Influence of Br⁻/S²⁻ site-exchange on Li diffusion mechanism in Li₆PS₅Br: a computational study

Marcel Sadowski and Karsten Albe

Technical University of Darmstadt, Institute of Materials Science, Otto-Berndt-Straße 3, 64287 Darmstadt, Germany

We investigate how low degrees of Br⁻/S²⁻ site-exchange influence the Li⁺ diffusion in the argyrodite-type solid electrolyte Li₆PS₅Br by ab initio molecular dynamics simulations. Based on the atomic trajectories of the defect-free material, a new mechanism for the internal Li⁺ reorganization within the Li⁺ cages around the 4d sites is identified. This reorganization mechanism is highly concerted and cannot be described by just one rotation axis. Simulations with Br⁻/S²⁻ defects reveal that Li⁺ interstitials (Li⁺ᵢ) are the dominant mobile charge carriers and originate from Frenkel pairs. These are formed because Br⁻/S²⁻ defects on the 4d sites donate one or even two Li⁺ᵢ to the neighbouring cages. The Li⁺ᵢ then carry out intercage jumps via interstitial and interstitialcy mechanisms. With that, one single Br⁻/S²⁻ defect enables Li⁺ diffusion over an extended spatial area explaining why low degrees of site-exchange are sufficient to trigger superionic conduction. The vacant sites of the Frenkel pairs, namely V⁺₄Li, are mostly immobile and bound to the Br⁻/S²⁻ defect. Because S⁺Br⁻ defects on 4a sites act as sinks for Li⁺ᵢ they seem to be beneficial only for the local Li⁺ transport. In their vicinity T₄ tetrahedral sites start to get occupied. Because the Li⁺ transport was found to be rather confined if S⁺Br⁻ and Br⁻/S²⁻ defects are direct neighbours, their relative arrangement seems to be crucial for effective long-range transport.

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1. Introduction

Sulfide solid electrolytes (SE) are promising candidates to be used in lithium all-solid-state batteries due to their high ionic conductivity that competes with conventional liquid organic electrolytes. Especially, argyrodite-type Li₆PS₅X (X = Cl, Br, I) materials first proposed by Deiseroth et al. in 2008 [1] have recently attracted much attention [2–5]. Their basic crystal structure is cubic with F43m symmetry (figure 1a). The rock-salt arrangement of anions can be described as a face-centred cubic lattice of X⁻ anions (Wyckoff 4a) and a shifted face-centred cubic lattice of PS₃⁻⁴ units (P ion centred on Wyckoff 4b). Half of the tetrahedral sites spanned by the 4a and the 4b sites are occupied by S²⁻ (Wyckoff 4d). We note that the nomenclature of the 4d sites varies between different reports and is sometimes denoted as 4c, which originates from different choices of the origin of the coordinate system. For the positions of Li⁺ various tetrahedral sites (T1, T2, T3, T4 and T5) for Li⁺ have been defined [6]. Forming an octahedron, each S²⁻ on 4d is surrounded by six Li⁺ sites (Wyckoff 24g, also called T5a). Each T5a site is located on the face of two face-sharing tetrahedra that comprise the T5 sites (Wyckoff 48h). Due to the close distances inside such a T5-T5a-T5 triplets, it is often argued that it is only occupied by one Li⁺ at a time.

Based on this structure, three main jump types have been identified: (1) motion inside a T5-T5a-T5 triplet, also referred to as doublet jump, (2) intracage jumps between two different T5-T5a-T5 triplets of the same cage and (3) intercage jumps between T5-T5a-T5 triplets of neighbouring cages. The doublet jump has a small migration barrier, and therefore the T5-T5a-T5 triplets can also be viewed as a local basin of sites with a flat potential energy surface similar to that found in other superionic conductors [7]. The intracage jump was found to be highly concerted and two mechanisms, a rigid octahedral rotation and a trigonal-prismatic internal reorganization, have been identified recently [8]. Effective Li⁺ transport, however, can only be achieved via intercage jumps. These have been reported to be the bottleneck for long-range diffusion [9] and seem to be facilitated by T2 and potentially also T4 sites [8,10].

