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Computationally-guided discovery of a new compound in the Li-Al-S phase field, Li$_3$AlS$_3$: structure and lithium conductivity

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Abstract

With the goal of finding new lithium solid electrolytes by a combined computational-experimental method, the exploration of the Li-Al-O-S phase field resulted in the discovery of a new sulphide Li$_3$AlS$_3$. The structure of the new phase was determined through an approach combining synchrotron X-ray and neutron diffraction with $^6$Li and $^{27}$Al magic angle spinning nuclear magnetic resonance spectroscopy, and revealed a highly ordered cationic polyhedral network within a sulphide anion hcp-type sublattice. The originality of the structure relies on the presence of Al$_2$S$_6$ repeating dimer units consisting of two edge-shared Al tetrahedra. We find that, in this structure type consisting of alternating tetrahedral layers with Li-only polyhedra layers, the formation of these dimers is constrained by the Al/S ratio of 1/3. Moreover, by comparing this structure to similar phases such as Li$_5$AlS$_4$ and Li$_{4.4}$Al$_{0.2}$Ge$_{0.3}$S$_4$ ((Al+Ge)/S = 1/4), we discovered that the AlS$_4$ dimers not only influence atomic displacements and Li polyhedral distortions, but also determine the overall Li polyhedral arrangement within the hcp lattice, leading to the presence of highly ordered vacancies in both the tetrahedral and Li-only layer. AC-impedance
measurements revealed a low lithium mobility, which is strongly impacted by the presence of ordered vacancies. Finally, a composition-structure-property relationship understanding was developed to explain the extent of lithium mobility in this structure type.

1. Introduction

All solid-state batteries (ASSB) are of considerable current interest because they are a potential route to the use of lithium metal anodes while avoiding dendrite formation.\textsuperscript{1,2} Solid-state electrolytes (SSE) offer advantages over liquid electrolytes, such as large electrochemical stability windows and better thermal stability,\textsuperscript{3,4} and have a lithium transport number of unity. Moreover, inorganic crystalline lithium ion conductors have superior ionic conductivity compared to organic polymers.\textsuperscript{5} Recent reviews compare the different families of Li electrolytes\textsuperscript{5–9} and sulphides have the highest Li ion conductivity. For instance, members of the thio-LISICON family\textsuperscript{10–14} such as the Li\textsubscript{7}P\textsubscript{3}S\textsubscript{11} crystalline phase discovered in the Li\textsubscript{2}S-P\textsubscript{2}S\textsubscript{5} system\textsuperscript{15,16} and the Li-argyrodites Li\textsubscript{6}PS\textsubscript{5}X (X = Cl, Br, I)\textsuperscript{17,18} have superior ionic conductivities, $\sigma \sim 1$–20 mS cm\textsuperscript{-1} at RT and low activation energies, $E_\text{a} \sim 0.20$ eV. These values are competitive with those of liquid electrolytes and make them promising candidates for integration in ASSB. The sulphide anion is larger than oxide, more polarizable and affords lower frequency lattice vibrations, all favouring higher lithium mobility,\textsuperscript{19–21} while superior mechanical properties offer lower grain boundary resistance\textsuperscript{6} and allow easier processing into dense pellets. While these characteristics indicate superiority of sulphides over oxides, the usually narrower electrochemical stability window of the former can lead to parasitic reactions at the electrodes and considerably limit the performance and life cycle of ASSB containing sulphide electrolytes.\textsuperscript{5,11,22} Moreover, sulphide materials are often not stable in air, which makes them more difficult to handle. Further improvement of SSE is needed for their commercialisation which implies finding materials showing good ionic conductivity as well as being able to form stable and conducting interfaces at the cathode and anode sides.\textsuperscript{8,14,23}

Given the large number of candidate material compositions for potential new SSE, computation has been extensively used to guide experimental work. On the one hand, some studies focus on currently known materials in order to produce an
understanding of the underlying mechanisms for ion transport thanks to Density Functional Theory (DFT) energy landscape methods and molecular dynamics.\textsuperscript{20,24,25} The need for higher throughput screening methods led to database-driven approaches where models of ion transport, such as the development of predictive performance metrics,\textsuperscript{26} are used to prioritise existing materials for evaluation as SSE. This can be done for example through the use of machine learning algorithms combined with first principle calculations\textsuperscript{27,28} or with bond valence mapping analysis.\textsuperscript{18,29–31} On the other hand, the discovery of new materials, with unique compositions and/or structures, can be accelerated by predicting the most stable compounds within a chosen phase field prior to experimentation. The crystal structure for which the energy is calculated can be either thought to be isostructural to a known material in which original substitutions are performed,\textsuperscript{32–34} or can be determined through crystal structure prediction techniques.\textsuperscript{35–37}

Relatively few mixed anion systems have been studied as SSE. Such materials can combine the advantages of each individual anion and may also offer new structure types for ion transport. The good performance of argyrodite sulphide halide materials demonstrates the potential of such mixed anion systems.\textsuperscript{18,38} Oxysulphide phases, especially for lithium solid electrolyte applications, however remain less explored\textsuperscript{39–42} and could be a promising approach to yield new materials. In particular, the oxygen for sulphur substitution in LGPS structures has been an area of investigation.\textsuperscript{40,42} For instance, Kim \textit{et al.} reported the study of the Li\textsubscript{10}SiP\textsubscript{2}S\textsubscript{12}–xO\textsubscript{x} (0 < x < 1.75) solid solution which resulted in an optimal conductivity for x = 0.7. Another interesting example is the theoretical study by Wang \textit{et al.} presenting O doping into β-Li\textsubscript{3}PS\textsubscript{4} which showed that the oxygen insertion enabled lower activation energy barriers, improved electrochemical stability and create a beneficial 3D connection pathway for Li diffusion.\textsuperscript{41} Moreover, among non-crystalline materials, oxysulphide glasses such as combinations of Li\textsubscript{2}S–P\textsubscript{2}S\textsubscript{5}–P\textsubscript{2}O\textsubscript{5}\textsuperscript{43} or Li\textsubscript{2}S–SiS\textsubscript{2}–LiBO\textsubscript{2},\textsuperscript{44} have been studied as potential lithium solid electrolytes and showed promising properties.

In this study, we evaluate oxysulphides of aluminium as candidate lithium ion conductors, due to the earth abundance, low cost and toxicity, high polarizability and redox inactivity. The composition LiAlOS was previously identified as a new potential interesting solid electrolyte target in a computation-only study.\textsuperscript{37} The study of the Li-
Al-O-S phase diagram was guided by computational evaluation of the stability of candidate compositions, which both highlights where new phases are likely to be found, and allows assessment of the amount of experimental effort to be invested at each composition. Within this phase diagram, the new sulphide phase Li₃AlS₃ was identified and its structure and lithium ion conductivity were characterised.

2. Experimental

2.1. Synthesis

2.1.1. Materials

Li₂S (99.98 % pure), LiNO₃ (> 99 %), Li₂CO₃ (> 99 %), ⁷Li₂CO₃ (99 % ⁷Li), Al(OH)₃ (reagent grade) were purchased from Sigma Aldrich, while Li₂O (99.5 %), urea (99.0 %), Al₂S₃ (99+%), Al(NO₃)₃·9·H₂O (98 %) were obtained from Alfa Aesar.

