canonical ensemble (NVT) and were thermostated with Nosé-Hoover chains to maintain the constant temperature.³⁴ Volumes were fixed to zero-temperature atomic relaxations unless stated otherwise. Prior to the thermostated production runs, all calculations were thermalized to the specified temperature, and then equilibrated within a microcanonical ensemble (NVE) for a minimum of 2 ps. Data was collected over a minimum of 50 ps at 800 K. This temperature ensured adequate statistical data collection while preserving the underlying mechanism.²² Intermittent Born-Oppenheimer steps using conjugate gradient minimization of the electronic degrees of freedom were performed every 0.5 ps to ensure that the electronic energy did not drift from the Born-Oppenheimer surface over the long CP trajectories.

All calculations for fcc packing of the B₁₂H₁₂ icosohedra in both the low-temperature α and high-temperature superionic β phases of Li₂B₁₂H₁₂ were performed on 208-atom supercells generated from a $(\sqrt{2} \times \sqrt{2} \times 1)$ repetition of the optimized unit cell. The bcc packing of the B₁₂H₁₂ icosohedra in Na₂B₁₂H₁₂ in the superionic $Im\bar{3}m$ space group was performed on 208-atom supercells generated from a $(\sqrt{2} \times \sqrt{2} \times 2)$ repetition of the optimized unit cell. The calculated cubic lattice parameters of 9.63, 10.05, and 7.980 Å for α -Li₂B₁₂H₁₂, β -Li₂B₁₂H₁₂, and superionic $Im\bar{3}m$ Na₂B₁₂H₁₂ are in good agreement with their respective experimentally measured lattice parameters of 9.58 Å (300 K), 10.02 Å (355 K), and 8.10 Å (675 K).^{17,24,35} Similar calculations were performed for K₂B₁₂H₁₂, Rb₂B₁₂H₁₂, and Cs₂B₁₂H₁₂, giving lattice constants of 10.71, 11.00, and 11.40 Å, respectively, in reasonable agreement with the experimental values of 10.63, 10.87, and 11.28 Å.^{36,37}

For static total-energy calculations of isolated $\rm Li_2B_{12}H_{12}$ and $\rm Na_2B_{12}H_{12}$ molecules, we used the DFT module implemented in the NWChem package. 38 Polarization consistent local basis sets at the double- ζ level with diffuse augmentation (aug-pcseg-1) were used for all atoms. 39,40

Activation energy barriers for cation diffusion were extracted from linear fits to Arrhenius plots of diffusion coefficients derived from AIMD at temperatures ranging from 400 to 900 K. Diffusion

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Figure 2. Cation diffusion pathways. (a) Left panel: Map of linear (red), trigonal (blue), and tetrahedral (green) interstitial sites in fcc-Li₂B₁₂H₁₂. Center panel: Isosurface of time-averaged cation density from AIMD showing the diffusion pathways. Right panel: Cross-sectional view of the time-averaged cation density contours. (b) Analogous quantities for bcc-Na₂B₁₂H₁₂. (c) Isosurfaces of time-averaged cation density for Li₂B₁₂H₁₂ upon volume contraction (-12% relative to the superionic β phase; top panel) and volume expansion (+14% relative to the superionic β phase; bottom panel). Isosurface values for the cation densities are identical for all cases. The time-averaged positions of the anion centers of mass are shown as small gray balls.

coefficients were obtained from the slope of the time dependence of the cation mean squared displacements using the Einstein relation. Full Arrhenius plots are shown in Figure S1 in the Supporting Information. Additional details can be found in ref 22.

RESULTS AND DISCUSSION

Structural Factors. $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ undergo a phase transition to a cation-disordered superionic phase at elevated temperatures. The superionic $Li_2B_{12}H_{12}$ structure (β phase) features an fcc arrangement of the anions, whereas the superionic $Na_2B_{12}H_{12}$ structure features a bcc arrangement.²⁴ Although the average anion positions adopt the high-symmetry cubic structures in both cases, the specific orientations of the anions are also known to disorder. Figure 1 shows a conventional unit cell taken from AIMD snapshots of the $H_{12}H_{12}^{-2-}$ molecule that forms the anion sublattice in each case. The bcc $Na_2B_{12}H_{12}$ structure exhibits higher ionic conductivity than fcc $Li_2B_{12}H_{12}$ at equivalent temperatures;^{13,35} this is consistent with reports favoring Na^+ conductivity over Li^+ conductivity in certain other systems.⁴¹

In a conventional solid-state diffusion picture, cation mobility requires the existence of open neighboring sites. The density of cation vacancies can be straightforwardly computed on the basis of the stoichoimetry of the material, as well as the total number of preferred interstitial sites. In ionic salts, the interstitial site preference can usually be predicted according to Pauling's rules,^{42,43} which are based on the ratio $R^+/R^$ between the radii of the cation (R^+) and the anion (R^-) within a hard-sphere, close-packed approximation. The cation radius should exceed the interstitial site radius to ensure contact with nearest-neighbor anions; otherwise, the coordination structure becomes unstable since it cannot effectively screen the anion– anion repulsion. As R^+/R^- increases, the cation coordination also increases, leading to lower theoretical limits for R^+/R^- of 0.155, 0.225, and 0.414 for trigonal, tetrahedral, and octahedral site occupation, respectively.

Theoretical cutoffs of R^+/R^- for different interstitial site preferences can be compared to the computed ratio for $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ based on the structures shown in Figure 1. To compute R^+/R^- , we use the reported R^+ of 0.59 Å for Li⁺ and 0.99 Å for Na^{+,44} and determine R^- by assuming hard-sphere packing of the anions in the appropriate fcc or bcc lattice. In the superionic phase, we find that R^+/R^- is 0.167 for $Li_2B_{12}H_{12}$ and 0.286 for $Na_2B_{12}H_{12}$ based on the computed $R^$ of 3.53 and 3.46 Å in the two respective materials (note that the radius of the molecular $B_{12}H_{12}^{2-}$ anion differs slightly for the Li and Na compounds due to the hard-sphere assumption). Accordingly, Li⁺ and Na⁺ are predicted to preferentially occupy trigonal and tetrahedral interstitial sites in their respective M₂B₁₂H₁₂ closo-borates. In the fcc crystal structure adopted by Li₂B₁₂H₁₂, there are four trigonal interstitial sites available per cation, implying 1/4 occupancy. In the bcc structure adopted by Na2B12H12, there are three tetrahedral sites per cation, implying 1/3 occupancy. Accordingly, both structures should have high vacancy concentrations that are intrinsic to the lattice without the need for extrinsic doping, opening possible pathways for cation diffusion. By contrast, M2B12H12 closoborates of larger K⁺, Rb⁺, and Cs⁺ cations are known to adopt an fcc lattice structure (similar to $Li_2B_{12}H_{12}$) with tetrahedral site occupation (similar to Na₂B₁₂H₁₂).⁴⁵ This combination leads to structures with all possible cation sites fully occupied; the lack of cation vacant sites for these materials may explain their poor ionic conductivity.²³

While having vacant sites is necessary to ensure a possible pathway for cation diffusion, it is not a sufficient condition for time scales.

