In chemically complex materials, including but not limited to ceramics with multiple cations and/or anions and concentrated solid-solution alloys such as high entropy alloys (HEAs)\(^1\) and high entropy oxides (HEOs),\(^2-6\) the chemical variations within the material can dramatically modify the potential energy landscape experienced by defects. As defects migrate through the crystal lattice, the local chemical environment varies. While this effect is greatest in random solid solutions, it is still present in ordered multi-component compounds, such as complex oxides. In complex oxides, at least in their ordered state, each species resides on a specific sublattice of the crystal. (For the purposes of this paper, we define a complex oxide as any oxide that has more than one cation in its formula unit). As the chemical complexity of the compound increases, the potential energy surface that defects must navigate also becomes more complex.

Because of the enormous importance that defect migration has on describing and predicting the properties of materials for numerous applications, there has been a huge effort to quantify the relevant migration mechanisms via atomistic modeling. As just a few examples, past work has examined defect migration in perovskites,\(^7,8\) corundum-structured compounds,\(^9,10\) pyrochlore,\(^11,12\) and spinels,\(^13,14\) among a myriad of other cases. In most cases, particularly regarding oxides, studies have focused on relatively simple structures and chemistries. Often, however, real materials either contain more complex chemistries or chemical order than often assumed in computational studies. Thus, in order to understand transport under a range of conditions, these variables must also be considered. This is particularly true of compounds such as spinels.

1 | INTRODUCTION

Spinels with the generic chemical formula \(\text{AB}_2\text{O}_4\) have potential applications in nuclear energy and batteries. In both cases, their functionality is related to mass transport through the crystal. Here, using long-time atomistic simulations, we examine the impact of the cation structure on interstitial transport in two spinel chemistries, inverse \(\text{MgGa}_2\text{O}_4\) and double \(\text{MgAlGaO}_4\). We emphasize two aspects of the transport properties: the unit mechanisms that are described by individual barriers, for which we introduce pole-figure-like plots, and the aggregate behavior of those unit mechanisms. Compared to previous work on normal spinels, we find that inversion significantly reduces the rate of interstitial transport in these structures and has an impact on the stability of defects as they move through the lattice. In particular, B cation interstitials are found to be kinetically stable only in the inverse \(\text{MgGa}_2\text{O}_4\). These results provide new insight into relationship between structure, chemistry, and transport in spinels.

**KEYWORDS**
accelerated molecular dynamics, cation order, interstitials, migration, spinels
spinel where cation inversion—the mixing of cations across sublattices—can depend on both chemistry and temperature.

Previously, we examined the kinetic behavior of point defects in Mg-bearing spinels as it pertained to radiation damage.\textsuperscript{15} Using temperature accelerated dynamics (TAD),\textsuperscript{16,17} we characterized the migration mechanisms and energies for all six elemental point defects that can induce mass transport in MgAl\textsubscript{2}O\textsubscript{4}, MgGa\textsubscript{2}O\textsubscript{4}, and MgIn\textsubscript{2}O\textsubscript{4}. (Antisites, which are also point defects, cannot, in and of themselves, induce mass transport). While we did explore the potential effect of cation disorder on defect migration in that prior work, the detailed defect behavior was limited to fully ordered and, more importantly, normal structures. While this might be reasonable for MgAl\textsubscript{2}O\textsubscript{4}, it is not so for the other spinels. Here, we expand upon that work by considering the effect of inversion on defect transport in MgGa\textsubscript{2}O\textsubscript{4}. We then consider an entirely new structure, one recently predicted by density functional theory (DFT) calculations, that is a mixture of MgAl\textsubscript{2}O\textsubscript{4} and MgGa\textsubscript{2}O\textsubscript{4}. This new double spinel structure\textsuperscript{18} is also inverse in nature and dynamics (AMD),\textsuperscript{22} method that allows for longer times to fully ordered and, more importantly, normal structures.

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2 | METHODOLOGY

We use TAD to simulate the transport of interstitial species in MgGa\textsubscript{2}O\textsubscript{4} and MgAlGaO\textsubscript{4}. TAD is an accelerated molecular dynamics (AMD)\textsuperscript{22} method that allows for longer times to be simulated than possible with conventional molecular dynamics (MD) while retaining near-full fidelity to the underlying interatomic potential. While TAD has been discussed in many papers, we briefly summarize the algorithm here for convenience.