2.1.2. Exploratory synthesis of the compounds in the Li-Al-O-S phase field

For all sulphide-containing materials, precursors and resulting powders were handled in a He-filled glovebox. Compositions belonging to the Li-Al-O-S phase diagram were synthesized from stoichiometric mixtures of Li₂O, Al₂S₃, and, when needed Li₂S and pre-synthesized LiAlO₂ (according to a procedure from Gao et al.⁴⁵ cf. Supplementary Information, SI). The precursors were weighed in the appropriate amount in order to obtain a total mass of 300 mg. The powders were then mixed and ground in an agate mortar for 15 min, transferred to an alumina crucible and placed in a quartz tube before sealing under vacuum (10⁻⁴ mbar). The tube containing the sample was heated to 800 °C at a ramp rate of 5 °C·min⁻¹, held at 800 °C for 48 hours, and then quenched in water. The resulting powder was then manually ground in order to obtain a fine powder.

2.1.3. Final synthesis of Li₃AlS₃

After identifying Li₃AlS₃ as a new phase through the described synthesis method above, its synthesis was slightly modified in order to improve purity. Li₂S (1.4358 g, 31.2 mmol), and Al₂S₃ (1.5642 g, 10.4 mmol) were weighed according to the stoichiometry 3:1 ratio. The resulting powders were then mixed and ground in an agate mortar for 15 min, transferred in an alumina crucible and placed in a quartz tube before sealing under vacuum (10⁻⁴ mbar). The tube containing the sample was heated at 700 °C for 12 hours and then to 800 °C for 12 hours with an intermediate grinding step in between both firings. The heating ramp rates of the furnace was
5 °C·min⁻¹, and cooling was performed by quenching the tube in water. Neutron powder diffraction (NPD) experiments were conducted on ⁷Li-enriched samples of ⁷Li₃AlS₃, using ⁷Li₂S as precursor material which was synthesized according to a method described by Leube et al.⁴⁶ starting from ⁷Li₂CO₃. For consistency of the structural analysis, the ⁷Li₃AlS₃ sample was also used for synchrotron diffraction experiments.

The importance of the quenching step was investigated by either letting the sample cool down by turning off the furnace, and by setting the cooling ramp rate to 1 °C·min⁻¹. The sample cooled down by turning the furnace off did not show any extra impurity peaks in the X-Ray diffraction pattern, however, the sample cooled with the 1 °C·min⁻¹ ramp resulted in the partial decomposition into Li₅AlS₄ and LiAlS₂. This decomposition was also observed when a formerly prepared Li₃AlS₃ sample was heated slowly to 700 °C at 1 °C·min⁻¹, maintained at this temperature for 30 min and quenched to room temperature. We therefore maintained the 5 °C·min⁻¹ fast heating ramp rate and the quenching step for the synthesis of the material.

### 2.2. Probe Structure Generation and Energy Calculations

All energies were computed using periodic Density Functional Theory (DFT) with the VASP programme.⁴⁷ The PBE functional was used with the projector augmented wave approach to treat core electrons.⁴⁹

A probe structure approach was used to sample compositions in the Li⁺-Al³⁺-O²⁻-S²⁻ phase space.³⁶ Crystal structure prediction (CSP) was used to generate a probe structure at each composition. Each probe structure was assumed to have an energy close enough to the global minimum energy structure to assess the thermodynamic stability of a hypothetical compound at that composition against the formation of an assemblage of known phases.

The CSP was performed using the in-house code ChemDASH (Chemically Directed Atom Swap Hopping). Cells containing hexagonally close packed (hcp) and cubic close packed (ccp) anion lattices hosting O²⁻ and S²⁻ were constructed, and some octahedral and tetrahedral interstitial sites occupied by Li⁺ and Al³⁺ cations. The hcp cells contained eight anions, and the ccp cell nine anions, with a correct number of cations to satisfy charge neutrality at each composition. Structures were initialised with a random decoration of the anion and cation sublattices, and their
structures optimised. To generate new structures, the positions of some anions were swapped on the anion sublattice, or in the interstitial sites the positions of some cations were either swapped or moved to previously vacant interstitial sites. The new structure was then optimised by relaxation of the atomic positions to the nearest local minimum. At each step a Monte Carlo sampling algorithm was used to accept swaps which lowered the energy of the system or increased it by an amount lower than the Monte Carlo energy threshold. The process was continued until 1000 structures had been generated and the lowest energy structure at each composition taken forward for calculating the stability.

One of the features of ChemDASH is to perform structural optimisations in a number of stages which can use different parameters. This was done when optimising each of the structures generated during the CSP process, with each stage using an increasing level of accuracy. In the first stage of each geometry optimisation Γ point-only calculations were used with a plane wave cut-off of 400 eV. By the final stage of each geometry optimisation, a 2×2×2 k-point grid was used with a plane wave cut-off of 600 eV. The cell vectors and atomic positions were optimised until forces fell below 0.02 eV·Å⁻¹.

Once a probe structure had been obtained, its energy was re-calculated at a more accurate level, which was also the level of accuracy used to calculate the energies of previously reported phases. These energies were used to generate the convex hulls of chemical stability. A plane wave cut-off of 700 eV was used with a k-point spacing of 0.15 Å⁻¹. Cell vectors and atomic positions were optimised until forces fell below 0.001 eV·Å⁻¹. The convex hull of chemically stable compositions was generated using pymatgen.⁵⁰

DFT calculations were also performed on an ordered analogue of the experimentally refined crystal structure of Li₃AlS₃. The split Li sites were merged onto a single high symmetry site and all sites given full occupancy. The structure was then optimised in VASP using the more accurate parameters detailed above. No imaginary frequency modes were found in phonon calculations, showing that the structure is stable against displacement of ions from their relaxed positions. The computed phonon frequencies are presented in Table S2 of the supplementary information.
2.3. Elemental analysis

Elemental analysis of Li₃AlS₃ was performed by Mikroanalytisches Labor Pascher at Remagen-Bandorf, Germany, after dissolution in a HF/HCl solution at elevated temperature and pressure.

2.4. Diffraction

2.4.1. X-Ray diffraction

Synchrotron X-ray diffraction (SXRD) was performed at Diamond Light Source UK, on high resolution beamline I11, at λ = 0.82465 Å. The sample was introduced into a 0.7 mm diameter borosilicate glass capillary to record the pattern in transmission mode [0 ° < 2θ < 150 °, and Δ(2θ) = 0.004 °] using the high resolution multianalyser crystal (MAC) detector. The experiment was performed at room temperature. For the Rietveld refinement, the Thompson-Cox-Hastings function with spherical harmonic expansion implemented in FullProf was used to model the peak shape anisotropy. In particular, the (-311), (-402), (-602) and (331) reflections showed a pronounced anisotropic peak shape broadening, which could be due to the presence of structural defects such as antiphase domains and stacking faults. The improvement of the fit thanks to the use of spherical harmonics is illustrated in Figure S3.

2.4.2. Neutron diffraction

Time of flight neutron powder diffraction (NPD) data were collected on Li₃AlS₃ using the High Resolution Powder Diffractometer (HRPD) instrument at ISIS, UK. Experiments were carried out at ambient temperature on the ⁷Li enriched sample sealed in thin-walled vanadium cans of diameter 8 mm, sealed with an indium gasket under 1 atm of helium gas. For the Rietveld refinement, all banks were fitted simultaneously with the T.O.F. pseudo-Voigt back-to-back exponential function with spherical harmonic expansion as for the SXRD data refinement. The structure determination was performed using Jana2006 in order to utilise the charge flipping method implemented in the software to yield an initial model, followed by refinement in FULLPROF owing to user preference.