Table 1. Cation Site Occupancy and Entropy Analysis

	tetrahedral		trigonal		linear			
$M \ in \ M_2 B_{12} H_{12}$	P_1	P ₂	P ₁	P ₂	P_1	P ₂	$\tilde{S}(k_{ m B})$	$E_{\rm a}~({\rm meV})^a$
Li	0.14	0.14	0.57	0.14	0.29	0.10	3.00	136
Li (contracted)	0.03	0.03	0.87	0.22	0.10	0.03	2.67	910
Li (expanded)	0.09	0.09	0.45	0.11	0.45	0.15	3.00	190
Na	0.60	0.20	0.24	0.04	0.16	0.04	3.16	137
K	0.95	0.95	0.05	0.01	0.00	0.00	0.43	high
Rb	0.96	0.96	0.04	0.01	0.00	0.00	0.37	high
Cs	0.92	0.92	0.07	0.02	0.01	0.00	0.68	high
^a Computed activation er	nergy barriers ((E_a) from ref 22	; see Figure S1	in Supporting	Information. "	High" indicate	s no diffusion o	bserved on AIME

superionic behavior. In fact, the premise that ions occupy a single type of interstitial site can itself become flawed in the limit of liquid-like cation diffusivity. Instead, superionic behavior implies that the energy landscape must have low-barrier pathways for diffusion, including any intermediate metastable sites that may be visited. This liquid-like diffusion behavior can be observed in our AIMD simulations of $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$, from which the associated pathways and site occupancies were directly mapped. Figure 2a,b shows the time-averaged cation density for the two materials. For both cases, although the overall cation site preference matches the predictions using Pauling's rules (trigonal sites for $Li_2B_{12}H_{12}$ and tetrahedral sites for $Na_2B_{12}H_{12}$), the occupation density forms a nearly continuous diffusion pathway across multiple linear, trigonal, and tetrahedral interstitial sites.

Although both materials exhibit diffuse occupation densities, upon comparing the density cross sections in Figure 2a,b, it becomes clear that Na⁺ exhibits a stronger preference than Li⁺ for a particular type of interstitial site. This is consistent with the calculated R^+/R^- for the two materials. In particular, R^+/R^- = 0.167 for the superionic phase $Li_2B_{12}H_{12}$ is very close to the lower limit of 0.155 for a trigonal site. This implies that trigonal site occupancy should be only weakly preferred over linear site occupancy, permitting ready diffusion between trigonal and linear sites. Note that the continuous diffusion pathway also passes through tetrahedral sites, leading to occupancy of all three types of interstitial sites. It follows that values of $R^+/R^$ that lie close to the boundary between the Pauling-predicted interstitial occupancies may have a natural advantage for promoting conductivity, since they minimize clear interstitial site preferences and create degenerate minima in the overall energy landscape. On the other hand, for Na2B12H12, the calculated $R^+/R^- = 0.286$ lies further from the lower limit of 0.225 for a tetrahedral site, which gives a stronger preference of the tetrahedral site over other sites.

To further confirm the relevance of the R^+/R^- ratio for promoting a flat energy landscape for cation diffusion, we adjusted the effective R^- size by varying the volume of $\text{Li}_2\text{B}_{12}\text{H}_{12}$. As shown in the top panel of Figure 2c, reducing the volume by 12% effectively increases R^+/R^- , leading to a far stronger preference for trigonal sites over linear sites, as predicted (this reduced volume matches that of the lowtemperature α phase, which shares the fcc structure of the superionic β phase but exhibits ordered cation and anion configurations). On the other hand, if we decrease the $R^+/R^$ ratio by increasing the volume by approximately 14% relative to the superionic β phase, the linear sites become far more preferred over the trigonal sites, as shown in the bottom panel of Figure 2c. We can get a clearer picture of the interstitial site occupancy by extracting probabilities from the densities in Figure 2, as shown in Table 1. The positions of interstitial sites were first calculated using the instantaneous positions of the anion centers of mass in the AIMD trajectories. Site occupancies were then computed by weighting the distance between the cation and adjacent interstitial sites by a normalized Gaussian function (see Supporting Information for details). As one type of relative probability measure, we consider the probability (P_1) of a cation occupying each type of interstitial site (linear, trigonal, and tetrahedral). This quantity reflects the relative site preference from the point of view of each cation. Defining N_i and n_i as the number of total and occupied interstitial sites of type *i*, respectively (*i* = linear, trigonal, tetrahedral), we can write $P_1^i = n_i / \sum_i n_i$.

As shown in Table 1, changing the volume of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ results in the cation's shifting from a strong trigonal site preference ($P_1 = 0.87$) at small volume to a weak linear site preference ($P_1 = 0.45$) at large volume, with the superionic $\text{Li}_2\text{B}_{12}\text{H}_{12}$ volume lying in between. Na₂B₁₂H₁₂ exhibits some preference for tetrahedral sites ($P_1 = 0.60$), but this preference increases to $P_1 \ge 0.92$ for the nonconductive K, Rb, and Cs variants.

However, P_1 obscures the fact that each type of interstitial site exists in a different overall concentration in the lattice; accordingly, we also compute a second probability P_2 that represents the average cation occupation of each individual interstitial site. This quantity is calculated from the point of view of the *site* rather than the cation, and is given by $P_2^i = n_i/N_i$.