TAD assumes harmonic transition state theory (HTST) to use high temperature MD trajectories to extrapolate behavior to a lower temperature of interest. A high temperature trajectory is evolved in the current state of the system, defined as the basin of attraction around a given minimum-energy configuration. Once a transition from that state to any neighboring state is detected, the trajectory is interrupted and the barrier for that process calculated using the climbing-image nudged elastic band (CI-NEB) method.\textsuperscript{23} Using that barrier, the time of the event at the high temperature can be extrapolated to the lower temperature (with the assumption of HTST). The trajectory is then restarted in the current state. Once a stopping criterion has been met (defined by a user-defined confidence level and an assumed minimum prefactor), the shortest time event at low temperature is accepted, the system placed in the corresponding state, and the procedure repeated for that new state. In the simulations reported here, we used an assumed minimum prefactor of 10\textsuperscript{12}/s and a confidence level of 0.05. The high temperature used to explore the landscape was 2000 K while the low temperature to which the dynamics were extrapolated was 1000 K. We note that the relative rates of different events that comprise the final trajectory would change with the low temperature. The speed-up, or the amount of time simulated using TAD versus the amount of time that could have been simulated using MD if all force calls (including those used in the CI-NEB calculations to determine the barriers of all observed events) were used to advance the MD time step, varied between eight and 26 times for the simulations discussed below.

Finally, the simulation cell, a 2 × 2 × 2 expansion of the cubic unit cell of spinel, contained 449 atoms. Adding the interstitial ion introduces a net charge into the system. We use Ewald summation\textsuperscript{24} to calculate the electrostatic interactions. Normally, for a non-neutral cell, a constant term must be added to the Ewald sum to compute the energy of the system. However, this term depends only on the net charge and is otherwise constant for a system of constant size and composition.\textsuperscript{25} As in the TAD simulations we are only interested in relative energies, such as barriers, we neglect this term.

To simulate the properties of a material at the atomic scale, we must specify the interatomic interactions. While, conceptually, there is nothing that prevents coupling the TAD algorithm with DFT-quality forces, the computational expense of DFT precludes this coupling in practice. Thus, we are forced to rely upon classical potentials. Here, to describe these ionic oxides, we use Buckingham potentials, particularly a parameter set previously used to study the same types of compounds.\textsuperscript{26} While these potentials are certainly not perfect, past experience has shown that they provide a good qualitative description of strongly ionic materials.\textsuperscript{27-29} Thus, we expect that they are reasonable descriptions for understanding how the chemical structure of cations in these spinels impacts interstitial transport.

Each simulation begins by placing an extra atom of the chosen element in the simulation cell. We then evolve the kinetics of the resulting system forward in time, generating a long trajectory that is characterized by the state-to-state evolution of the defect and the connecting barriers. We then analyze this trajectory to determine the salient features that describe the migration of the interstitial. Often, during the course of a given simulation, the defect persists in what one might call a super-basin of states, a subset of states that are connected by relatively low barriers. The defect might visit many of these states repeatedly before eventually leaving that super-basin and finding another neighboring one. These
FIGURE 1  Examples highlighting how the trajectories from TAD simulations are processed for analysis. (A) Schematic of the clipping and reducing process. First, side trajectory loops (thinner black lines) that do not lead to evolution between minimum energy states (green circles) are “clipped”. Then, among the states that remain, the highest barrier between subsequent minimum energy states is identified, leading to the “reduced” trajectory containing only one barrier between such states (the red line in the first and last schematic image). This is illustrated with specific examples in what follows. (B) First, the trajectory containing all visited states is “clipped” such that events that repeat or loop -- where the trajectory moves on a side branch but then returns to the main branch -- are removed. This leads to a reduced sequence of events that contribute to the net evolution of the trajectory. (C-D) These clipped trajectories are further reduced to identify the events and barriers that lead to net center of mass motion of the atoms in the system. From the clipped path, for each pair of minimum-energy states, the minimum highest barrier connecting them is identified. These are then analyzed to understand the motion of the corresponding defect in the system. Two different cases are shown, highlighting how different types of landscapes are identified. In (C), corresponding to the migration of O\textit{i} in MgGa\textsubscript{2}O\textsubscript{4}, the defect constantly visits new states that correspond to net migration through the crystal. In contrast, in (D), representing Mg\textit{i} in Mg(AlGa)O\textsubscript{4}, the defect tends to get stuck in “super-basins” of low energy states, connected by relatively small barriers, and must overcome larger barriers of just over 0.9 eV to migrate through the crystal. In these plots, the “state ID” is a unique number given to each unique minimum visited during the simulation [Color figure can be viewed at wileyonlinelibrary.com]
repeated events do not describe net migration of the defect and their existence complicates analysis of the trajectory.