NMR spectroscopy

The ⁶Li Magic Angle Spinning (MAS) NMR spectra were recorded at 9.4 T on a Bruker DSX spectrometer using a 4 mm HXY MAS probe (in double resonance
mode). The $^6$Li MAS spectrum was obtained using a pulse length of 3 $\mu$s at radio-frequency (rf) field amplitude of $\omega_1/2\pi = 83$ kHz and a MAS rate of $\omega_r/2\pi = 10$ kHz. The $^{27}$Al MAS NMR data were recorded at 9.4 T on a Bruker Avance III HD under MAS at a rate of $\omega_1/2\pi = 12$ kHz using a 4 mm HXY MAS probe (in double resonance mode). The $^{27}$Al spectrum was obtained with a short pulse angle of 30° of duration 0.33 $\mu$s at an rf amplitude of $\omega_1/2\pi = 83$ kHz. The $^{27}$Al triple quantum magic angle spinning (MQMAS)$^{57}$ was obtained with a z-filtered sequence$^{58}$ and using rf field amplitude of $\omega_1/2\pi = 83$ kHz for the excitation and reconversion pulses, and of 4 kHz for the selective 90° pulse. All spectra were collected at room temperature and obtained under quantitative recycle delays of more than 5 times longer than the spin-lattice relaxation times $T_1$ which were measured using the saturation recovery pulse sequence and fitted with a stretch exponential function of the form $1 - \exp[-(t/T_1)^\beta]$ (with $\beta$ ranging from 0.3 to 1). The $^6$Li and $^{27}$Al shifts were referenced to 10 M LiCl in D$_2$O and 0.1 M Al(NO$_3$)$_3$ in H$_2$O at 0 ppm, respectively.

### 2.5. AC impedance spectroscopy

A pellet of the Li$_3$AlS$_3$ powder was made by uniaxial pressing ~30 mg of powder in a 5 mm diameter cylindrical steel die at a pressure of 125 MPa, followed by sintering in evacuated quartz tube at 800 °C for 12 h. A relative density of 80 % was obtained by this method.

A.C. impedance measurements were performed using an impedance analyser (Solartron 1296 dielectric interface coupled with the Solartron 1255B frequency response analyser) in the frequency range from 1 MHz to 100 mHz (with an amplitude of 50 mV). Silver paint (RS silver conducting paint 186-3600), brushed on both sides of the pellet and dried under vacuum at room temperature, was used as ion blocking electrodes. Variable temperature conductivity measurements were carried out under argon (flow rate 50 mL·min$^{-1}$), using a custom built sample holder, in the temperature range 25-125 °C. The impedance spectra were fitted with an equivalent circuit using the ZView2 program.$^{59}$

### 3. Results and discussion

#### 3.1. Computational/experimental study of the Li-Al-O-S phase field

We explored the Li-Al-O-S phase field using probe structure-based materials discovery.$^{35,36}$ This method involves identifying a set of unexplored compositions on
the phase field of interest and computationally generating a probe structure for each one. By determining the energy of each of the probe structures compared to the convex hull, we can identify low-energy regions of the phase diagram and hence target synthetic efforts towards regions of the phase field where new compounds are more likely to be found. To ensure fully occupied anion sublattices, the compositions of unit cells used in calculations were constrained to contain eight or nine anions with a stoichiometric number of cations to satisfy charge neutrality. Under these constraints a range of compositions were chosen to span the phase field, with more compositions at the Li rich end (Figure 1a). We sampled all of the possible compositions for the cells containing eight anions, and then only considered the Li:Al ratios closest to 1:1 for the cells containing nine anions, since these were the lowest energy regions following the initial screen. All possible S:O ratios were considered. The computed energy of the probe structure at each computed composition is presented in Figure 1a.

A valley of lower energy is observed at a Li/(Li+Al) ratio of 0.5 (LiAlS$_2$-LiAlO$_2$ solid solution line), with a local energy minimum at 42 meV·atom$^{-1}$ above the convex hull for the previously proposed composition of LiAlOS. When using the full convex hull construction, LiAlOS is predicted to decompose into LiAl$_5$O$_8$, LiAlS$_2$ and Li$_2$S. In comparison, the probe structure in the previous study was also determined to be thermodynamically unstable, but with respect to LiAlS$_2$ and LiAlO$_2$, with a calculated formation reaction energy of 46 meV·atom$^{-1}$ at 0 K. Because these calculated energies are relatively low, LiAlOS could be a metastable structure possibly synthesizable, and was therefore selected as a candidate composition for experiment.

Near the sulphur and oxygen rich regions of the LiAlS$_2$-LiAlO$_2$ solid solution line, the calculated energy is interestingly low compared to other regions close to the borders in the overall phase diagram. For instance, the energy of composition LiAlS$_{1.8}$O$_{0.2}$ is 34 meV·atom$^{-1}$ above the convex hull. This value is close to the value of the known phase LiAl$_5$S$_8$ (38 meV·atom$^{-1}$ above the convex hull), which has been synthesized in the literature. Composition LiAlS$_{1.8}$O$_{0.2}$ was therefore selected for experimental synthesis. The symmetrical composition near the oxide end member, LiAlS$_{0.2}$O$_{1.8}$, shows a higher energy (51 meV·atom$^{-1}$), but is close to that of LiAlOS and was also synthesized as a matter of comparison.
Plateaus with energies below 60 meV·atom\(^{-1}\) above the convex hull are observed in regions close to the terminal Al\(_2\)S\(_3\) and Li\(_2\)O. Within the former, the composition Li\(_3\)Al\(_9\)O\(_2\)S\(_{13}\) was previously suggested by the Materials Project\(^{61}\) as an interesting analogue candidate of Ga\(_9\)Tl\(_3\)O\(_2\)S\(_{13}\).\(^{62}\) The energy calculated for this compound in this work is 46 meV·atom\(^{-1}\) above the convex hull, which is also close to that calculated for LiAlOS. The plateau close to Li\(_2\)O, as well as presenting relatively low energies, attracted our interest due to the high content of lithium, possibly favourable to attain higher conductivities. Two compositions, Li\(_5\)AlO\(_3\)S and Li\(_7\)Al\(_2\)O\(_4\)S, were selected for experimental synthesis in this region of the phase diagram.

Figure 1b and
summarize the six compositions (labelled A to F and represented by red squares) that were chosen, in a first stage, after analysis of the results from calculations. The experimental procedures for all samples were the same, and are described in the experimental section. In particular, we used Li$_2$O and LiAlO$_2$ as oxide precursors whenever the composition enabled it, in order to improve the reactivity compared to the use of Al$_2$O$_3$. Moreover, a relatively high temperature of 800 °C and cooling by quenching procedure were chosen in order to both facilitate the access to high energy phases, and to kinetically trap them and prevent the decomposition into binary or ternary phases during cooling.