For superionic β -Li₂B₁₂H₁₂, the probabilities P_2 for the three different site types are nearly the same, indicating that all individual tetrahedral, trigonal, and linear sites are occupied with near equal probability. This matches the distributions in Figure 2. Larger probability differences among sites are observed for the volume-contracted Li₂B₁₂H₁₂ case. However, the probabilities in Table 1 do not account for the configurational entropy arising from the many different ways ions can be patterned onto the multiplicity of sites and site types. Accordingly, we use our site probabilities P_2 to introduce a new metric based on the configurational entropy \tilde{S} of a mixture of cations and vacancies, patterned onto a lattice of available interstitial sites. Specifically, we define \tilde{S} as

$$\tilde{S} = -k_{\rm B} \sum_{i} \left(\frac{N_i}{n} \right) [P_2^i \ln P_2^i + (1 - P_2^i) \ln(1 - P_2^i)]$$
(1)

Here $n = \sum_{i} n_i$ is the total number of occupied sites of all types, where the index *i* runs over the three types of interstitial sites

that we consider (linear, trigonal, and tetrahedral). A full derivation of eq 1 can be found in the Supporting Information. We caution that \tilde{S} carries some temperature dependence, in part because the underlying energy landscape itself depends on temperature, and in part because thermal broadening (combined with our Gaussian weighting function) creates ambiguity in the determination of instantaneous site probabilities, particularly at higher temperatures. Nevertheless, systematic comparisons performed at the same temperature should have physical significance.

We point out that \tilde{S}_{i} , which is derived from P_{2i} , implicitly considers two factors. The first factor is the multiplicity of different types of sites, weighted by their respective concentrations in the lattice structure; this is accounted for by the summation over the index *i*. This factor should correlate with the number of available diffusion pathways, since ions typically hop via networks that consist of different types of interstitial sites. The second factor considered by S is the multiplicity of individual sites within each type. In eq 1, each type of site is treated as a sublattice onto which cations and vacancies can be patterned, with the cation concentration determined by the corresponding site probability P'_2 . This factor accounts for the different ways of arranging the cations on the sublattice, which is related to the breadth of the available phase space. For a given structure and stoichiometry, the quantity \tilde{S} increases when many sites are available, each of which is occupied with similar probability; this implies a flatter energy landscape. At the opposite extreme, a zero value of \tilde{S} implies a completely ordered configuration with full occupation of only one type of site.

We suggest that \tilde{S} , which provides a thermodynamic measure of the availability and accessibility of local minima in the energy landscape, can also act as a potential predictor of structures that may facilitate rapid local cation mobility. Although the value does not explicitly quantify the barrier heights or available pathways that play a role in determining diffusion kinetics, it contains information about the complexity of the energy landscape in terms of the *density* of closely spaced accessible minima (i.e., interstitial sites with sufficiently low energies) in the available phase space. It is therefore reasonable to assume that systems with high values of \hat{S} should have a higher likelihood of exhibiting connected pathways of low-barrier transitions. In this regard, \tilde{S} should correlate with a high probability of facile kinetics. One advantage of this timeaveraged statistical approach for describing the shape of the energy landscape is that it avoids conventional energetic analyses based on single-ion hopping, which are sensitive to the instantaneous configurations of the surrounding cations. Moreover, using \tilde{S} in lieu of direct computation of diffusion coefficients can have practical advantages in molecular dynamics simulations, since relative site occupancy should equilibrate much faster than the statistical convergence of longranged atomic displacements.

Values of \tilde{S} at T = 800 K for each of our tested systems are shown in Table 1. As expected, the nonconductive systems containing K, Rb, and Cs have very low \tilde{S} , since these systems exhibit almost exclusively tetrahedral site occupancy. On the other hand, the superionic materials have values of \tilde{S} close to $3k_{\rm B}$. Furthermore, the calculated \tilde{S} of ${\rm Li}_2{\rm B}_{12}{\rm H}_{12}$ at different volumes agrees well with the volume dependency on the Li diffusivity. We point out that ${\rm Na}_2{\rm B}_{12}{\rm H}_{12}$ has the highest \tilde{S} among the compounds we studied, implying a high density of available sites that is consistent with a low barrier and a high experimental conductivity. By contrast, an analysis of $Na_2B_{12}H_{12}$ based only on the probabilities in Table 1 would have detected a strong preference for tetrahedral site occupancy while failing to consider the high multiplicity of such sites in the bcc structure. Instead, our use of \tilde{S} as a descriptor presents a more complete picture, suggesting that the high density of tetrahedral sites should be beneficial for conductivity. Indeed, the wealth of tetrahedral sites within the bcc structure is known to form a highly connected pathway,⁴⁶ which can facilitate cation diffusion. Note that, within our interpretation, the high \tilde{S} values in the $\mathrm{Li}_2B_{12}H_{12}$ and $\mathrm{Na}_2B_{12}H_{12}$ structures have fundamentally different microscopic origins: in Li₂B₁₂H₁₂, the high \tilde{S} arises from the simultaneous accessibility of multiple types of sites with similar energies; in Na2B12H12, it can be traced predominantly to the high number of available tetrahedral sites in the structure.

Chemical Factors. Although \tilde{S} is useful as a thermodynamic descriptor for structures that may be intrinsically conducive to superionic behavior, it focuses on the energy and dispersion of occupied interstitial sites. It does not contain any explicit information about the shape of the energy landscape, including transition states and anharmonic features that help to determine the kinetics of low-barrier transitions. In this section, we explore such factors and their underlying physicochemical origins by considering the nature of the interaction between the anion and cation more directly.

We previously showed that ultrafast diffusion in *closo*-borates is connected to correlated diffusive events, which originate from the introduction of "coordination defects" that alter the standard cation coordination about an anion.²² These defects are necessary precursors for cation diffusion, and may be introduced extrinsically via doping, or else spontaneously by cation hopping to form a Frenkel-type defect. Note that examining diffusion from a local coordination perspective prompts a more liquid-like view of conduction, which may be more appropriate for examining ultrafast ion conduction than conventional solid-state approaches based on rare diffusive events.²⁹

Within this view, the ease of forming coordination defects is closely related to the barriers for cation migration, since both reflect the shape of the energy landscape. As we will show, cations that are nearest the anions tend to pattern themselves according to the icosahedral symmetry of the anion, a consequence of the local chemical interaction between the two. For Li₂B₁₂H₁₂ and Na₂B₁₂H₁₂, this symmetry is incompatible with the preferred symmetry of the occupied lattice interstitial sites. We propose that this incompatibility introduces an intrinsic frustration that lowers the barrier for coordination defect formation, thereby aiding cation migration. Such frustration has been discussed previously for superionic halides,^{25,28,29} where covalent character in the anion-cation interaction prompts local bond symmetry preferences that are incongruous with the distribution of electrostatically preferred interstitial sites.