In order to isolate the events that are critical to the net migration of the defect, we first “clip” and then “reduce” the trajectory, as described in Figure 1. By clipping (Figure 1B), we prune all of the side branches in which the defect moves from one state through a series of states and back to the original state. These loops describe excursions of the defect into local minima of the super-basin and are superfluous. Once the trajectory is clipped, it is then reduced (Figure 1C,D) by first identifying the sequence of lowest (or minimum) energy states of the defect along the trajectory. The highest barrier connecting structurally equivalent but translationally different minimum-energy states is also identified. These might be connected via other intermediate (but not looping or side-branching) states—those states are ignored. We filter those states out, leaving only a series of barriers that connect distributed minimum-energy states. This final trajectory is then analyzed to determine what the barriers are for migration and how those barriers depend on the structure of the crystal. It is important to emphasize that this clipping and reducing process occurs after the simulation is complete, so does not in any way affect the course of the trajectory produced by the TAD simulation.

We note that this process is not perfect, due to the evolution of the TAD trajectory itself. As the trajectory evolves, the center of mass of the system can drift due to thermal effects. Further, periodic boundary conditions are applied sporadically, which makes reconstructing the unit processes in an automatic way somewhat ambiguous. For most events, this is not an issue as they are not separated by significant amounts of times, but there are cases where the system visits thousands of states between minimum-energy structures and, in these cases, the drift can become significant. However, even in those cases, the error introduced by the drift is relatively small, and impacts only the estimated direction of the event, not the magnitude of the barrier.

3 | RESULTS

The structures of the two compounds studied here are schematically illustrated in Figure 2, along with the normal structure of MgAl2O4 for reference. In a normal spinel (Figure 2A), all of the A cations (as defined by the formula unit AB2O4) reside in tetrahedral positions while the B cations are on octahedral sites. In an inverse spinel, such as shown in Figure 2B for MgGa2O4, the tetrahedral sites are filled with B cations and the A cations share the octahedral sublattice with the remaining B cations. At low temperature, the A and B cations on the octahedral sublattice order, forming intertwined helices.

The inversion parameter $i$ describes the degree to which B cations fill the tetrahedral sites, with $i = 0$ being normal and $i = 1$ being fully inverse. However, most spinels do not achieve these limits. In particular, due to a combination of configurational and vibrational entropy, MgGa2O4 is, experimentally, close to a random spinel with $i \sim 0.66$. In prior work, we examined how intermediate levels of inversion impacted oxygen vacancy migration in MgGa2O4. Here, however, we treat the material as a fully ordered inverse structure. Thus, by comparing the inverse structure with previous work on the normal structure, we examine the two limiting cases and the effect on transport.

Finally, Figure 2C shows the structure of the MgAlGaO4 double spinel. This is also an inverse structure, with the tetrahedral site filled with Ga. However, the octahedral sublattice contains both Mg and Al, which order in the same helical structure as the inverse single spinel in Figure 2B. We note that, while normal spinels are cubic, inverse spinels have a slight tetragonal distortion—a consequence of the ordering of the cations on the octahedral sublattice—and thus have a different symmetry along that direction (which is always $z$ in the structures studied here) as compared to the other two directions ($x$ and $y$).

We used TAD to simulate the transport of interstitial species in inverse MgGa2O4 and double MgAlGaO4. We analyze the resulting trajectories from two perspectives. First, we identify the unit mechanisms by which the defects move from one position in the lattice to a neighboring one. We then look at the resulting aggregate trajectories that describe net transport through the crystal.

3.1 | Unit mechanisms

The lowest energy configurations for both the oxygen and cation interstitials are shown schematically in Figure 3. In both compounds, the ground state for the oxygen interstitial is the same—if one considers a 111 plane of oxygen ions, which form a triangular lattice, the extra ion resides on one of the edges of one of the triangles, pushing two other oxygen ions slightly off their lattice position. As will be discussed below, there are three different cation interstitials that are relevant in these compounds: Mg$_i$ in both compounds and Ga$_i$ in MgGa$_2$O$_4$. In all cases, the cation interstitial forms a $<110>$ split structure with a cation on the tetrahedral sublattice. In the case of Mg$_i$, this spilt interstitial is mixed chemistry, but in the case of Ga$_i$, both ions in the split structure are Ga ions.

To visualize and interpret the unit mechanisms of migration for these defects, we borrow the concept of pole figures from microscopy. In particular, once we have clipped and reduced the trajectories as described above, we then extract
the migration energy and the direction of the migrating event from those trajectories. Assumptions have to be made to do this. In particular, to assign a direction to a given migration event, we look at the ion that moved the greatest distance, using the vector connecting its initial position to its final position as the direction of the event. If more than one atom moved, as is always the case for interstitialcy mechanisms in solids, this is not a complete description of how the atoms moved. Further, there are some issues related to the thermal drift of the trajectory and the application of periodic boundary conditions, as noted above. However, this analysis does provide a simple metric that is easy to understand for characterizing how ions are moving in the system.