Compositions highlighted with the filled red squares on Figure 1b, consisted of a mixture of already reported phases after annealing which is detailed in
However, two points along the LiAlO$_2$-LiAlS$_2$ solid solution line (Figure 1b, points B and C) showed the presence of an unknown phase along with the already reported phases. Figure S1 shows the XRD patterns of samples A to F after reaction made in the first stage. For composition LiAlOS, the unknown phase seemed to be in relatively high amount, thus, in a second stage, four new compositions were tested around this point (black squares on Figure 1b, composition given in caption and
For composition number 4 in particular (Li$_2$Al$_4$O$_5$S$_2$), this new phase was present along with Al$_2$O$_3$ as a single impurity. Figure S2 shows the XRD patterns of the samples 1 to 4 after reaction made in the second stage. Li$_2$Al$_4$O$_5$S$_2$ can then be written as Li$_2$Al$_4$O$_5$S$_2$ = a Al$_2$O$_3$ + Li$_2$Al$_{2/3(1+y)}$O$_y$S$_2$ (0 ≤ y < 5), highlighting that the unknown phase must have a Li/S ratio of 1. By considering the two end members (y = 0 and y = 5), this result lead us to investigate the solid solution line x Li$_2$Al$_4$O$_5$S$_2$ + (1−x) Li$_2$Al$_{2/3}$S$_2$, on which is located the composition Li$_2$Al$_{2/3(1+y)}$O$_y$S$_2$. The synthesis of the pure sulphide end-member (point number 5) gave the phase pure new compound sought, which was thus revealed to be a pure sulphide material, rewritten as Li$_3$AlS$_3$. The energy calculated for Li$_3$AlS$_3$ was found to be 16 meV·atom$^{-1}$ above the convex hull. No other calculated energies in the phase diagram which do not already correspond to known phases drop below this threshold. We therefore concluded that no other oxysulphide phases are likely to form in the Li-Al-O-S field. The oxide analogue Li$_3$AlO$_3$ could not be stabilized by a similar quenching method (cf. SI) and leads to a calculated energy of 27 meV·atom$^{-1}$ above the convex hull. The calculated energy of Li$_3$AlS$_3$ is slightly above the hull, which suggests the phase is metastable.
Figure 1. (a) Calculated energy of different compositions in the Li-Al-O-S phase field using cells containing hexagonally close packed (hcp, black triangles) and cubic close packed (ccp, black filled circles) anion lattices. $E_{\text{hull}}$ is the energy above the convex hull. Reported oxide and sulphide phases in the Li-Al-O-S phase field (black rectangles). (b) First stage experimentally tested compositions which resulted in a mixture of already reported compounds (empty red squares), and a mixture of already reported compounds along with the presence of the new phase (filled red squares). Second stage experimentally tested compositions (numbered black circles). Composition of points are: A ($\text{Li}_3\text{Al}_9\text{O}_2\text{S}_{13}$), B ($\text{LiAlOS}$), C ($\text{LiAlO}_{0.2}\text{S}_{1.8}$), D ($\text{LiAlO}_{1.8}\text{S}_{0.2}$), E ($\text{Li}_7\text{Al}_2\text{O}_4\text{S}$), F ($\text{Li}_5\text{AlO}_2\text{S}$), 1 ($\text{Li}_4\text{Al}_2\text{O}_2\text{S}_3$), 2 ($\text{Li}_6\text{Al}_8\text{O}_{10}\text{S}_5$), 3 ($\text{Li}_2\text{Al}_4\text{O}_4\text{S}_3$), 4 ($\text{Li}_2\text{Al}_4\text{O}_5\text{S}_2$), 5 ($\text{Li}_5\text{AlS}_3$).
In the Li-Al-S phase field, phases with compositions LiAlS$_2$, Li$_5$AlS$_4$, and LiAl$_5$S$_8$ have previously been reported. Moreover, an amorphous phase with composition Li$_3$AlS$_3$ was identified previously as the discharge product of an Al-S battery. Although no experimental structural data was presented for this model, a local structure of this amorphous phase was modelled with DFT, and displayed a network of isolated 4 and 5-coordinated aluminium. Both the LiAlS$_2$ and Li$_5$AlS$_4$ structures possess nearly close-packed anion layers arranged in a hexagonal stacking sequence. LiAl$_5$S$_8$ is dimorphic and comprises a low temperature modification with a normal spinel type structure and a high temperature modification related to the ZnIn$_2$S$_4$ structure. Both LiAl$_5$S$_8$ structures have a cubic closed packed arrangement of the anion lattice. The integrated computation-experiment approach described here enabled the identification of a new crystalline phase with the composition Li$_3$AlS$_3$. This phase was isolated by synthesis and its structure and lithium transport properties experimentally investigated.

3.2. Synthesis and structure of Li$_3$AlS$_3$

3.2.1. Synthesis

Polycrystalline Li$_3$AlS$_3$ was synthesized via solid state reaction of Li$_2$S and Al$_2$S$_3$ (described in the experimental section). The powder XRD profile of the product could be indexed to a phase whose structure does not match any of the compounds previously reported for Li-Al-S systems. A small quantity of Li$_5$AlS$_4$ (3.3(5) mol %) was also identified in the XRD pattern. Elemental analysis gave an overall composition of Li$_{3.1(1)}$Al$_{1.1(1)}$S$_{3.0(1)}$ (Table S3), but the ICP measurement is not sufficiently precise to distinguish between the nominal reaction stoichiometry (Li$_3$AlS$_3$), the measured composition and the presence of the secondary Li$_5$AlS$_4$ phase further complicating its interpretation: consequently, the compound is referred to as Li$_3$AlS$_3$ hereafter.

3.2.2. Structure determination

The crystal structure of Li$_3$AlS$_3$ was solved by first indexing the SXRD pattern using the first 22 reflections using GSAS-II. The unit cell was indexed in the space group C12/c1 with approximate lattice parameters 14.3*12.0*6.6 Å with $\beta \sim 117^\circ$. The lattice parameters were then refined across the d-spacing range 16 – 0.67 Å ($2\theta = [3^\circ – 75^\circ]$) via a Lebail fit in Jana2006. The structure was solved initially by locating the S and Al atoms using superflip implemented in Jana2006. From this
solution, a Rietveld model was refined against the SXRD and NPD patterns. Once converged the Li atoms were located using Fourier Difference mapping on the NPD patterns searching for peaks in the difference map located at greater than 1 Å from existing atoms within the model. When no more new sites could be located, an initial Rietveld model was constructed and refined.

Final Rietveld refinement of the neutron and synchrotron diffraction data was carried out using the program FULLPROF.\textsuperscript{70} First, the SXRD pattern was fitted on its own. Position, site occupancy factor (sof), and atomic displacement parameters (ADPs) of lithium atoms remained fixed in the refinement of the synchrotron data. The sof of aluminium refined to 0.974(1) on its site and significant drops in the conventional reliability factors were obtained: $R_{\text{Bragg}}$ decreased from 2.79 to 2.68. Figure 2a shows the final fit of the SXRD pattern and the following results were obtained for the cell parameters: $a = 14.31901(5)$ Å, $b = 11.98037(3)$ Å, $c = 6.62700(2)$ Å, and $\beta = 116.9231(3)^{\circ}$. The values of the refined cell parameters were then implemented and fixed in the refinement of neutron data. The final model of the structure was obtained through the combined refinement of the neutron data coming from the three neutron datasets. Figure 2b-d shows the final fits of the patterns. Refinement details and outcome as well as the crystallographic data are summarized in Table S4 and S5.
Figure 2. Final Rietveld refinement of (a) the synchrotron X-ray diffraction pattern of $^7\text{Li}_3\text{AlS}_3$ (Diamond light source, I11 beam line) with fixed Li positions, and of (b) $^7\text{Li}_3\text{AlS}_3$ against neutron powder diffraction data (ISIS neutron source, HRPD) from (b) bank 1 ($2\theta = 168.330^\circ$), (c) bank 2 ($2\theta = 89.580^\circ$), and (d) bank 3 ($2\theta = 30.000^\circ$), with $I_{\text{obs}}$ (red dots), $I_{\text{calc}}$ (black line), $I_{\text{obs}}-I_{\text{calc}}$ (blue line), and Bragg reflections (red tick marks for $\text{Li}_3\text{AlS}_3$, black tick marks for $\text{Li}_5\text{AlS}_4$ and blue tick marks for the vanadium can).