We begin with a discussion of the ease with which coordination defects are formed in superionic $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$. We first calculate from our AIMD results the radial distribution function g(r) for the anion-cation pairs, as well as its integral to obtain the corresponding coordination numbers n(r). The results are shown in Figure 3a. The peak of g(r) is broad and asymmetric. It also exhibits a non-negligible population in the long tail region and a weakly defined second peak, reflecting liquid-like structure with primarily short-range



Figure 3. Local coordination environments. (a) Anion–cation radial pair distribution functions g(r) (—) and corresponding integrated coordination numbers n(r) (---). The center of mass position of the $B_{12}H_{12}^{2-}$ molecule is used as the anion center. (b) Instantaneous first-shell coordination numbers for superionic $L_{i2}B_{12}H_{12}$ (red) and $Na_2B_{12}H_{12}$ (blue) along with volume-contracted $Li_2B_{12}H_{12}$ (orange; see text). Cutoffs for the first shell correspond to the distance *r* at which g'(r) = 0: 5.5, 6.0, and 5.3 Å for $Li_2B_{12}H_{12}$, $Na_2B_{12}H_{12}$, and volume-contracted $Li_2B_{12}H_{12}$, respectively.

order. As a result, the anion-cation coordination number does not show a clear plateau, suggesting a possibly large variation of local coordination environments. The average first-shell coordination of cations around an anion is calculated to be 6.3 and 8.2 for $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$, respectively; however, the distribution of instantaneous coordination numbers for the superionic materials is widely distributed from the average value, as shown in Figure 3b. In contrast, the weakly conducting, volume-contracted Li₂B₁₂H₁₂ (shown in orange) shows a much sharper distribution that is closer to a typical ionic salt. The large variation in instantaneous coordination number for the superionic Li₂B₁₂H₁₂ and Na2B12H12 phases can be interpreted in terms of a flexible coordination environment. Accordingly, the energy cost of creating an off-stoichiometric local configuration that deviates from the average coordination number should be comparatively small

To explore the nature of the cation–anion interaction more directly, we first rely on static total-energy computations of stoichiometric $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ molecules in isolation. The results, shown in Figure 4, allow us to temporarily exclude the influence of the lattice environment and focus instead on the cation–anion pairwise interaction. The potential energy landscape for the cations near an anion was mapped by first relaxing a single $\text{B}_{12}\text{H}_{12}^{-2}$ anion with one Li⁺ cation to form a $\text{LiB}_{12}\text{H}_{12}^{-1}$ ion. In the optimized $\text{LiB}_{12}\text{H}_{12}^{-1}$ molecule, Li⁺ binds to the center of a triad of B atoms (see Figure 1) at an equilibrium distance of 3.2 Å from the center of mass of the anion (corresponding to 1.86 Å from the centroid of the B triad). This Li⁺ cation and its three closest B atoms were then kept fixed, and a second Li⁺ was added to achieve a charge-



Figure 4. Potential energy landscape of cation—anion interactions. (a, b) Relative potential energy as a function of the anion—cation distance *r* and cation—anion—cation angle θ along the path shown in the center-left schematic for (a) Li₂B₁₂H₁₂ and (b) Na₂B₁₂H₁₂. Panel c shows the corresponding energy profile as a function of θ at the optimized distance *r*. (d) Difference between the potential energy after and before full anion relaxation, plotted as a function of *r* at fixed $\theta = 180^{\circ}$ for Li₂B₁₂H₁₂ (red) and Na₂B₁₂H₁₂ (blue); see text for details. (e) Cross-sectional view of total charge density in the plane containing two Li and four B atoms (B1–B4; see schematic at lower left). The two Li⁺ cations at the left and right are positioned at distance) from the anion center, respectively.

neutral configuration, with all remaining atoms fully relaxed. A similar procedure was followed for Na⁺ cations interacting with $B_{12}H_{12}^{2-}$, which bind with an equilibrium distance of 3.7 Å from the center of mass of the anion (corresponding to 2.36 Å from the centroid of the B triad). The potential energy landscape in Figure 4a,b was mapped by varying the position of the second Li⁺ and Na⁺, both by adjusting the distance *r* from the anion and by adjusting the cation—anion—cation angle θ along the path shown in Figure 4. For easier viewing, the energy profiles for Li⁺ and Na⁺ as a function of θ at the optimized distance *r* are also shown in Figure 4c.

From Figure 4c, the strong preference for closely coordinated Li^+ to bind to the triad of B atoms is clear, with wellpronounced local minima appearing at angles θ that match the geometric distribution of these sites on the $B_{12}H_{12}^{2-}$ anion. This suggests that cations that approach an anion closely will tend to reflect the symmetry of the latter and "dock" at preferred sites, whereas at somewhat larger distances the rotationally invariant point-charge electrostatic behavior becomes manifested. Such docking behavior of cations on $B_{12}H_{12}{}^{2-}$ anions has also been suggested in previous studies. 47,48 Indeed, the binding of $\rm Li^+$ to the triad center is not surprising, since it maximizes interaction with the pseudoaromatic electron cloud in $B_{12}H_{12}^{2-}$ and echoes cation $-\pi$ interactions with alkali metal ions in aromatic carbons.^{49,50} The barrier for moving cations to a neighboring triad site is approximately 200 meV according to Figure 4c, which is consistent with observations that docking events persisted at the temperatures simulated with AIMD. As θ decreases, the minima in the energy landscape increase, evidencing the effects of cation-cation repulsion and suggesting that cations will tend to bind to triad sites in a way that maximizes their distance from one another. Accordingly, both cation $-\pi$ -type and electrostatic interactions are important for determining the cation-anion chemistry at short-range. At longer distances, the angular preference diminishes, and the interaction approaches the electrostatic limit with no specific dependence on θ (see Figure 4a,b).

To better understand the underlying physicochemical factors that contribute to the binding of the cation to the anion, we ran a second set of calculations in which *r* was varied (for $\theta = 180^{\circ}$) but with the internal $B_{12}H_{12}^{-2}$ geometry fixed to the optimized $LiB_{12}H_{12}^{-1}$ (NaB₁₂H₁₂⁻¹) with no additional relaxation allowed upon introduction of the second Li⁺ (Na⁺) ion. The energy difference between the calculations with and without the rigid anion approximation is shown in Figure 4d. This curve describes the additional stabilization that is induced by distortions of the atoms within the anion, and therefore places a lower limit on interactions that go beyond the point-charge Coloumb potential. At the local minima in Figure 4d (3.9 Å for Li⁺ and 4.5 Å for Na⁺), these interactions amount to 30-50 meV. Note that the values in Figure 4d represent the contribution from one cation-anion pair, whereas the crystalline environment features several cation neighbors per anion. Accordingly, it is reasonable to expect that the actual cation-induced contributions to the anion distortion should result in much greater perturbations to the underlying energy landscape.