The basic crystal structure of Li₆PS₅X can be modified in different ways in order to enhance the materials properties. Several approaches such as (i) varying the X⁻/S²⁻ content towards Li₆₋nPS₅₋nX₁+n (influence on Li content), (ii) replacing S with elements such as Se or Te (influence on the lattice softness and polarizability), (iii) replacing P with aliovalent elements such Si, Ge or Sn (influence on Li content) and/or (iv) replacing Li with Na have been successfully applied [11–17]. However, even in the non-modified Li₆PS₅X systems (X = Cl, Br) the basic structure can be influenced and structural site-disorder between X⁻/S²⁻ on the 4a/4d sites is achieved depending on the synthesis conditions. For Li₆PS₅Br, this was recently shown using quenching experiments from elevated temperatures. The quenching kinetically freezes a certain degree of Br⁻/S²⁻ site-exchange that is present at higher temperatures without the need for changing the composition [18,19]. The site-exchange influences the Li⁺ substructure which in turn leads to enhanced transport properties.

In summary, a variety of optimization strategies have already been successfully applied to Li₆PS₅X and related systems. In this regard, atomistic computer simulations helped to understand the material and the influence of the applied optimization strategies [8,9,12,15,18,20–26]. For the development of further reliable optimization strategies, however, an even more detailed understanding of the atomistic processes is necessary.

Therefore, we are using ab initio molecular dynamics simulations (AIMD) in this contribution to study the Li⁺ diffusion mechanism and how it is influenced by the X⁻/S²⁻ site-exchange on the 4a/4d sites. We restrict the analysis to Li₆PS₅Br, but the generated knowledge should be transferable to other halide ions and will also be helpful for the development and optimization of other superionic conductors whose properties are largely influenced by structural disorder.

2. Computational details

Density functional theory (DFT) calculations have been performed using Version 5.4.4. of the Vienna ab initio simulation package (VASP) [27–30] with plane-wave basis sets and the
Figure 1. (a) Basic unit cell of \(\text{Li}_6\text{PS}_5\text{Br}\). The T5a sites form octahedra (\(\text{Li}^{+}\) cages) around the 4d sites. (b) Used \(\sqrt{2} \times \sqrt{2} \times 2\) supercell model for all simulations. For simplicity, only \(\text{PS}_4^{3-}\) tetrahedra (purple), \(\text{Li}^{+}\) cages (grey) and the 4d sites are shown. In the centre of the supercell one original unit cell is indicated. Unique names A1, A2, ..., D4 have been assigned to each nominal 4d site as labelled in the figure. Their fractional coordinates can be read from electronic supplementary material, table S1. (Online version in colour.)

Figure 2. Schematic snapshots of the newly observed internal reorganization mechanism within the \(\text{Li}^{+}\) cages around the 4d sites. Arrows indicate the different diffusion paths. For clarification, \(\text{Li}^{+}\) are illustrated as differently coloured spheres. The large grey sphere in the centre of the octahedron represents the 4d site. For better comparison, the form of representation was adopted from reference [8]. (Online version in colour.)

Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [31,32]. Projector-augmented-wave (PAW) [33,34] pseudopotentials for Li, P, S and Br have been used as provided by VASP that explicitly treat the outer 3, 5, 6 and 7 electrons as valence electrons, respectively. The pseudopotential versions were PAW_PBE Li_sv 10Sep2004, PAW_PBE P 06Sep2000, PAW_PBE S 06Sep2000 and PAW_PBE Br 06Sep2000.

During geometry optimizations of atomic structures the cut-off energy for the plane-wave basis set was $600 \text{eV}$. The convergence criteria for the energy of self-consistent electronic calculations was $10^{-6} \text{eV}$ and $0.01 \text{eV/Å}$ for atomic forces. The k-spacing was set to $0.25 \text{Å}^{-1}$ resulting in a $3 \times 3 \times 3$ k-mesh for one unit cell as shown in figure 1a. In order to get an initial starting structure only the T5a sites on Wyckoff 24g were occupied in a unit cell of \(\text{Li}_6\text{PS}_5\text{Br}\) without \(\text{Br}^\text{-}/\text{S}^2\text{-}\) site-exchange. The atomic positions and the simulation box volume were then optimized while the box was kept cubic. The resulting lattice constants of $10.2855 \text{Å}$ was used as the basis for all cells described in the following.