The resulting “pole figure” plots for interstitial migration in inverse MgGa₂O₄ are shown in Figure 4. In each panel, the barriers that move the defect from one minimum-energy configuration to an equivalent (by energy) but translated state are colored by their energy. The direction of the event is indicated by the position of the corresponding point on the pole figure. A point at the highest position of the circle, for instance, would indicate that the event corresponded to migration along the [010] direction while a point in the center of the circle means the defect moved in the [001] direction.

Figure 4 provides these polar plots for the potential interstitial species in inverse MgGa₂O₄: (a) Oᵢ, (b) Mgᵢ, and (c) Gaᵢ. We first consider the behavior of the oxygen interstitial in Figure 4A. There are many distinct pathways for Oᵢ in this compound and they tend to move the defect in many different directions. The lowest barriers for migration are about 0.96 eV and they move the defect in <101> and <011> directions. Other low-energy pathways exist that move the ions more directly along [001] or the c-axis of the crystal (these are the teal points that are slightly closer to the center of the plot). Thus, the fast pathways for the migration of Oᵢ move the defect, at least partially, along z, the direction of the helices on the octahedral sublattice. Migration within the x – y plane, perpendicular to [001], is characterized by higher barriers between 1.1 and 1.2 eV. Thus, there is a preference for oxygen migration via interstitials to occur along the z axis of the material.

The behavior of cation interstitials is much simpler than that of Oᵢ, as revealed in Figure 4B,C. However, it also reveals a complication in interpreting these pole figures. Figure 4B suggests that the fastest pathway for Mgᵢ migration in inverse MgGa₂O₄ is along the <111> direction. However, upon closer inspection, we find that these barriers do not lead to net migration. That is, even after clipping and reducing the trajectories, there are still events that take the system from one minimum-energy state to another but do not lead to net migration. This is evident in Figure 1C where barriers with heights of about 0.8 eV move the defect, but not in a way that allows for net migration. That is, these events just “oscillate” the defect between two different minimum-energy states. An even larger barrier, in this case of 0.99 eV, must be overcome for the defect to migrate long distances in the crystal. There are two types of pathways, one along <111>, just like the 0.8 eV process (the points representing these paths are barely visible under the 0.8 eV points in Figure 4B) and another that is intermediate between the <101> and <100> (roughly <313>) directions, tending to move the defect both in the x – y plane and along the z direction.

The case of Gaᵢ is even simpler. The dominant path is actually along <111>, much like the apparent fast pathway for Mgᵢ, though, in this case, the defect can translate
through the crystal along this direction. The migration barrier for Ga\(_i\) along this direction is only 0.32 eV. As will be discussed below, however, the interstitial cannot move along a single <111> direction over multiple steps, but rather alternates between different <111> directions, resulting in a complex but essentially 1D migration path along <001>. This emphasizes the need to look beyond unit mechanisms to determine net migration paths through the crystal.

Figure 5 shows the pole figures for interstitials in the double spinel MgAlGaO\(_4\). In contrast to the case of MgGa\(_2\)O\(_4\), only two defects are shown. This is because the two B interstitials – Al\(_i\) and Ga\(_i\) – are actually not kinetically stable as migrating defects. That is, they are thermodynamically stable defects, but they do not migrate as independent species, as they do in MgGa\(_2\)O\(_4\). Rather, their behavior is reminiscent of the behavior we observed previously for B cation interstitials in normal spinels [15], in some pyrochlore chemistries [33], and even in perovskites [34]. The fastest kinetic processes associated with these defects are the ejection of A interstitials, in which the B cation becomes a substitutional antisite. Because of the relative charge state of the antisite (+1) and the resulting Mg\(_i\) (+2), the new interstitial is repelled by the antisite and migrates as an independent Mg interstitial. Thus, the pole figure for Mg\(_i\) shown in Figure 5B essentially describes all three cases for cation interstitials, at least in the dilute limit of antisite concentrations. For the B cations to migrate, the Mg interstitial has to kick out B cations, as described in Ref. [35].