The existence of these local minima points to a secondary effect that is likely connected to the direct interaction of the cation with the pseudoaromatic $B_{12}H_{12}^{2-}$ electron cloud. This is also hinted in the charge density plot in Figure 4e, which shows a Li $-B_{12}H_{12}-Li$ complex with the two cations at different distances. At shorter distance, a Li⁺ cation induces some additional charge delocalization, whereas a Li⁺ cation at longer (nonbinding) distance has no effect on the charge density.

The presence of short-range cation—anion interactions introduces a preferred cation distribution that is templated by the icosahedral symmetry of the anions. Although this presents no challenges for the isolated anion—cation pairs shown in Figure 4, when we consider the anion—cation pair within the crystalline environment, the situation may be very different. In this instance, there may be a fundamental incompatibility between the anion symmetry and the crystallographic interstitial site preference, resulting in a frustrated energy landscape that helps to mitigate the dominance of purely electrostatic factors.²⁹ This frustration can partially destabilize otherwise strongly preferred interstitial sites, resulting in a flatter energy landscape overall and more facile diffusion kinetics.

As shown in Figure 4, in an ideal $B_{12}H_{12}^{2-}$ icosahedron, there are 10 3-fold rotational axes (C_3 point-group symmetry), each of which goes through the centers of two opposite triad faces.

Possible angles between them are 41.8° , 70.5° , 109.5° , 138.2° , and 180° . However, the crystal environment introduces another geometric template that is related to the distribution of interstitial sites around each anion, which is in turn derived from the lattice symmetry. The full distributions of linear, trigonal, and tetrahedral interstitial sites for ideal fcc and bcc lattices are shown in the top panels of Figure 5a,b, with dashed



Figure 5. Frustration between anion geometry and lattice symmetry. Top panels of parts a and b show the angular distributions of linear, trigonal, and tetrahedral interstitial sites in ideal fcc $(Li_2B_{12}H_{12})$ and bcc $(Na_2B_{12}H_{12})$ lattices, respectively. Bottom panels of parts a and b show the normalized probability density of averaged cation—anion—cation angle θ obtained from AIMD of $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$. For each case, the data are plotted for three different distance ranges within the first coordination sphere, and the probability is normalized for each distance range. Red and blue lines show the shortest and intermediate distance ranges, and the gray shaded region shows the longest distance range. Possible angles (41.8°, 70.5°, 109.5°, 138.2°, and 180°) between two C_3 axes in an ideal icosahedron are shown in dashed lines in the bottom panels of parts a and b.

vertical lines in the corresponding bottom panels indicating the angles between C_3 sites for the assessment of symmetry compatibilities. It can be seen that, for the fcc lattice, tetrahedral site occupancy is fully compatible with the anion geometric preference. In this case, the C_3 axes in the $B_{12}H_{12}^{2-}$ anion can align along the 8-fold cubic distribution of tetrahedral sites; this allows the anion to orient in a way such that each neighboring cation can dock into a triad site while still retaining its electrostatically preferred interstitial site occupation. For a bcc lattice, only the linear sites have some symmetry compatibility with the icosahedral anion.

For the $B_{12}H_{12}^{2-}$ salts with larger cations (K⁺, Rb⁺, and Cs⁺), which adopt an fcc structure, tetrahedral interstitial sites are always preferred (see Table 1). This ensures that there should be no symmetry incompatibility between the anion and the lattice. These systems are indeed nonconductive. On the other hand, in the case of the smaller Li⁺ cations within Li₂B₁₂H₁₂, Pauling's rules instead dictate a preference for trigonal sites. This is confirmed by the probabilities in Table 1, which also show a secondary preference for linear sites and a much lesser preference for tetrahedral sites. According to Figure 5, trigonal and linear site distributions in the fcc lattice are intrinsically incompatible with the possible anion orientations, triggering symmetry frustration.

To visualize the frustration between the symmetries of the anion and the lattice more explicitly, we directly computed the distribution of cation-anion-cation angles (θ) for Li₂B₁₂H₁₂ and Na₂B₁₂H₁₂ from the AIMD simulations. The data are plotted in the bottom panels of Figure 5a,b for three different distance ranges within the first coordination sphere (as determined from Figure 3a). For the Li₂B₁₂H₁₂ and $Na_2B_{12}H_{12}$ structures, cations nearest to the anion (red solid lines in Figure 5) tend to adopt a symmetry that reflects the distribution of B triad docking sites on the anion (peaks near 70.5° and 109.5°), in agreement with the static calculations in Figure 4 (the fact that the larger 138.2° and 180° angles have lower overall probability can be easily understood given that each anion is coordinated with multiple cations). We emphasize that the distributions at short distances are very similar for $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ despite their different crystal structures, which points to a common factor based on the anion symmetry. On the other hand, Figure 5 also demonstrates that cations that are slightly farther from the anion begin to show additional peaks that are more reflective of the distribution of interstitial sites in the lattice. For instance, for fcc $Li_2B_{12}H_{12}$, peaks near 60° and 120° are signatures of linear sites, and peaks near 80° and 100° are signatures of trigonal sites.

Dynamical Factors. The three ingredients discussed above, namely, vacant sites for jumping, a high density of accessible sites that remove any clear site preference, and frustration between anion symmetry and lattice symmetry, are important for creating cation excitations that can lead to diffusion. However, these factors do not address dynamical contributions such as anion rotation or distortion, which have been shown to be important considerations for diffusion.

Using AIMD simulations, we previously showed that Li^+ diffusivity in β -Li₂B₁₂H₁₂ was reduced by 3 orders of magnitude when the anions were constrained to be immobile.²² There is no reason to believe that static or time-averaged structural descriptors alone can capture this subtlety. In fact, we find that the computed \tilde{S} for β -Li₂B₁₂H₁₂ is predicted to identical (3.00k_B) regardless of whether or not the anions are held fixed in the simulation. Thus, we can conclude that the relative occupation and density of available interstitial sites may by itself be an insufficient predictor of ionic conductivity. One limitation of such analyses is that they average out any dynamical factors that may alter the energy landscape on shorter time scales.

Although facile short-ranged hopping (i.e., *local* mobility of cations) is necessary for high ionic conductivity, it does not necessarily guarantee long-ranged diffusion (i.e., fast macroscopic mass transport).⁵¹ Among the factors that can inhibit long-ranged diffusion is the possibility that locally mobile ions can become trapped in regions of phase space due to high escape barriers. We propose that lattice dynamical contributions, such as collective modes or low-frequency distortions introduced by anion rotations, introduce flucutations in the local energy landscape. This increases the instantaneous probability that a viable low-barrier pathway can be found, thereby facilitating escape from local-minimum traps. As a result, the efficiency with which the global phase space is

explored by the cations is enhanced, thereby promoting facile long-ranged diffusion.