The unit cell shows three sulphur sites (S1, S2 and S3), three tetrahedral sites on general positions 8f (Table S5), two of them occupied by Li (Li1 and Li4) and one by Al and Li ions (Al and Li_{Al}), and two occupied octahedral lithium sites (Li2 and Li3) located on two 4e Wyckoff positions on the 2-fold rotation axis (at the beginning of the refinement). The isotropic atomic displacement parameters ($B_{\text{iso}}$) refined to large values: 3.3(5) Å² for Li2 and 3.7(5) Å² for Li3. In order to improve the model, the displacement was modelled as anisotropic, which lead to the decrease of $\chi^2$ from 1.74, 6.46, 1.54 to 1.73, 6.06, 1.54 for bank 1, 2 and 3 respectively. The anisotropic ADPs for Li2 and Li3 remained high, and a marked anisotropic displacement along the a axis was found for Li3 in particular, as highlighted by the Fourier difference map in the (ab) plane on Figure S4a, thereby prompting us to consider site splitting. Li3 was moved from its fully occupied 4e position (0, y, 0.25) to a half occupied...
general 8f position (x, y, z) which then generates a second Li3 atom of coordinate (-x, y, z) from the other side of the rotation axis, within the same coordination polyhedra. For Li2, as the anisotropic displacement was not as straightforwardly along one single direction, moving the atom to one half occupied 8f position did not improve the fit. This site was split into two 8f positions (Li2 and Li2b), each allocated first with an occupancy of 0.25, generating 4 Li positions within the same coordination polyhedron, in order to model its large displacement. The occupancies of Li2 and Li2b were then refined by constraining their sum to be equal to 0.5. In that way, the total occupancy within each polyhedron is equal to one. The site splitting of Li2 and Li3 led to much smaller isotropic ADPs of 1.2(7) Å² for Li2 (and Li2b) and 1.7(4) Å² for Li3, along with a reduced residual density in the Fourier difference map around the sites (Figure S4b). Another indication for preferring the modelling of both sites with multiple atoms was the increase in the bond valence sum (BVS) from 0.76(1) to 0.83(16) for Li2 and 0.82(4) for Li2b, while keeping it to 0.80(3) for Li3.

Through occupancy refinement, a lithium antisite defect was identified and occupies 6.7% of the aluminium site. No other Li or Al antisite defects were found. Details of the refinement procedure are presented in the SI page 7 and results of the final refinement of the occupancies are given in Table S4.

NMR spectroscopy was deployed to further confirm the overall pattern of site occupancy of the lithium atoms. The $^6$Li MAS NMR spectrum for Li$_3$AlS$_3$ is shown in Figure 3a and displays three well-resolved resonances at 1.7, 1.3 and -0.2 ppm which fit yield signals of equal integration. A small shoulder is also observed at 1 ppm (Figure S8) and corresponds to the Li$_2$AlS$_4$ impurity seen in the diffraction and $^{27}$Al NMR data (see below); this signal was found to integrate 3.0(5) mol% of Li$_3$AlS$_3$ in agreement with the 3.3(5) mol% value from diffraction. Based on the well-established semi-empirical correlations relating lithium coordination environment and $^6$Li NMR shifts, further aided by calculations of the NMR parameters using the GIPAW approach as implemented in CASTEP (cf. SI, Table S7), the signal at -0.2 ppm has been attributed to the octahedrally coordinated Li2/Li2b and Li3 sites while the resonances at 1.3 and 1.7 ppm correspond to Li4 and Li1, respectively. These assignments agree well with the structural refinement described above which identified the sum of the contents of the three octahedrally coordinated sites Li2 (0.8(3)), Li2b (3.2(3)) and Li3 (4.0(4)) to 8.0(7) Li per unit cell, and the contents of the
two tetrahedrally coordinated Li4 and Li1 to 7.8(3) and 8.00 per unit cell, respectively.

The $^{27}$Al one-dimensional MAS spectrum for Li$_3$AlS$_3$ is shown in Figure 3b and reveals a broad second order quadrupolar lineshape that resonates at $\sim$ 100 ppm, typical of tetrahedrally coordinated Al sites, and a very sharp signal at $\sim$ 130 ppm corresponding to the small amount of Li$_5$AlS$_4$ impurity (Figure S7). Note that no signal in the octahedral region (around 0 ppm) of the $^{27}$Al MAS NMR spectrum is present as expected. The z-filtered triple quantum MAS$^{53,54}$ NMR spectrum of Li$_3$AlS$_3$ is also shown in Figure 3b and demonstrates that the $\sim$ 100 ppm signal corresponds to one resonance only with an isotropic chemical shift of 117 ppm (cf. SI) and a quadrupolar coupling constant ($C_Q$) of 5.8 MHz in close agreement with the computed value of 5.1 MHz (cf. SI, Table S7).

Figure 3. (a) $^6$Li MAS spectrum of Li$_3$AlS$_3$ obtained at a magnetic field of 9.4 T and under MAS at 10 kHz. The experimental spectrum (full line), total fit (dashed line) spectral deconvolution (dotted lines), Li$_5$AlS$_4$ impurity (red dotted line) and GIPAW simulated spectrum (green line) are shown. (b) $^{27}$Al MQMAS NMR spectrum of Li$_3$AlS$_3$ recorded at a magnetic field of 9.4 T and at a MAS rate of 10 kHz. The black dotted line and the red dotted line represent the spectral deconvolution of Li$_3$AlS$_3$ and Li$_5$AlS$_4$ respectively. The black dashed line shows the total fit for the sample and
the solid black line shows the anisotropic one-dimensional $^{27}$Al spectrum, while the vertical spectrum shows the non-quantitative isotropic $^{27}$Al spectrum. The solid green line shows the GIPAW simulated spectrum with an isotropic shift of 117 ppm, a quadrupolar coupling constant of 5.1 MHz and an asymmetry parameter of 0.44 (Table S7).

The final model led to the overall refined composition $\text{Li}_{3.13(2)}\text{Al}_{0.958(4)}\text{S}_3$, slightly different from the composition determined by ICP. The small differences can be explained by the presence of the $\text{Li}_5\text{AlS}_4$ impurity which prevents the ICP measurement from producing an accuracy to the nearest two decimal places. The refined composition is different from the ideal, which will be discussed hereafter.

3.2.3. Structure description

a) Polyhedral arrangement

$\text{Li}_3\text{AlS}_3$ adopts a structure related to that of $\text{Na}_3\text{InS}_3$ reported by Eisenmann et al. where $\text{In}^{3+}$ and $\text{Na}^+$ cations are replaced by $\text{Al}^{3+}$ and $\text{Li}^+$, respectively.\(^{72}\) The only other isostructural phases reported are $\text{Na}_2\text{Mn}_2\text{S}_3$,\(^{73}\) $\text{Na}_2\text{Mn}_2\text{Se}_3$\(^{74}\) and $\text{Li}_x\text{Na}_{1-x}\text{Mn}_2\text{S}_3$ ($x\sim0.7$),\(^{75}\) in which half of the Mn$^{2+}$ ions are replaced by aluminium atom whereas the other half along with the sodium atoms are replaced by Li$^+$. The structure is constructed from a hcp arrangement of sulphur atoms with an AB A*B* stacking of anion layers, where B is the equivalent of A through the c glide plane and 2-fold axis symmetry operations. A* and B* are the equivalent of A and B through the C centring translation (Figure 4a). In the tetrahedral layer, Li1 and Al atoms occupy 2/3 of the tetrahedral interstices between a pair of sulphur atom layers (B and A*, equivalent to the B*A pair). Between the second pair of sulphur layers (A and B, equivalent to the A*B* pair), Li2 and Li3 occupy octahedral interstices, whereas Li4 occupies a tetrahedral interstice, generating a mixed polyhedral (octahedral-tetrahedral) layer. The two different polyhedral layers are stacked alternately perpendicular to the (bc) plane (Figure 4a). Bond distances and angles of the different polyhedral, and BVS calculations performed for all atoms are summarized in Table S6.