The pole figure for O\(_i\) migration in MgAlGaO\(_4\) shown in Figure 5A is similar to but even more complex than that for O\(_i\) in MgGa\(_2\)O\(_4\) (Figure 4A). As for the cations discussed above, the lowest barrier pathways do not lead to net migration. Rather, barriers of 0.82 eV must be overcome for net migration. However, there are multiple pathways that are competitive with this barrier that move the defect in <110> and roughly <311> directions. Thus, we predict that, even though the chemical structure is more anisotropic in MgAlGaO\(_4\), oxygen interstitial migration is more isotropic in that material.

The behavior of Mg\(_i\) in MgAlGaO\(_4\) (Figure 5B) is very similar to that in MgGa\(_2\)O\(_4\), with the fastest migration pathways that actually move the defect through the crystal being along both <111> and, roughly, <313> with barriers of 0.93 eV (as for Mg\(_i\) in MgGa\(_2\)O\(_4\), the larger barrier along <111> is hidden under the points for the smaller barrier process in Figure 5B). This landscape is almost identical to that in MgGa\(_2\)O\(_4\), only with barriers slightly lower in magnitude (0.93 eV vs 0.99 eV).

Finally, we more carefully inspect the migration of O\(_i\) in MgAlGaO\(_4\). Figure 6A-C show the net migration of
oxygen ions as they move along the paths represented in Figure 5A that result in net migration of the defect through the crystal. Table 1 summarizes the motion of the atoms that move more than 1 Å during the course of the event. These figures and table highlight the fact that, while in the pole figures we used one atom to characterize the direction associated with a migration event, in reality several atoms can move during one of these events (which, we note, can also consist of multiple saddles). In particular, the event shown in Figure 6B involves five oxygen ions moving more than 1 Å in a variety of directions. Thus, again, the pole figures in Figures 4 and 5, while containing valuable information, offer only a partial picture of the dynamics in these systems.

### 3.2 Aggregate motion

As noted above, while the pole figures provide a high-level perspective of the migration characteristics of defects in these structures, it is incomplete at best. We illustrate this by analyzing the trajectory of Ga in inverse MgGa2O4 since, as revealed in Figure 4D, it has a relatively simple energetic landscape. The trajectory for this defect is shown in Figure 7. The defect's trajectory clearly reveals that it

| Case (barrier, eV) | Mechanism | Distance moved (Å) | Direction moved |
|-------------------|-----------|--------------------|-----------------|
| 0.82              | A 1.40    | B 1.89             | C 2.12          |
|                   | (9,−2,30) | (19,−30,−7)        | (30,−9,10)      |
| 0.93              | A 1.42    | B 2.17             | C 2.28          |
|                   | (7,16,−30)| (−4,10,213)        | (−2,30,−3,30)   |
| 1.05              | A 1.50    | B 2.28             | C 2.68          |
|                   | (1,3,6)   | (−4,11,20,30)      | (3,−1,−5)       |

Table 1: Distances and directions moved for the oxygen ions that moved more than 1 Å during net migration of O in MgAlGaO4. The mechanisms refer to the pathways illustrated in Figure 6.
events that move the defect through the crystal move it in directions, which are chemically opposed to those 3+ defects, as Mg_{i} has a charge of 2+, when
it fills the Ga lattice site to create an MgGa anti-site, it has an effective charge of 1-, which attracts the 3+ charged Ga_{i} that results. Thus, in this case, the Ga interstitial cannot escape from the anti-site defect and they continuously kickout and replace one another, ultimately leading to a coupled migration of Mg and Ga through the lattice along the [001] direction. This is an interesting contrast to what we previously observed for Mg_{i} migration in normal MgAl_{2}O_{4} and MgGa_{2}O_{4} where the defect migrated without pushing out B cations. Clearly, regardless of the inversion and chemistry, Mg_{i} prefers to migrate on the tetrahedral sublattice.

While the event landscape revealed by Figure 4A for O_{i} in MgGa_{2}O_{4} is more complex than for the two cation interstitials, the resulting trajectories are more uniformly 3-D through the crystal. This might be a consequence of the fact that the oxygen sublattice in spinels is densely packed (while the cation sublattice is not), leading to greater interconnectivity of the oxygen sites. Regardless of the origin, the disparity in barrier heights between events is not so great and the defect is able to traverse a 3-D path. However, even so, the trajectory is a complicated aggregate of unit processes. For example, there are instances in which the interstitial migrates along a series of metastable states that move it along a 001 direction for the full span of the simulation cell without ever returning to the ground state structure. The maximum barrier along this chain of events is 1.24 eV. These types of events, when combined with the lower energy events, promote 3-D migration through the crystal. This behavior is illustrated in Figure 8A in which the ground-state minima are plotted versus the time at which they are visited. While the overall migration of the interstitial is 3-D, it is punctuated by long chains of 1D migration in 1 10 or similar directions.