The energetic influences of cation docking and of anion distortion discussed in the previous section suggest that anion rotation and thermal vibration dynamically alter the energy landscape by introducing fluctuations in the local potential. Our calculations provide a means for estimating the order of magnitude of the energy modulation due to these local perturbations. For instance, the results of Figure 4c show that a single anion rotation may alter the local energy landscape by as much as 200 meV as the orientation changes. Notably, this value is about 3–5 times the thermal energy at the simulation temperatures, and is of similar magnitude to the collective diffusion barrier.²²

Furthermore, Figure 4d implies that anion distortion can help to dock nearby cations, with each cation contributing around 30-50 meV to the anion-cation interaction energy beyond the limit suggested by Coulomb attraction of hard ions. As already discussed, this originates from a combination of atomic (nuclear) reconfiguration and its accompanying electronic distortion. By considering the standard deviation of the B and H atomic positions averaged across the $B_{12}H_{12}^{-2}$ molecule for the optimized Li-B₁₂H₁₂-Li and Na-B₁₂H₁₂-Na configurations, we can compute a metric for the degree of the geometric anion distortion associated with the presence of the cation. The calculated standard deviation for B (H) atomic positions of the optimized complex is 0.026 Å (0.014 Å), significantly below the average standard deviation of 0.060 Å (0.081 Å) computed from the AIMD simulations at 800 K. Accordingly, it is reasonable to assume that thermal vibrations (even at lower temperatures) should be sufficient to induce anion distortions that non-negligibly fluctuate the underlying potential energy landscape of the cation. These fluctuations can facilitate cation docking and undocking, and collectively can introduce dynamical variations in the underlying energy landscape which we propose may aid long-ranged diffusion.

Moreover, the instantaneous orientation of the anions affects the potential experienced by *all* cation neighbors. Because cation docking at a $B_{12}H_{12}^{2-}$ triad site is coupled to the rotation of the anion, this has the effect of correlating the motion of nearby cations. Note that this is closely related to the "paddlewheel" mechanism of ionic conductivity. Such cation correlation has been widely discussed in the context of superionic conductors, and can have a significant impact on the ionic conductivity and diffusive prefactor.^{28,29,52-56} The dynamical correlation between cation hops can be directly seen using van Hove correlation analysis, shown for Li₂B₁₂H₁₂ in Figure S3 of the Supporting Information; the time to refill a site following a hopping event is found to be on the order of a few hundred femtoseconds.

The above discussion points to a close connection between anion rotation and cation mobility, which has been suggested previously for *closo*-borate salts,^{21,24} as well as several other classes of superionic conductors.^{57–60} This connection is revisited in Figure 6, which assesses how the anion rotation mobility is changed upon substitution of cations from superionic Li₂B₁₂H₁₂ and Na₂B₁₂H₁₂ to nondiffusive $K_2B_{12}H_{12}$, Rb₂B₁₂H₁₂, and Cs₂B₁₂H₁₂. The superionic Li₂B₁₂H₁₂ and Na₂B₁₂H₁₂. The superionic Li₂B₁₂H₁₂ and Na₂B₁₂H₁₂ systems have considerably faster anion rotation than the far less diffusive systems associated with other cations (K, Rb, and Cs), consistent with the relevance of anion dynamics in diffusion. We point out that the behavior in Figure 6 cannot be explained on the basis of volume



Figure 6. Anion rotation. Angular autocorrelation function $(\langle \hat{\mathbf{r}}(t) \cdot \hat{\mathbf{r}}(t + \Delta t) \rangle)$ for M₂B₁₂H₁₂ at 800 K (M = Li, Na, K, Rb, and Cs), where $\hat{\mathbf{r}}(t)$ is the unit vector from the anion center of mass to a constituent boron atom. The angular autocorrelation curves for the superionic and the nonconducting systems are indicated by the solid and dashed lines, respectively.

considerations alone, since the larger cations tend to expand the lattice and provide more free volume for rotation. Instead, this discrepancy points to the role of other factors, such as the specific interaction between anion and cation.⁵⁸ It is further interesting to note that although $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ have very similar calculated activation barriers for cation diffusion in Table 1, $Li_2B_{12}H_{12}$ exhibits faster anion rotation. We can therefore also conclude that anion rotational rates alone, while certainly relevant, cannot be the sole determining factor for cation diffusion rates.

Possible interactions between the anion dynamical modes and cation diffusion are explored further in Figure 7a,b which shows the vibrational power spectrum of $Li_2B_{12}H_{12}$ and Na2B12H12 derived from AIMD. From these data, specific vibrational and librational modes associated with particular anion frequency regimes can be identified: high-frequency B-H stretching and bending modes (f > 60 THz, not shown); midfrequency internal anion B-B fluxional and torsional modes (6 < f < 30 THz); and low-frequency vibrational, librational, and rotational modes (f < 6 THz). Focusing on the lowfrequency regime, we find that the cation-derived modes have significant overlap with librational B12H12²⁻ modes, implying probable momentum transfer between the anion dynamics and low-frequency cation vibrations precursory to diffusive events. Specifically, modes associated with collective angular motion of entire $B_{12}H_{12}^{2-}$ molecules are the dominant contributors to low-frequency anion dynamics; this is evident upon comparing the power spectra to the anion-derived angular rotational/ librational modes in Figure 7c. In combination with the results in Figure 4, this suggests a picture in which cations dock to anions, are carried by the rotational mobility of the latter, and are subsequently released. Note that the Li₂B₁₂H₁₂ spectrum (Figure 7a) is significantly more dispersed than the $Na_2B_{12}H_{12}$ spectrum (Figure 7a); this probably reflects the tendency of Li₂B₁₂H₁₂ to display a wider variety of site occupancies (see Table 1), each of which should exhibit a different characteristic dynamical frequency.