Next, a \(\sqrt{2} \times \sqrt{2} \times 2\) supercell containing 16 formula units of \(\text{Li}_6\text{PS}_5\text{Br}\) was generated and used as the starting structure for AIMD simulations using VASP. For AIMD calculations, the cutoff energy for the plane-wave basis set was reduced to the default value as specified by the pseudopotentials and the convergence criterion for the self-consistent electronic calculations was set to $10^{-5} \text{eV}$. Calculations were performed only at the gamma point with timesteps of...
1 fs. Besides the plain supercell defective structures have also been used and an S-rich system containing a $S_{Br}$ defect was generated by placing an S on a Br 4a site in the supercell model. One Li$^+$ interstitial (Li$^+_i$) was added in the vicinity of the substituted ion to ensure charge neutrality. Similarly, also a Br-rich system with a Br$_5$ defect was generated that was compensated by a Li$^+$ vacancy (V$^\prime_{Li}$) in its vicinity. Furthermore, by combining a $S_{Br}$ and a Br$_5$ defect different structures with formally 6.25% site-exchange have been generated using the Supercell Program [35].

By inspection of the Li$^+$ trajectories using the Ovito software [36], we identified intracage and intercage jumps. Furthermore, the python interface of Ovito has been used to determine the occupancies of the T1, T2, T3, T4 and T5 sites. Atomic structures are visualized using VESTA [37] and Ovito [36].

3. Results and discussion

(a) Li$^+$ diffusion without Br$^-$/S$^2-$ site-exchange

In order to discuss how Br$^-$/S$^2-$ site-exchange on 4a/4d sites affects Li$^+$ diffusion the non-disturbed system without site-exchange needs to be analysed first as a reference. Thus, we conducted ab initio molecular dynamics (AIMD) simulations using a $\sqrt{2} \times \sqrt{2} \times 2$ supercell (see figure 1b) of Li$_6$PS$_5$Br without Br$^-$/S$^2-$ site-exchange. Two independent runs of approximately 60 ps length have been performed for improved statistics. Unless specified differently, all results presented in the following refer to simulations conducted at 600 K.

The Li$^+$ motion was found to be dominated by doublet and intracage jumps. The observed intracage jumps are based on two recently reported mechanisms, the rigid octahedral rotation and trigonal-prismatic reorganization mechanisms [8]. Besides these two types of reorganization mechanisms, we furthermore identified a third type which is depicted in figure 2. This mechanism cannot be described by only one rotation axis and involves four Li$^+$. During the reorganization, however, the remaining Li$^+$ also partly show extended displacements (see blue sphere in figure 2). The whole process takes place within approximately 2.0 ps at 600 K and substantiates that Li$^+$ motion inside the cages is highly concerted.

In contrast to the high mobility of Li$^+$ within the cages the observation of intercage jumps is rare. In order to characterize intercage jumps in the following, we have labelled all 4d sites as indicated in figure 1b. During the two independent simulations without Br$^-$/S$^2-$ site-exchange only one single intercage jump was observed which is shown in figure 3a. At a simulation time of approximately 12.7 ps one Li$^+$ jumps from the cage centred around position C4 to the cage around D2 creating a situation in which the number of Li$^+$ around C4 and D2 are 5 and 7, respectively. As normally the number of Li$^+$ would be 6 in both cages this configuration can be seen as a Frenkel pair with a Li$^+$ vacancy (in Kröger-Vink notation: V$^\prime_{Li}$) around C4 and a Li$^+$ interstitial (Li$^+_i$) around D2. The unfavourable Li$^+$ distribution is restored by a back jump of the same Li$^+$ only 2 ps later demonstrating the highly correlated character of intercage jumps in the absence of Br$^-$/S$^2-$ site-exchange.