The trajectory of O_{i} in MgAlGaO_{4}, as shown in Figure 8B, differs, as now the long excursions in 1 10 directions no longer occur, a consequence of the more complex chemistry of the material. That is, as highlighted in Figure 2C, the chemical environments of a defect in the double spinel are more complex than in the inverse MgGa_{2}O_{4} structure (Figure 2B), with three different cations defining the local environment rather than just two. As reflected in the unit mechanisms, there is even less disparity in the barriers in different directions in the double spinel than in the inverse spinel, leading to a more uniform 3-D migration of the defect. If we contrast this to what we previously saw for normal MgAl_{2}O_{4}, where pure 1D migration was possible with a barrier of 0.29 eV, it seems that one consequence of the more complex chemistry and structure of MgAlGaO_{4} is the elimination of the fast 1D migration pathways present in the simpler material.15 That pathway lies along 1 10 directions, which are chemically simpler in MgAl_{2}O_{4} than in MgAlGaO_{4}.

Finally, a similar effect occurs for Mg_{i} in double MgAlGaO_{4} (not shown). As opposed to in MgGa_{2}O_{4}, where
Mg$_i$ diffuses along the $z$ axis, now its migration is more 3-D in nature. Presumably, this is again a consequence of more competing interactions due to three versus two cations in the structure. Thus, these trajectories reveal that even when the unit mechanism landscapes are similar, the resulting trajectories can be complex. Further, as the chemical complexity and ordering in the material increases, migration first becomes restricted but, as even more order is imposed, it becomes less restricted again. There is a delicate balance between the cation ordering in the system and the impact on defect migration.

4 | DISCUSSION

The TAD simulations reveal a complex dependence of the migration of interstitial defects on both chemistry and inversion. The ordering along the $z$ axis of the crystal breaks symmetry and leads to preferential migration directions, but only when the structure contains two cations. Introducing more cations, even if they are arranged in a similar ordering, leads to sufficient chemical complexity that the migration becomes more isotropic. This is reminiscent of the behavior seen in HEAs in which the addition of more alloying elements leads to more isotropic diffusion.36 In the case of HEAs, this makes sense as the uniform landscape of the single component material is essentially randomized as multiple species are added to the alloy. Here, in the case of these spinels, the result is more surprising as the structure, with the addition of the third cation, is even more strongly ordered along $z$ than when only 2 cations are present. However, the interatomic interactions must disrupt the channels that are present in the simpler spinel to provide more isotropic migration. A more fundamental explanation eludes us at this time.

Table 2 summarizes the migration energies for the various interstitial species in these two compounds and compares them to previous results on normal MgAl$_2$O$_4$ and MgGa$_2$O$_4$ using the same potential parameters. The most interesting result is that migration tends to be faster in normal spinels than inverse spinels, even for the same chemistry, by about 0.5 eV or more. One reason for this is that, as noted above, in the normal spinel the fast migration pathways are

![Figure 6](http://example.com/figure6.png)

**Figure 6** Paths taken by the oxygen ions that move more than 1 Å during the course of events that take the oxygen interstitial from one lowest energy state to an equivalent but translated state in MgAlGaO$_4$. The larger spheres represent the paths of these oxygen ions, with the shade indicating the position along a linear interpolation of ions between minima along the path. All minima along the respective paths are represented and can be identified as kinks, when present, in the pathways. The net barrier for the overall path is indicated for each case. The structures are viewed down a [110] axis. The labels highlighted in the blue circles correspond to properties describing that part of the migration path as listed in Table 1 [Color figure can be viewed at wileyonlinelibrary.com]
1D along <110> and these pathways no longer exist in the more complex double spinel. Thus, these results indicate that normal spinels would be much more attractive from a battery perspective in terms of the operating temperature needed to move species around. Inversion not only leads to slower migration, but as noted above, can lead to anisotropic diffusion. Thus, migration in the directions perpendicular to the $z$ axis would be even slower. Moving to the double spinel would alleviate the anisotropy, but would not enhance the fastest migration paths.

Another interesting result revealed in Table 2 is that B cation interstitials are kinetically unstable in all but one compound, inverse MgGa$_2$O$_4$. They are unstable in both normal spinel structures as well as the inverse double spinel. There does not seem to be any evident trend on B$_i$ stability versus either inversion or chemistry. When they are stable, as they are in inverse MgGa$_2$O$_4$, their migration rates are very different, with this compound exhibiting the highest cation mobilities of all of those considered. Granted, it is one-dimensional along the $z$ axis of the crystal, but it suggests that, by choosing the right chemistry that supports an inverse structure, high mobilities can be achieved.