DISCUSSION

Ultrafast ion conduction relies on the lack of cation ordering in the anion lattice, which is intrinsically connected to a frustrated landscape that lacks deep local minima. Each of the factors



Figure 7. Dynamical modes. (a, b) Power spectrum calculated via the Fourier transform of the AIMD velocity autocorrelation function $(\langle \hat{\mathbf{v}}(t) \cdot \hat{\mathbf{v}}(t + \Delta t) \rangle)$ for (a) $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and (b) $\text{Na}_2\text{B}_{12}\text{H}_{12}$. Separate contributions from the anions and cations are shown in red and blue, respectively. (c) Fourier transform of the angular velocity autocorrelation function for $\text{B}_{12}\text{H}_{12}^{2-}$ anions in $\text{Li}_2\text{B}_{12}\text{H}_{12}$ defined as $\langle \hat{\omega}(t) \cdot \hat{\omega}(t + \Delta t) \rangle$. In part c, the red line indicates the quantity derived from the average angular velocity of individual B and H atoms (ω_i) , whereas the shaded region indicates the analogous quantity derived from the net angular velocity of each entire $\text{B}_{12}\text{H}_{12}^{2-}$ molecule $(\omega_{\text{tot}} = \sum_i \omega_i)$.

highlighted in the above sections can be thought of as introducing a source of frustration into the system, as shown schematically in Figure 8. A high density of accessible sites (e.g., the lack of a strongly preferred interstitial site) implies the existence of many local minima, which serve to flatten the overall energy landscape and decrease the tendency toward



Figure 8. Effect of structural, chemical, and dynamical frustration on energy landscape. (a) Geometric site frustration removes strong site preferences, creating multiple minima in the energy landscape. (b) Frustration between the local anion geometry and crystal lattice symmetry creates additional local minima. (c) Anion dynamics introduces fluctuations in the perturbing potential.

cation ordering (Figure 8a). The short-ranged cation—anion interactions that lead to cation docking create shallow local minima, which introduce frustration between the local geometry of the anion and the broader crystal symmetry (Figure 8b). Finally, the existence of soft dynamical modes serve to fluctuate the underlying energy landscape, which likely aids long-ranged diffusion as well as local cation mobility (Figure 8c). In the case of $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ these soft modes come in the form of anion rotations, which dynamically alter the nature of the symmetry incompatibility.

The factors in Figure 8 also prompt the development of meaningful descriptors that can be used to optimize polyboratebased solid electrolytes, as well as to discover other similar materials with attractive properties as solid electrolytes. For instance, \tilde{S} in Table 1 describes the energy landscape in terms of the variety of interstitial sites that may be involved in the diffusion pathway. Accordingly, maximizing this quantity should generate systems and structures that are intrinsically favorable for ultrafast local cation mobility. Moreover, interstitial site preferences (or lack thereof) are implicitly connected to structural characteristics, including the ratio of anion-to-cation sizes (which depends on lattice volume) and the number of possible interstitial sites (which depends on crystal structure). These quantities could be used to collectively describe a structural descriptor for improving and optimizing superionic behavior. Indeed, polyborate-based solid electrolytes are known to exhibit dependence of ionic conductivity on crystal structure.^{14,22} Similar frustration-oriented structural metrics have also been proposed to explain superionic conductivity in certain fluoride and garnet compositions.^{61,62}

Among chemical factors, the key to descriptor development may lie in the energetic magnitude of the specific interactions that give rise to cation docking. In ionic salts, these interactions must be significant enough to ensure that docking is feasible at operating temperatures, yet small enough such that cation release becomes thermally possible. Indeed, descriptors based on bond ionicity and degree of covalent character in cation anion interactions have already shown some success in other superionic systems.^{25–29,63} For systems with polyatomic anions that exhibit cation docking, the degree of symmetry incompatibility between the anion geometry and preferred cation interstitial site could also form the basis of a quantifiable descriptor.

Another possible descriptor relies on the frequency associated with the dynamical behavior of the soft rotational modes that fluctuate the underlying energy landscape.⁶⁴ It is critical that these fluctuations occur on time scales that are accessible to diffusion. If they are too fast, the cations will see only their mean-field effect instead of the instantaneous perturbations that are important for driving local diffusion. If they are too slow, then the cations will see a fixed potential. In this case, the fluctuations cannot be leveraged in order to escape possible local-minimum traps for enhanced diffusion. Many other investigations have similarly shown that ionic conductivity in superionic systems can be connected to the frequency of soft or floppy modes, suggesting a much broader phenomenon. $^{2,51,57-60,65}$ Although such soft-mode disortions can arise from a variety of physical origins, in polyborate salts, they are likely a direct result of the unusually low anion packing density and the associated free volume. Accordingly, substitution with chemical species of different sizes or masses may offer a pathway for tuning the time scale of the anion soft-mode dynamics and thereby optimize cation mobility.

However, we caution that each of the above descriptors alone may be insufficient for predicting ionic conductivity. For instance, it may be possible to have structural factors that favor multiple competing sites, yet have high barriers for cation migration between the sites. Alternatively, a favorable cationanion interaction may be present, but a confined or vacancyfree lattice structure may prevent the cation from taking advantage of this property. Finally, facile anion rotation could be ineffective if the cation-anion interaction is either too strong (i.e., cation pinning) or too weak. We therefore suggest that multiple factors collectively determine superionic behavior, which must be considered in the development of a general descriptor. Moreover, we emphasize that our analysis is rooted in understanding fundamental structural and dynamical factors that contribute to frustration and therefore give rise to lowbarrier transitions. In this way, it is intended to offer a more microscopic picture of the origins of facile local diffusion kinetics. However, to accurately predict macroscopic ionic conductivity, it may also be necessary to further consider how the available sites can interconnect to create a percolating lowbarrier pathway, as has been widely discussed in the case of sulfur-containing superionic conductors.^{46,66}

CONCLUSIONS

In conclusion, we have shown that superionic behavior in closoborate Li₂B₁₂H₁₂ and Na₂B₁₂H₁₂ solid electrolytes arises from a combination of structural, chemical, and dynamical factors. Structurally, the materials possess intrinsic vacancies: a direct consequence of a mismatch between the stoichiometry of the crystal and the preferred interstitial sites, the latter of which are determined largely by the ratio between cation and anion ionic radii. Moreover, the materials feature a high density and variety of accessible interstitial sites, meaning they exhibit a naturally flattened energy landscape and a high tolerance for disordering. Chemically, the cation-anion interaction transcends simple point-charge descriptions, with the cation "docking" to specific sites on the $B_{12}H_{12}^{2-}$ anion. Cation docking can generate an incompatibility between the preferred interstitial lattice site symmetry and the symmetry of the anion itself. Finally, the reorientational dynamics of the ${B_{12}}{H_{12}}^{2-}$ anions leads to fluctuations in the energy landscape that prevent cation ordering. We propose that, collectively, these processes introduce intrinsic frustration that enhances cation conductivity and leads to superionic behavior in polyborate solid electrolytes.