The jump sequence of figure 3a is summarized in part b of the figure using a flow chart notation that will also be used for more complex jump sequences below. The flow chart always shows the time axis on the bottom. Above the time axis, the jump sequences are illustrated and the arrows indicate an actual Li$^+$ jump from one cage belonging to the labelled 4d site (A1, A2, ..., D4) to another. A red arrow is used for consecutive jumps of the same Li$^+$. The blue background colour of the bar labelled with D2 indicates that the cage around D2 now accommodates a Li$^+_i$. In order to keep track of the V$^\prime_{Li}$ situation, the uppermost yellow bar summarizes around which 4d site(s) a V$^\prime_{Li}$ can be found at the given simulation time.

These results show that intercage jumps are rare processes in the absence of Br$^-$/S$^2-$ site-exchange. Only at temperatures of 700 K or above a sufficient number of intercage jumps (and with that truly long-range Li$^+$ transport) can be observed within reasonable simulation time scales [18,26]. The situation changes as soon as Br$^-$/S$^2-$ site-exchange is introduced into the system. In order to analyse its effect on the underlying atomistic processes, we will in the
Figure 3. (a) Snapshots of the only intercage jump observed in the supercell without Br\(^{-}\)/S\(^{2-}\) site-exchange. The jumping Li\(^{+}\) is shown as a deep blue sphere together with its trajectory in light blue. The simulation time in ps is labelled in the upper left corner of the individual snapshots. The remaining colour coding is the same as in figure 1a and the majority of ions are not shown for clear visibility. (b) Flow chart of the observed intercage jump. The labels C4 and D2 refer to Li\(^{+}\) cages around the corresponding 4d sites as defined in figure 1b. The uppermost yellow bar displays around which 4d sites V\(^{'}\)Li are present at the current simulation time. (Online version in colour.)

Following first divide the site-exchange into its individual parts: a substitutional S\(^{2-}\) on nominal Br\(^{-}\) sites on 4a (S\(_{\text{Br}}\)) and a substitutional Br\(^{-}\) on nominal S\(^{2-}\) sites on 4d (Br\(_{S}\)), where charge compensation was realized by adjusting the Li content.

(b) Li\(^{+}\) diffusion induced by S on 4a

A S\(_{\text{Br}}\) defect was positioned in the supercell structure on the 4a site which is tetrahedrally coordinated by the C3, C4, D2 and D4 sites as sketched in figure 4a. The charge compensation was ensured by adding a Li\(_{i}\) between C3 and C4 in the vicinity of the defect.

The flow chart shown in figure 4b depicts all observed intercage jumps during the simulation. Immediately after the simulation was started the Li\(_{i}\) moves towards C4 and only 0.6 ps later another Li\(^{+}\) jumps from C4 to D4 which is similar to an interstitialcy mechanism. Furthermore, an additional Frenkel pair is formed by an Li\(^{+}\) jump from D2 to C3 but is annihilated again only 1 ps afterwards with a back jump. In the meantime, another Li\(^{+}\) jumps from D4 to C3 creating a situation in which even two Li\(_{i}\) are residing around C3 for a short time until one Li\(^{+}\) moves to the next cage and D2 is refilled. For the rest of the simulation, only one Li\(^{+}\) is traveling at a time via interstitial and interstitialcy jumps. Some of these jump sequences are correlated and mostly result from a Li\(^{+}\) jump followed by a back jump only shortly afterwards (see red arrows in figure 4b).

In conclusion, the majority of Li\(^{+}\) intercage jumps can be attributed to Li\(_{i}\) that jump between the cages. Because most jumps involve the cages C3, C4, D2 and D4, we find that the Li\(_{i}\) mainly resides in the vicinity of the S\(_{\text{Br}}\) defect which is summarized in figure 4c. Both observations are not unexpected: compared to ordinary 4a sites occupied with Br\(^{-}\) the S\(_{\text{Br}}\) defect can be viewed as an additional negative charge that will more strongly attract the positively charged Li\(^{+}\). Therefore, any Li\(_{i}\), which can be viewed as an additional positive charge, will preferentially stay in the orbit of S\(_{\text{Br}}\). This is confirmed by analysis of the average number of Li\(^{+}\) and the occupation of tetrahedral sites discussed in §(e). Sporadically, the second nearest neighbour cages (here C1)
have also been reached by an Li\textsuperscript{i}. A second independent simulation (see electronic supplementary material, figure S1) reproduces these observed features but the generation of Frenkel pairs with V\textsuperscript{′}Li in cages that are not direct neighbours to the S\textsubscript{Br} defect have also been observed.