In the tetrahedral layer, one tetrahedral site in every three is vacant in an ordered manner (Figure 4b). Each T$^+$ and T$^-$ interstice forms a network of alternating Al, Li1, and vacancy corner shared tetrahedra. The T$^+$ and T$^-$ networks interlock in such a way that each AlS$_4$ unit shares one edge (S3-S3) with another Al tetrahedron and a second edge with the Li1S$_4$ unit within the layer. These 4 edge-shared tetrahedra ($\text{Li1S}_4(T^+)$-$\text{AlS}_4(T^-)$-$\text{AlS}_4(T^+)$-$\text{Li1S}_4(T^+$)) form a unit that is connected to
other units of this type by corner-sharing (Figure 5a, circled part on Figure 4b). The Li1 tetrahedron has two S that share corners with a Li1 and Al and there is no corner-sharing of Al tetrahedra.

In the mixed polyhedral layer, each of the Li2, Li2b, and Li3 atoms is surrounded by six sulphur atoms to form LiS₆ octahedra (Figure 4c, Figure 5b). Li2 and Li2b polyhedra form an infinite chain of edge-shared octahedra along the c axis, which are also connected to three Li3 octahedra also through three shared edges. Thus both octahedra form infinite two octahedra-wide chains along the c axis. Each chain is separated along the b axis by a chain of edge-shared LiS₄ T⁺ and T⁻ tetrahedra occupied by the Li4 atom (Figure 4c). Li3 octahedra are linked to two consecutive T⁺ and T⁻ Li4 tetrahedra, sharing one face with each of them (Figure 4c). These two Li4 tetrahedra form a unit (Figure 5b) and each T⁺ and T⁻ of the unit shares one corner with one Li2/Li2b octahedron from the same chain as the face-shared Li3 octahedra, as well as one corner with one Li3 octahedron of the chain on the other side of the Li4 chain. Along the Li4 chain, octahedral interstices are vacant, so that only 2/3 of the octahedral sites are occupied in the layer. As a result of crystallization, the ordered structure obtained experimentally in this study strongly differs with the structure modelled for the amorphous discharged product with the same composition described by Lu et al.⁶⁶

Figure 4c shows the connection between the polyhedra of both layer types. Each of the Al and Li1 T⁺ (T⁻) tetrahedra is connected to the layer below (above) by sharing the face at the base of the tetrahedron with a vacant tetrahedral site of the mixed polyhedral layer. For the Al tetrahedra, this face shares one edge with the Li2 octahedra and another edge with the Li3 octahedra of the same chain, while the third edge is shared with the vacant octahedral site. For the Li1 tetrahedra, this face shares two edges with the Li2 octahedra and one edge with the Li3 octahedra of the same chain. The S3 atom, which is at the vertex of the Al T⁺ (T⁻) tetrahedra, is shared with one Li2, one Li3 and four Li4 of the above (below) mixed polyhedral layer, whereas the S1 atom, which is at the vertex of the Li1 T⁺ (T⁻) tetrahedra, is shared with one Li3 octahedron and four Li4 of the above (below) mixed polyhedral layer. The chain of vacant T⁺ (T⁻) sites along the c axis in the tetrahedral layer lies above (below) the chain of Li4 tetrahedra of the mixed polyhedral layer.
Figure 4. (a) Crystal structure of Li$_3$AlS$_3$ showing the alternating arrangement perpendicular to the (bc) plane of the tetrahedral layers containing AlS$_4$ and LiS$_4$ tetrahedra and of the mixed polyhedral layers containing Li-only polyhedra. (b) T$^+$ and T$^-$ interstices in the tetrahedral layer, showing the corner sharing arrangement of the Li1, Al, and vacant (empty) tetrahedra in each network, as well as the interconnection (following the yellow arrow) of each T$^+$ (thin lines) and T$^-$ (thick lines) network so that AlS$_4$ dimers are formed. The highlighted yellow face of the Li1 tetrahedron corresponds to the only face that shares two edges with two vacant sites. (c) View of both the mixed polyhedral layer and the tetrahedral layer in the (bc) plane and of their interconnection (following the yellow arrow). Polyhedra colours: blue: Al tetrahedra, orange: Li tetrahedra, red: Li2 octahedra, light red: Li3 octahedra.
Figure 5. Coordination polyhedra of (a) Li1 and Al in the tetrahedral layer, (b) Li4, (c) Li2 and Li2b and (d) Li3 in the mixed polyhedral layer.

b) Polyhedral distortions and atom displacements

Figure 6 shows the bonding environment of each of the cations. In the tetrahedral-only layer, Li1 atoms are strongly off-centred towards the S1-S2-S2 face that both does not share any edges with the AIS₄ tetrahedra in the same layer, and does not belong to the octahedral layer (Figure 6). This face is also the only one that shares two edges with two vacant sites of the tetrahedral layer as opposed to one for the other two faces that do not belong to the octahedral layer (highlighted yellow face on Figure 4b and Figure 6). Moving away from the nearby Al cations as well as from the Li2 and Li3 atoms of the octahedral layer provides the electrostatic driving force for its displacement (Figure 6). The BVS of Li1 is 0.97(2), which is very close to the ideal value of +1, considering the oxidation state of lithium.
Figure 6. Crystal structure of Li$_3$AlS$_3$ showing the arrangement of octahedral (red) and tetrahedral (orange) lithium and tetrahedral aluminium (blue). The direction of the displacement of atoms is symbolized by arrows: blue for Al, orange for Li1 and Li4 and yellow for S.

The tetrahedral Li4 site in the mixed layer shares a face with the vacant tetrahedral site of the tetrahedral layer. The Li4 position is strongly displaced towards the base of the tetrahedron and the adjacent sulphur layer, towards this vacant tetrahedral interstice (Figure 6). Li4 thus adopts a pseudo trigonal bipyramid environment with one short axial Li4-S1 and one long axial Li4-S2 bond. BVS for Li4, is slightly lower than that of Li1, of 0.93(2), which is consistent with its pseudo 5-coordinated environment making it more loosely bound to the S atoms compared to the 4-coordinated Li1.

This is reflected in the NMR resonance frequency of Li4 (1.3 ppm), for which the five-coordinate environment provides this site with an intermediate chemical shift between the lithium atoms occupying a tetrahedral site (Li1 at 1.7 ppm) and octahedral sites (Li2/L2b and Li3 at -0.2 ppm). The NMR shift calculation also suggests that the resonances of Li3 and Li2/L2b should be resolved as the isotropic
chemical shifts differ by 0.3 ppm, however this is not observed experimentally due to the larger full width at half maximum (18 compared to 10 and 11 Hz for Li4 and Li1 respectively) observed for this Li3/Li2/L2b resonance. The presence of the occupied Li4 sites distinguishes both Li3 and Li2/Li2b sites: Li3 shares faces with Li4 whereas Li2 does not (Figure 4c). The shift of the Li4 toward the adjacent sulphur layer pushes the Li4 atom further away from the octahedral Li3 atoms, and therefore reduces the structural difference between Li2 and Li3, further explaining the similar shifts observed experimentally for these octahedral sites (Table S7). On the contrary, the difference in the environment of Li1 and Li4 is more pronounced (tetrahedral vs. trigonal bipyramid), which explains the resolution of their respective NMR peaks. The consistency between the experimental NMR data and the computed ones from described structure further reinforces the accuracy of the selected structural model.