In addition to physical understanding, we suggest that these mechanisms may be useful for deriving new descriptors for ionic conductivity in polyborate salts. These may be based on structural symmetry and stoichiometry, the energy and nature of the cation-anion interaction, and the time scale of dynamical fluctuations associated with soft-mode processes. We propose that these factors may be used to optimize ionic conductivity and order-disorder transition temperatures in polyborates. It is worth noting that similar descriptors have been suggested for ionic conductivity in other solid electrolyte candidates, including recent studies based on machine learning approaches and meta-analysis of available literature data across broad ranges of superionic materials.^{2,62,63} Our controlled study, which is based on chemical analysis and underlying mechanistic understanding, provides additional insight into the origins of these proposed descriptors. Accordingly, we suggest that our findings may apply more generally to other classes of solid electrolytes and superionic conductors.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.7b02902.

Arrhenius plots for $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$, additional details on the derivation of \tilde{S} , and van Hove correlation plots for $Li_2B_{12}H_{12}$ (PDF) Trajectory file for $Li_2B_{12}H_{12}$ (XYZ) Trajectory file for $Na_2B_{12}H_{12}$ (XYZ)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was performed under the auspices of the U.S. Department of Energy at Lawrence Livermore National Laboratory (LLNL) under Contract DE-AC52-07NA27344 and funded by Laboratory Directed Research and Development Grant 15-ERD-022. Computing support came from the LLNL Institutional Computing Grand Challenge program. Sandia National Laboratories is a multi-mission laboratory managed by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the DOE's National Nuclear Security Administration under contract DE-NA0003525.

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Supplementary Information for Structural, chemical, and dynamical frustration: Origins of superionic conductivity in *closo*-borate solid electrolytes

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Diffusion coefficients and barriers for $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ from AIMD. Figure S1 shows the Arrhenius plots for the systems shown in Table 1 of the main text, from which the activation barriers for cation diffusion were extracted.



Figure S1: Arrhenius plot of the computed diffusion coefficients of superionic $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$, and volume-contracted (by 12%) and volume-expanded (by 14%) $Li_2B_{12}H_{12}$.

Derivation of the configurational entropy (\tilde{S}) . To determine \tilde{S} , we first project the different types of interstitial sites onto independent statistical systems, as shown in Fig. S2 for linear, trigonal, and tetrahedral sites. The number of possible arrangements of cations within each type of interstitial sites is then counted for the given number of cations.



Figure S2: Schematic description of the projected statistical systems for three different types of interstitial sites.

Each system in Fig. S2 contains N_i sites (*i*=linear, trigonal, tetrahedral), within which n_i and n_i^{ν} sites are occupied and unoccupied, respectively, by cations. The number of possible configurations (Ω_i) for each system is given by $\Omega_i = N_i!/(n_i! n_i^{\nu}!)$. Therefore, the total number (Ω_{tot}) of configurations of the entire system becomes

$$\Omega_{tot} = \prod_{i} \Omega_{i} = \prod_{i} \frac{N_{i}!}{n_{i}! n_{i}^{\nu}!}$$

By definition, the configurational entropy S' for the total $N (=\sum_i N_i)$ sites is written as the following:

$$S' = k_B \ln \Omega_{tot} = k_B \ln \left[\prod_i \frac{N_i!}{n_i! n_i^{\nu}!} \right]$$

where k_B is the Boltzmann constant. Employing Stirling's approximation, the entropy is expressed by

$$S' = -k_B \cdot \sum_i \left[n_i \cdot \ln\left(\frac{n_i}{N_i}\right) + n_i^{\nu} \cdot \ln\left(\frac{n_i^{\nu}}{N_i}\right) \right]$$

Note that this entropy is defined as an extensive quantity with a magnitude proportional to the total number of interstitial sites (N). Since the N interstitial sites include $n (=\sum_i n_i)$ cations, the intensive quantity (\tilde{S}) per cation is given by

$$\tilde{S} = \frac{S'}{n} = -k_B \cdot \left(\frac{N}{n}\right) \cdot \sum_i \left(\frac{N_i}{N}\right) \cdot \left[\frac{n_i}{N_i} \cdot \ln\left(\frac{n_i}{N_i}\right) + \frac{n_i^{\nu}}{N_i} \cdot \ln\left(\frac{n_i^{\nu}}{N_i}\right)\right]$$

Using the definition of probability P_2^i (= n_i/N_i) in the main text, the configurational entropy \tilde{S} per a cation is written as

$$\tilde{S} = -k_B \cdot \left(\frac{N}{n}\right) \cdot \sum_i \left(\frac{N_i}{N}\right) \cdot \left[P_2^i \cdot \ln P_2^i + (1 - P_2^i) \cdot \ln(1 - P_2^i)\right]$$

where we have used the relation $n_i^{\nu} = N_i - n_i$. The entropies in Table 1 are computed using this equation. Note that P_2^i can be easily computed from P_1^i via the algebraic relation $P_2^i = n \cdot (P_1^i/N_i)$, while P_1^i is equivalent to $n_i/\sum_i n_i$.

In computing site occupancies, we added Gaussian smoothing to correct for finite statistics and site ambiguity. First, we found all possible tetrahedral, trigonal, and linear interstitial sites within a 4 Å cutoff distance of each cation, based on the instantaneous positions of the anion centers of mass. Next, we applied a 1-D Gaussian function f(d) with $\sigma^2 = 0.1$ to the distance (d) between the cation and the interstitial site:

$$f(d) = \frac{1}{\sqrt{2\pi^2}} e^{-\frac{d^2}{2\sigma^2}}$$

For each cation, the f(d) values were gridded and summed, and the sum was renormalized to unity before computing P_1 and P_2 .

Van Hove correlation analysis of $Li_2B_{12}H_{12}$. Figure S3 shows the "self" and "distinct" parts of the van Hove correlation function based on AIMD data for $Li_2B_{12}H_{12}$ at 800 K, generated using the **pymatgen** package.^{1,2} The "distinct" part of the correlation function $G_d(r,t)$ describes the radial distribution of (N-1) particles after time *t* with respect to the initial reference particle, and therefore can be used to assess the timescale with which cation sites are refilled after being emptied. The data show that the timescale of site refilling is short, with the process beginning after ~500 fs, confirming significant cation-cation correlation. The "self" part $G_s(r,t)$ describes the diffusion of a particle from its initial position by a distance of *r* after time *t*, and confirms fast diffusion for $Li_2B_{12}H_{12}$.



Figure S3: (a) Self and (b) distinct parts of the van Hove correlation function, computed from AIMD of $Li_2B_{12}H_{12}$ at 800 K.

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