(c) Li\textsuperscript{+} diffusion induced by Br on 4d

Without changing the composition of Li\textsubscript{6}PS\textsubscript{5}Br the natural counterpart of a S\textsubscript{Br} defect is Br\textsubscript{5}. In order to study its effect on the transport properties separately one nominal S on a 4d site (here: C3) was replaced with Br. A V\textsuperscript{′}Li was created by removing one Li\textsuperscript{+} from the cage around C3 to ensure charge neutrality for the starting structure. This initial configuration is depicted in figure 5a together with the corresponding flow chart of the observed intercage jumps in figure 5b.

At the beginning of the simulation, the first jump is performed by an Li\textsuperscript{+} from C3 to C4 thereby creating an Li\textsuperscript{i} around C4 and leaving back a second V\textsuperscript{′}Li on C3. Two subsequent jumps later the Li\textsuperscript{i} has returned to C3 via an interstitialcy mechanism. Overall, the majority of intercage jumps are governed by moving Li\textsuperscript{i} and during the simulation of approximately 20 ps Li\textsuperscript{i} were found in the Li\textsuperscript{+} cages around B1, B3, C1, C4, D1, D2 and D3 as summarized in figure 5c. All these cages are the nearest neighbour cages of C3 hosting the Br\textsubscript{5} defect. A second, independent simulation with the identical initial set-up (see electronic supplementary material, figure S2) shows similar features.
During the simulation shown in figure 5 only in one other cage (C2), not directly next to C3, a Li$_i$ was present for a short time that was generated as part of a Frenkel pair with a V'$_{Li}$ on C1. Similar to the Frenkel pair observed above for the S'$_{Br}$ defect its lifetime again is approximately 1 ps after which it was annihilated again. Later at around 8.9 ps, when again two V'$_{Li}$ have been present around C3, a Li$^+$ jumped from C1 to C3 to refill one of them. This is the only jump which, instead of an interstitial jump mechanism, could likewise be regarded as a vacancy jump mechanism.

In summary, we found that a Br$_5^-$ defect facilitates the generation of Frenkel pairs with rather mobile Li$_i$. The V'$_{Li}$ by contrast, seem to be strongly bound to the Li$^+$ cage around the Br$_5^-$ defect. This defect-induced Frenkel pair is formed regardless of the fact that one V'$_{Li}$ has already been introduced to the system as compensating defect for Br$_5^-$ defect. The reason for this is most probably due to the electrostatics: the Br$^-$ on the 4$d$ site has a weaker attraction for Li$^+$ compared to the nominal S$^{2-}$. Moreover, the strong attraction of S$^{2-}$ on the surrounding 4$d$ sites is even able to regularly strip another Li$^+$ from the Li$^+$ cage around Br$_5^-$ leaving back two V'$_{Li}$. The generated Li$_i$ is highly mobile which is most likely due to a combination of high Li$^+$ mobility inside the Li$^+$ cages and structural frustration [8]. As a result, the Li$_i$ is able to travel easily through all 12 nearest neighbour cages around the Br$_5^-$ defect. With that, an extended spatial area is involved with Li$^+$ transport only because of one single Br$_5^-$ defect. A larger concentration of Br$_5^-$ defects
will, despite lowering the overall Li content, presumably induce a larger concentration of Frenkel pairs and with that also more mobile Li$^+$$. Such a behaviour most likely explains the increasing ionic conductivity observed in Li$_{6-x}$PS$_{5-x}$Br$_{1-x}$ with increasing $x$ [16].