Ultimately, the landscape of defects in these types of materials is very complex, as highlighted by the pole figures in Figures 4 and 5. Exacerbating this is the fact that
the aggregate trajectories comprised of these unit mechanisms are even more complex. While the TAD simulations were performed at a specific temperature, presumably the aggregate trajectories will be very temperature dependent. At lower temperatures, smaller barrier processes will become ever more dominant and the resulting migration characteristics more dictated by those types of events. In contrast, we speculate, with good reason, that at high enough temperatures (and/or over long enough time scales) migration that is 1D in the TAD simulations would become more 3-D-like.

5 | CONCLUSION

Using temperature accelerated dynamics, we simulate the migration of interstitials in inverse MgGa₂O₄ and double MgAlGaO₄ spinel. We find that the landscape of these defects is characterized by a wide range of migration energies that tend to move mass in different directions. In aggregate, this complexity results in 1D migration for some defects and 3-D migration for others. More importantly, we find that migration tends to be slower in these inverse structures than in normal spinels, with migration energies roughly 0.5 eV higher in the inverse spinels. Finally, B cation interstitials tend not to be kinetically stable in any but the inverse single spinel. Together, these results highlight the role that both cation order and chemistry play in driving the migration of defects in spinels.

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REFERENCES

1. Yeh JW, Chen SK, Lin SJ, Gan JY, Chin TS, Shun TT, et al. Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes. Adv Eng Mater. 2004;6(5):299–303.
2. Rost CM, Sachet E, Borman T, Moballegh A, Dickey EC, Hou D, et al. Entropy-stabilized oxides. Nat Commun. 2015;6:8485.
3. Sarkar A, Velasco L, Wang D, Wang Q, Talasila G, de Biasi L, et al. High entropy oxides for reversible energy storage. Nat Commun. 2018;9(1):1–9.
4. Dubrowa J, Stygar M, Mikula A, Knapik A, Mroczka K, Tejchman W, et al. Synthesis and microstructure of the (Co, Cr, Fe, Mn, Ni) 3O₄ high entropy oxide characterized by spinel structure. Mater Lett. 2018;216:32–6.
5. Jiang S, Hu T, Gild J, Zhou N, Nie J, Qin M, et al. A new class of high-entropy perovskite oxides. Scr Mater. 2018;142:116–20.
6. Musić BL, Gilbert D, Ward TZ, Page K, George E, Yan J, et al. The emergent field of high entropy oxides: design, prospects, challenges, and opportunities for tailoring material properties. APL Mater. 2020;8(4):040912.
7. De Souza RA, Islam MS, Ivers-Tiffée E. Formation and migration of cation defects in the perovskite oxide LaMnO₃. J Mater Chem. 1999;9(7):1621–7.
8. Eames C, Frost JM, Barnes PR, O’regan BC, Walsh A, Islam MS. Ionic transport in hybrid lead perovskite solar cells. Nat Commun. 2015;6(1):1–8.
9. Kislenko SA, Vlaskin MS, Zhuk AZ. Diffusion of cation impurities by vacancy mechanism in α-Al₂O₃: effect of cation size and valence. Solid State Ionics. 2016;293:1–6.
10. Medasani B, Sushko ML, Rosso KM, Schreiber DK, Bruemmer SM. First-principles investigation of native interstitial diffusion in Cr₂O₃. J Phys Chem C. 2018;122(24):12984–93.
11. Gunn DS, Allan NL, Foxhall H, Harding JH, Purton JA, Smith W, et al. Novel potentials for modelling defect formation and oxygen vacancy migration in Gd₅Ti₃O₁₀ and Gd₅Zr₃O₁₀ pyrochlores. J Mater Chem. 2012;22(11):4675–80.
12. Toyoura K, Nakamura A, Matsunaga K. First-principles analysis of proton conduction mechanism in pyrochlore-structured lanthanum zirconate. J Phys Chem C. 2015;119(16):8480–7.
13. Nakayama M, Kaneko M, Wakahara M. First-principles study of lithium ion migration in lithium transition metal oxides with spinel structure. Phys Chem Chem Phys. 2012;14(40):13963–70.
14. Verma AK, Karki BB. Ab initio investigations of native and protonic point defects in Mg₃SiO₄ polymorphs under high pressure. Earth Planet Sci Lett. 2009;285(1–2):140–9.
15. Uberuaga B, Bacorisen D, Smith R, Ball J, Grimes R, Voter A, et al. Defect kinetics in spinels: long-time simulations of MgAl₂O₄, MgGa₂O₄, and MgIn₂O₄. Phys Rev B. 2007;75(10):104116.
16. Sørensen MR, Voter AF. Temperature-accelerated dynamics for simulation of infrequent events. J Chem Phys. 2000;112(21):9599–606.
17. Zamora RJ, Uberuaga BP, Perez D, Voter AF. The modern temperature-accelerated dynamics approach. Annu Rev Chem Biomol Eng. 2016;7:87–110.
18. Pilania G, Kocovsky V, Valdez JA, Kreller CR, Uberuaga BP. Prediction of structure and cation ordering in an ordered normalized inverse double spinel. Commun Mater. 2020;1(1):1–11.
19. Kim DK, Muralidharan P, Lee HW, Ruffo R, Yang Y, Chan CK, et al. Spinel LiM₂O₄ nanorods as lithium ion battery cathodes. Nano Lett. 2008;8(11):3948–52.
20. Wang J, Purewal J, Liu P, Hicks-Garner J, Soukazian S, Sherman E, et al. Degradation of lithium ion batteries employing graphite negatives and nickel–cobalt–manganese oxide spinel manganese oxide positive: Part 1, aging mechanisms and life estimation. J Power Sources. 2014;269:937–48.
21. Shimokawa K, Atsumi T, Harada M, Ward RE, Nakayama M, Kumagai Y, et al. Zinc-based spinel cathode materials for
magnesium rechargeable batteries: toward the reversible spinel–rocksalt transition. J Mater Chem A. 2019;7(19):12225–35.