The geometry of the AlS4 dimer is represented in Figure 5a, and among the six edges of each AlS4 tetrahedron, four of them are directly connected to the S3-S3 edge shared with the other tetrahedron of the dimer. Consequently, the aluminium position is shifted towards the S1-S2 edge that does not share a common sulphur atom with the other edge shared Al tetrahedron of the dimer. This displacement is symbolized by blue arrows on Figure 6. This can be explained by the proximity to the other Al atom of the edge-shared dimers, with which it tends to maximize its distance. The Al-Al distance is 3.015(6) Å, which is similar to distances obtained in other sulphide materials (Na6Al2S6, Na3FeS3) presenting these dimers. This is also supported by the 27Al NMR data obtained experimentally and computed with GIPAW (cf. SI and Table S7) that yield a clear second order quadrupolar lineshape at 9.4 T and from which large quadrupolar coupling constants (CQ = 5.8 vs. 5.1 MHz) and distorted asymmetry parameter values (ηQ = 0.56 vs. 0.44) are obtained. These data clearly demonstrate the non-symmetrical dimeric Al coordination environment in Li3AlS3 and is in sharp contrast to the symmetric AlS4 tetrahedra observed in Li5AlS4 (CQ ~ 0 MHz, Figure S7) as evidenced by the NMR narrow line of this phase.

The dimerization leads to the strong repulsive force between both highly charged Al3+ cations. This in turn brings the S3 atoms inside the dimer towards each other, and therefore towards the interior of the tetrahedral layer, in order to keep the BVS of Al and S close to their ideal values (symbolized by yellow arrows on Figure 6b, c). The S3-S3 distance (represented by a thick line on Figure 6b,c,
\(d_{S3-S3} = 3.463(14) \text{ Å}\) is indeed the shortest in the structure. The compression of the S3-S3 edge of the Al2S6 dimer unit in the tetrahedral layer leads to the stretching of the S3-S3 edge of Li2(Li2b)S6 and Li3S6 octahedra in the mixed polyhedral layer (Figure 6b,c).

As shown in Figure 6a, the Li2b (and Li2) octahedron is highly distorted, the S3-S3 edge is considerably longer than the other edges \((d_{S3-S3} = 4.40(1) \text{ Å whereas the length of the other edges range from 3.66(1) Å to 3.951(7) Å}\). Also, the Li3 octahedron is elongated along an axis defined by two S3 atoms \((d_{S3-S3} = 5.729(14) \text{ Å}\), whereas the equatorial plane defined by two S1 and two S2 atoms is close to a square \((d_{S2-S2} = 3.893(13) \text{ Å}, d_{S1-S1} = 3.713(14) \text{ Å}, d_{S2-S1} = 3.682(8) \text{ Å}\). The explanation for the site splitting of Li2 can be linked to the distribution of the sulphur vacancies (SI, page 10). In contrast to the tetrahedral Li1 and Li4, the BVS for octahedral Li2, Li2b and Li3 are below the theoretical value \((0.83(16), 0.82(4)\) and \(0.80(3)\) for Li2, Li2b and Li3 respectively), which reflects that they are weakly bonded to the sulphur atoms. This observation has also been made in similar structures\(^{65}\).

A sulphur deficiency was found on two S sites. This deficiency accounts for the charge compensation with the Al defect. The majority of sulphur vacancies are located on the S3 site, which bridges the two aluminium tetrahedra of the dimer. As explained above, the S3-S3 distance is the shortest in the structure, hence vacancies here would reduce anion-anion repulsions. Again the presence of the dimers leading to the short S3-S3 distance could be the trigger for the deficiency of the S site. Further, the occupancy of the Al site cation vacancies by Li creates a negatively charged antisite defect which could also drive the localization of the positively charged sulphur vacancy on the S3 site.

The analysis of the Li3AlS3 structure highlights the importance that the Al2S6 dimers have on site geometries as well as on site occupancies of both lithium and sulphur atoms. Moreover, the comparison with the probe structure, that also shows the presence of these dimers (SI, page 11 and Figure S5), further suggests that the stability of the structure is connected to the presence of the Al2S6 dimers.

### 3.3. Comparison with known structures

Lithium sulphide materials showing different arrangement of cation polyhedra in hcp arrays are common and some interesting compositions and structures have
been described by Lim et al. Among them, one can cite Li$_2$FeS$_2$, which consist of an octahedral only layer whose interstices are 100% occupied by lithium atoms, alternating with a tetrahedral layer, where all the tetrahedral sites are occupied by Li and Fe atoms randomly distributed in a 50:50 ratio. Li$_5$AI$_4$ shows a similar structure, where only half of the Fe atom are replaced by Al$^{3+}$ ions, whereas the other half are occupied by Li$^+$ ions. The tetrahedral layer consists of ordered LiS$_4$ and AlS$_4$ units in a 3:1 arrangement. The authors note that these structures can be expressed as: [LiFe]$^T[Li]^O$S$_2$ and [Li$_{1,5}$Al$_{0,5}$]$^T[Li]^O$S$_2$ respectively. We added the superscripts “T” and “O”, which refer to the tetrahedral and octahedral coordination of the cation in alternating layers. Following this representation, the material reported in this study Li$_3$AlS$_3$ could be written as [Li$_{2/3}$O Li$_{2/3}$]$^T$[Li$_{2/3}$Al$_{2/3}$]$^T$S$_2$, where the cation in the same square bracket belong to the same layer. Recently, Leube et al. reported a family of compounds Li$_{4,4}$M$_{0,4}$M$'_0,6$S$_4$ ($M = Al^{3+}$, Ga$^{3+}$, M$' = Ge^{4+}$, Sn$^{4+}$) whose structure is closely related to that of Li$_5$AI$_4$. The highly charged cations share the same site in the tetrahedral layer, the octahedral layer is made of ordered partially occupied lithium sites and fully vacant sites in a 3:1 arrangement, and the remaining lithium atoms share two crystallographically distinct tetrahedral sites in both the tetrahedral and octahedral layer in a 74:26 ratio. Following the same convention, this structure can be written as [Li$_{0,66}$O Li$_{0,38}$]$^T$[Li$_{1,11}$M$_{0,2}$M$'_{0,3}$]$^T$S$_2$.

Other alkali metal sulphides with composition $A_3MS_3$, where $A$ is an alkali monovalent cation and $M$ a trivalent cation, have been reported in the literature. As stated above, Na$_3$InS$_3$ in particular shows a closely related structure to Li$_3$AlS$_3$ and be written as [Na$_{2/3}$□$1/3$]$^O$[Na$_{2/3}$]$^T$[Na$_{2/3}$In$_{2/3}$□$2/3$]$^T$S$_2$ where In and Na occupy the same sites as Al and Li in Li$_3$AlS$_3$. Moreover, both compounds show identical distortions of the alkali octahedra and the same direction of displacements for the tetrahedral alkali cations. This particularity is most probably coming from the high degree of constraint imposed by the presence of the $M^{2+}S_4$ dimers, and the fact that this observation is made in both phases reinforces the validity of this explanation. Rothenberger et al. reported a structure with the composition ($M$AlS$_2$)(GeS$_2$)$_4$ ($M = Na$, Ag, Cu) where 20% of the Al atoms are in similar dimeric tetrahedral units. However, these Al dimers were much less distorted with very similar Al-S interatomic distances within the tetrahedra (the average Al-S distance is 2.2117(5) Å and the standard deviation 1.3%). The absence of tetrahedral distortion in these dimers can be explained by
the 3D polyanionic rigid structure imposed by the three other Al or Ge sites. This lessening of the distortion from tetrahedral symmetry is also reflected in the $^{27}$Al NMR where the resonance observed clearly shows a smaller value of $C_Q$.

The splitting of the Li2 site in Li$_3$AlS$_3$ is not reported for Na$_3$InS$_3$, nor is the displacement from the Wyckoff position to a general position of the second octahedral alkali site. Lithium is smaller than sodium and the volume occupied by each atom considering a hard sphere model is 12 and 18% of the total volume of each octahedron for Li and Na, respectively. The displacements and splitting modelled for lithium might therefore be key to generate an appropriate bonding environment as defined by the BVS.