**d) Combining S on 4$a$ and Br on 4$d$**

The previous subsections revealed the effects of the individual S$'_{Br}$ and Br$'_{S}$ defects on 4$a$ and 4$d$. For the analysis, however, the Li content needed to be adjusted to keep the cell charge neutral which might affect the Li$^+$ transport. Therefore, the same analysis as presented above has been applied to supercells containing a defect pair of S$'_{Br}$ and Br$'_{S}$ at the same time that does not require any further charge compensation by adjusting the Li content. Based on the given supercell size, this structure corresponds to a Br$^-$/S$^2-$ site-exchange of 6.25%. Within this supercell only four symmetrically dissimilar configurations can be realized. These have been chosen in the way that the S$'_{Br}$ defect always resides on the tetrahedral site between C3, C4, D1 and D3 while the Br$'_{S}$ defect occupies A2, A3, C2 or C3 for the individual structures, respectively. The initial configurations, sketches that summarize which cages have been visited by Li$^+_i$ and/or V$'_i$, and the corresponding flow charts of these four simulations are shown in electronic supplementary material, figure S3–S10. Overall, the observations made for the individual S$'_{Br}$ and Br$'_{S}$ defects still hold true and can be summarized as follows.

At almost any time at least one Li$^+$ Frenkel pair is present in all supercells. Similar to that observed for the individual defects, the formation of the Frenkel pair again mainly originates from the Br$'_{S}$ defect which donates one Li$^+$ from its cage to a neighbouring cage. While the generated Li$^+_i$ is highly mobile and initiates further intercage jumps via interstitial and interstitialcy mechanisms the V$'_i$ is strongly bound to the Br$'_{S}$ defect. Periodically, even two Frenkel pairs with two immobile V$'_i$ around the Br$'_{S}$ defect and two mobile Li$^+_i$ are found.

The S$'_{Br}$ defect on the other hand acts as a sink for Li$^+_i$. Frequently, the mobile Li$^+_i$ is drawn close to the S$'_{Br}$ defect and in some cases the T4 sites (see also §(e)) that do not belong to the original cages around the 4$d$ sites become occupied. This is the onset of the cage shifting towards the 4$a$ sites which becomes more pronounced at higher degrees of site-exchange [8,19]. Occasionally, the S$'_{Br}$ defect is also able to strip an Li$^+$ from its regular neighbouring cages but the main source for mobile Li$^+_i$ still remains the Br$'_{S}$ defect.

If the Br$'_{S}$ and S$'_{Br}$ defects are close to each other, the intercage jumps are mainly confined to their vicinity as can be seen in figure 6$a$. In this set-up, the two defects are direct neighbours. As a result, the moving Li$^+_i$ jumps mostly between the cages C4, D1 and D3 or back to C3 where the Br$'_{S}$ defect is located. In rare cases, the Li$^+_i$ also shortly passes the cages B1, D2 and D4 (see electronic supplementary material, figure S4 for the flow chart of jump sequences). With that a Li$^+_i$ was found around only six of the 15 different 4$d$ sites (neglecting C3 which is the 16th site containing the Br$'_{S}$ defect itself) during the simulation.

A larger separation between the two Br$'_{S}$ and S$'_{Br}$ defects, as shown in figure 6$b$, seems to facilitate a more extensive distribution of the Li$^+_i$ (see electronic supplementary material, figure S10). For this set-up, a Li$^+_i$ was found around 10 of the 15 different 4$d$ sites (again neglecting the Br$'_{S}$ on C3). This observation indicates that in cases of low degrees of Br$^-$/S$^2-$ site-exchange as investigated here the local relative arrangement of Br$'_{S}$ and S$'_{Br}$ defects might determine whether or not extended low energy pathways for Li$^+$ are formed. Furthermore, the large spatial distribution of mobile Li$^+_i$ as seen in figure 6$b$ suggests that in cases of an optimal relative arrangement of the anion defects only rather low degrees of Br$^-$/S$^2-$ site-exchange might be necessary in order to establish long-range percolating networks for easy Li$^+$ transport. The evaluation of such an optimal arrangement, however, is beyond the scope of this work and needs to be done elsewhere.