22. Perez D, Uberuaga BP, Shim Y, Amar JG, Voter AF. Accelerated molecular dynamics methods: introduction and recent developments. Annu Rep Comput Chem. 2009;5:79–98.

23. Henkelman G, Uberuaga BP, Jónsson H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. J Chem Phys. 2000;113(22):9901–4.

24. Ewald PP. Die Berechnung optischer und elektrostatischer Gitterpotentiale. Ann Phys. 1921;369(3):253–87.

25. Leslie M, Gillan N. The energy and elastic dipole tensor of defects in ionic crystals calculated by the supercell method. J Phys C: Solid State Phys. 1985;18(5):973.

26. Bacorisen D, Smith R, Ball J, Grimes R, Uberuaga B, Sickafus K, et al. Molecular dynamics modelling of radiation damage in normal, partly inverse and inverse spinels. Nucl Instrum Methods Phys Res B. 2006;250(1–2):36–45.

27. Uberuaga B, Smith R, Cleave A, Montalenti F, Henkelman G, Grimes R, et al. Structure and mobility of defects formed from collision cascades in MgO. Phys Rev Lett. 2004;92(11):115505.

28. Benedek NA, Chua ALS, Elsässer C, Sutton AP, Finnis MW. Interatomic potentials for strontium titanate: an assessment of their transferability and comparison with density functional theory. Phys Rev B. 2008;78(6):064110.

29. Murphy S, Gilbert C, Smith R, Mitchell T, Grimes R. Non-stoichiometry in MgAl₂O₄ spinel. Philos Mag. 2010;90(10):1297–305.

30. Jiang C, Sickafus KE, Stanek CR, Rudin SP, Uberuaga BP. Cation disorder in MgₓOₓ (x=Al, Ga, In) spinels from first principles. Phys Rev B. 2012;86(2):024203.

31. Uberuaga BP, Sickafus KE. Interpreting oxygen vacancy migration mechanisms in oxides using the layered structure motif. Comput Mater Sci. 2015;103:216–23.

32. Randle V. Texture. In: Buschow KHI, Cahn RW, Flemings MC, Ilschner B, Kramer EJ, Mahajan S, editors. Encyclopedia of Materials: Science and Technology. Oxford: Elsevier; 2001. p. 9119–29. Available from: http://www.sciencedirect.com/science/article/pii/B0080431526016454

33. Uberuaga BP, Perriot R. Insights into dynamic processes of cations in pyrochlores and other complex oxides. Phys Chem Chem Phys. 2015;17(37):24215–23.

34. Uberuaga BP, Vernon LJ. Interstitial and vacancy mediated transport mechanisms in perovskites: a comparison of chemistry and potentials. Solid State Ionics. 2013;253:18–26.

35. Murphy S, Uberuaga B, Ball J, Cleave A, Sickafus K, Smith R, et al. Cation diffusion in magnesium aluminate spinel. Solid State Ionics. 2009;180(1):1–8.

36. Lu C, Niu L, Chen N, Jin K, Yang T, Xiu P, et al. Enhancing radiation tolerance by controlling defect mobility and migration pathways in multicomponent single-phase alloys. Nat Commun. 2016;7(1):1–8.

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