**e) Occupation of Li tetrahedral sites**

As the Li$^+$ transport at low degrees of Br$^-$/S$^2-$ site-exchange is mostly governed by Li$^+_i$, the question arises how the Li$^+$ sub-structure, or more specifically the occupation of the Li$^+$...
Figure 6. Summarizing sketch indicating around which $4d$ sites $\text{Li}_i^+$ and/or $\text{V}_i'$ have been observed during the simulation. The position of the $S'_{6}$ defect is the same in both systems and only the $\text{Br}_5^-$ position varies. For (a), it is located on the C3 position whereas for (b) the A3 position has been used. All initial structures started with a uniform $\text{Li}^+$ distribution with six $\text{Li}^+$ around each $4d$ site. (Online version in colour.)

Figure 7. Average number of $\text{Li}^+$ with respect to the specified $4d$ or $4a$ site and their allocation to the adjacent tetrahedral sites T2, T4 and T5 for the different structure models described in the previous sections. Note that the Kröger–Vink notation has been omitted for the labels of the bars for better readability. Therefore, $S_3$ and $\text{Br}_6$ represent the regular $4d$ and $4a$ sites not involved with $\text{Br}^- / S^2^-$ site-exchange. (Online version in colour.)

tetrahedral sites (T1, T2, T3, T4 and T5), is influenced. We have therefore determined $N_{\text{Li}}$, the average number of $\text{Li}^+$, occupying the tetrahedral sites. Moreover, the analysis has been performed based on different 'perspectives', meaning that we have distinguished between $4a$ and $4d$ sites and whether they are occupied with $\text{Br}^-$ or $S^2^-$. Therefore, $N_{\text{Li}}$ is always a result of only the tetrahedral sites directly adjacent to the investigated site. The results are shown in figure 7.

For the ordered $\text{Li}_6\text{PS}_5\text{Br}$ without $\text{Br}^- / S^2^-$ defects, we can only distinguish between the regular $4d$ sites occupied with $S^2^-$ (labelled as $S_3$ in figure 7) and regular $4a$ sites occupied with $\text{Br}^-$ ($\text{Br}_6$). Consistent with the picture of $\text{Li}^+$ cages surrounding the $4d$ sites we find exactly 6 $\text{Li}^+$
around each 4d site. The Li$^+$ are mostly distributed among the adjacent T5 sites but also partly on the T2 sites substantiating that the internal reorganization mechanism described above (see figure 2) and by Morgan [8] involves the T2 site. Because the T2 and T5 sites are not only connected to the 4d sites, but also spanned by 4a sites, we can likewise monitor the Li$^+$ distribution based on the point of view of 4a sites and their adjacent tetrahedral sites. Unsurprisingly, it shows the same result as for the 4d sites due to the non-defective and therefore symmetrical situation at hand.

With the introduction of a $S_{Br}$ defect and an additional Li$^+_i$ the symmetry of the system is disturbed and $N_{Li}$ starts to vary locally. Most notably, $N_{Li}$ around the $S_{Br}$ defect increases to 7.3, confirming that it acts as a sink for the additional Li$^+_i$. Because the value is above 7 the $S_{Br}$ defect even attracts additional Li$^+$ from its surrounding. This seems to influence the occupation ratio between T5 and T2 towards larger occupation of T2 in the remaining cages. Furthermore, a slight decrease of $N_{Li}$ around Br$_5$Br$^-$ is observed. The increased $N_{Li}$ around the $S_{Br}$ is distributed mostly among the adjacent T2 and T5 sites but also its adjacent T4 sites start to become occupied with 0.12 Li$^+$. This is clearly larger compared to the T4 occupation adjacent to regular 4a sites that remained below 0.01 in all other simulations.

For the Br$_5^-$ defect compensated by V$^-_{Li}$ the determined $N_{Li}$ decreases to 4.6. With the presence of only one V$^-_{Li}$ a value of 5 would be the expected value for $N_{Li}$. The clearly lower value of 4.6 fits to the observations of §(c) and reflects that the Br$_5^-$ occasionally even donates two Li$^+$ to the surrounding that leave back two V$^-_{Li}$. As a result, even though the system is missing one Li$^+$ compared to the defect-free structure, the average $N_{Li}$ of the regular 4d sites ($S_5^-$) slightly increases to 6.02. Also for this defective system, the occupation of T2 sites becomes again slightly more prominent.

Finally, the results from combining a $S_{Br}$ and Br$_5^-$ defect in the same structure fit almost perfectly to the superposition of their individual effects: $N_{Li}$ around $S_{Br}$ is larger than 7, lower than 5 around Br$_5^-$ and it slightly increases (decreases) for the regular $S_5^-$ sites on 4d (Br$_{Br}$ sites on 4a). Furthermore, a small general increase in the occupation of T2 sites is observed and around the $S_{Br}$ defect again the T4 sites become occupied to a small extent.

The analysis proves that a rather complex interaction between different anionic defects and the mobile Li-ions in superionic conductors can be understood by separating the problem into the individual defects. We believe that this approach should be easily transferable to other compounds and might be helpful for the further development of superionic conductors.

4. Conclusion

In this work, the Li$^+$ diffusion processes in the argyrodite-type solid electrolyte Li$_6$PS$_5$Br have been thoroughly analysed using ab-initio molecular dynamics simulations. Without Br$^-$/$S^{2-}$ site-exchange Li$^+$ diffusion is mostly restricted to ionic motion within the Li$^+$ cages (intracage jumps) around the 4d sites and only the T5 and to a lesser degree also T2 tetrahedral sites are occupied. A new cooperative mechanism for the internal reorganization of Li$^+$ was observed. This reorganization mechanism is highly concerted and cannot be described by one single rotation axis. Even at elevated temperature of 600 K only jump between different Li$^+$ cages (intercage jump) was observed during two simulations of approximately 60 ps length, each. This intercage jump, however, was followed by a back jump indicating a high correlation.

With the introduction of Br$_5^-$ and $S_{Br}$ defects on the 4d and 4a sites much more intercage jumps are initiated. Both defects have been analysed separately and in combination. From these simulations, we identified Li$^+$ interstitials (Li$^+_i$) as the main mobile charge carriers. They originate from Li Frenkel pairs which are formed mainly because of Br$_5^-$ defects on the 4d sites that donate one or even two Li$^+_i$ to the neighbouring 12 Li$^+$ cages. This is confirmed by an average number of Li$^+\times N_{Li} < 5$ of the nominal 6 Li$^+$ per cage around the Br$_5^-$ defect. The initiated Li$^+_i$ then carry out intercage jumps via interstitial and interstitialcy mechanisms. With that, one single Br$_5^-$ defect enables Li$^+$ diffusion over an extended spatial area explaining why low degrees of site-exchange are sufficient to trigger superionic conduction. The Li$^+$ vacancies (V$^-_{Li}$) that are formed as part of the Frenkel pairs are mostly immobile and bound to the Br$_5^-$ defect. Also, $S_{Br}$ defects induce
disturbances in the Li\textsuperscript{+} distribution. They mainly act as sinks for Li\textsuperscript{i+} \((N_{Li} > 7)\) and lead to a slight occupation of adjacent T4 sites. Therefore, the Li\textsuperscript{+} motion is mostly restricted to the vicinity of S\textsubscript{Br} defect at low degrees of Br\textsuperscript{-} /S\textsuperscript{2-} site-exchange. From simulations with a combination of a S\textsubscript{Br} and Br\textsubscript{S} defect, we deduce that their relative arrangement might be crucial in enabling long-range transport. Our analysis shows that rather complex interactions between different anion defects and the mobile Li-ions can be well understood by separating the problem into the individual defects first.

**Data accessibility.** Input files, raw data and codes for producing the output can be downloaded from https://github.com/Gitdowski/DFT-Data.git.

**Authors’ contributions.** M.S. performed all calculations and did the data analysis. All authors drafted, read and approved the manuscript.

**Competing interests.** The authors declare that they have no competing interests.

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