Interestingly, Na$_3$AlS$_3$ along with Na$_3$GaS$_3$ show a slightly different structure (Figure 7a,b). In between two sulphide layers, Al2 occupies 1/3 of the tetrahedral sites and form dimers between T$^+$ and T$^-$ tetrahedra of the same slab. In this layer Na4 occupies 1/3 of the distorted octahedral sites forming infinite chains along the c axis. In between the next two sulphide layers Na1 occupies one distorted octahedral site, whereas Na2 and Na3 form 5-coordinated sulphide polyhedra in a trigonal bipyramid configuration and all three Na sites are in a 1:1:1 arrangement. The next slab consists of similar AlS$_4$ and NaS$_6$ polyhedra arrangement as the first described slab, with a slight tilt of the polyhedra (Figure 7b). Na5 lies within each of the sulphide layers forming the Al2S$_4$ slab and is 6-coordinated to four of the sulphur atoms of the same layer, one in the layer above and one in the layer below, therefore forming a 2D network of edge and corner shared octahedra. The structure difference between Na$_3$InS$_3$ or Li$_3$AlS$_3$ (for which Na or Li are 4-coordinated in the tetrahedral layer) and Na$_3$AlS$_3$ or Na$_3$GaS$_3$ (for which Na is 6-coordinated in the tetrahedral layer) could be attributed to the size of the $M^{3+}$ cation with respect to that of the alkali cation. Indeed, the ionic radius of Al$^{3+}$ (0.39 Å) and Ga$^{3+}$ (0.47 Å) is considerably smaller than that of In$^{3+}$ (0.62 Å)$^{81}$, so the size of tetrahedral interstices will decrease and might not be suitable to host Na$^+$ cations, which would then prefer to occupy octahedral sites, in contrast with the smaller Li$^+$ cation.

Another known structure of similar composition showing different arrangement of metal and alkali cation within the hcp array is that of Na$_3$FeS$_3$, which is also adopted by Na$_3$FeSe$_3$, Na$_3$AlSe$_3$, and Na$_3$GaSe$_3$ among all (Figure 7c). In those phases, the $M^{3+}$ cation assembles in tetrahedral dimers in between each of the
sulphide layers, and the sodium atom occupies all of the octahedral sites in these layers (Figure 7c,d). Curiously, the absence of alkali-only layers and the stabilization of a single layer type containing both Fe or $M$ ($M = \text{Al}^{3+}, \text{Ga}^{3+}$ and $\text{In}^{3+}$) and Na or Li polyhedra seem to occur in all of the selenide compounds as well as both the iron sulphide and selenide phases. It seems that this could be linked to the less ionic character of the bonds in those structures. Indeed, the higher polarizability of $\text{Se}^{2-}$ compared to $\text{S}^{2-}$ anions generally leads to softer and more covalent bonds in selenides.\textsuperscript{85} It has also been shown, through magnetic property measurements, that the $3d$ orbitals of $\text{Fe}^{3+}$ in $\text{Na}_3\text{FeS}_3$ are more extended than that of ionic $\text{Fe}^{3+}$, which can be attributed to Fe-S covalency.\textsuperscript{86} Because $\text{Al}^{3+}, \text{Ga}^{3+}$ and $\text{In}^{3+}$, do not show this effect, the ionic character of the $M$-$\text{S}$ ($M = \text{Al}^{3+}, \text{Ga}^{3+}$ and $\text{In}^{3+}$) bond might be more pronounced in $\text{Na}_3M\text{S}_3$ than in $\text{Na}_3\text{FeS}_3$. Different layer type structures are often found in materials where ions have different chemical properties, in particular different polarizability which results in different ionicity of the cation-anion bond in each layer.\textsuperscript{87,88} A more covalent character of the bonds would then attenuate the difference in polarizability of the cations, and favour the single layer type structure.

![Figure 7](image_url)

Figure 7. (a) Crystal structure of $\text{Na}_3\text{AlS}_3$ showing the alternating arrangement, along $a$, of the tetrahedral layers containing $\text{AlS}_4$ and $\text{NaS}_4$ tetrahedra and of the mixed polyhedral layers containing Na only polyhedra. (b) View of the two consecutive tetrahedral layers of $\text{Na}_3\text{AlS}_3$ in the (bc) plane (c) Crystal structure of $\text{Na}_3\text{FeS}_3$ showing one type of layer along b (d) View of the layer along b of $\text{Na}_3\text{FeS}_3$ showing the fully occupied octahedral sites by Na atoms and the 1/3 occupied tetrahedral interstices by Fe atoms in a dimer arrangement.

### 3.4. Lithium conductivity

The ionic conductivity of $\text{Li}_3\text{AlS}_3$ was assessed by electrochemical impedance spectroscopy on sintered pellets with $80 \pm 2\%$ relative density. The Nyquist plot of
the sample measured at room temperature under an argon atmosphere in shown in Figure 8a. The presence of the two semicircles is characteristic of two unique time constants and therefore of the dissociation between different scattering contributions. The plot has therefore been fitted by a two component equivalent electrical circuit (inset in Figure 8a) that models these two contributions. Each component consists of a resistance associated in parallel with a constant phase element (CPE, a modified capacitor taking into account inhomogeneities in the sample, cf. SI). The values of the capacitance obtained for the semicircles at high and low frequencies were $8(1) \times 10^{-12}$ and $2.6(4) \times 10^{-9}$ F, and are characteristic of the bulk and grain boundary response, respectively. The high frequency intercepts of both semicircles give direct values of the bulk and total resistance ($R_{\text{bulk}}$ and $R_t = R_{\text{bulk}} + R_{\text{GB}}$ respectively, where $R_{\text{GB}}$ is the resistance resulting from the grain boundary scattering). A bulk and grain boundary room temperature conductivity of $1.3(1) \times 10^{-8}$ and $2.2(2) \times 10^{-9}$ S·cm$^{-1}$ respectively were obtained. The impedance of the pellet was measured over the temperature range [24 °C - 125 °C] and each Nyquist plot fitted with the described equivalent circuit. Table S8 and S9 present the results of the fits and the values of the different parameters obtained at each temperature. For each temperature, the conductivity of the bulk, $\sigma_{\text{bulk}}$, was therefore extracted and showed to follow the Arrhenius law (Figure 8b). The activation energy was 0.48(1) eV.

The room temperature bulk conductivity is of the same order of magnitude as that of Li$_5$AlS$_4$ ($\sigma = 9.7 \times 10^{-9}$ S·cm$^{-1}$)\textsuperscript{65}. In Li$_5$AlS$_4$, all Li sites are fully occupied, whereas in Li$_3$AlS$_3$, there are multiple ordered vacancy sites: one third of the octahedral interstices in the mixed polyhedral layer and two third of the tetrahedral interstices in the tetrahedral layer are vacant. Although the lowering of the activation energy (0.48 eV for Li$_3$AlS$_3$ and 0.61 eV for Li$_5$AlS$_4$) is indeed observed, the increase in Li mobility is not, which suggest that ordered vacancies sites are not sufficient to improve conductivity in this structure type.

In the recently reported related Li$_{4.4}M_{0.4}M'$$_{0.6}$S$_4$ compounds, which show considerably higher conductivities $\sigma = 10^{-5}$-10$^{-6}$ S·cm$^{-1}$, the presence of multiple disordered partially occupied lithium sites has been shown to play a major role in the improvement of the conductivity. In Li$_3$AlS$_3$, the only disordered vacancies can be found within the Li4 site which was determined to be 98 % occupied (Table S5), as
all other Li sites are completely occupied. In order to highlight the different types of vacancies within the structure, Li$_3$AlS$_3$ can be written as:

$$[\text{Li}_{2/3}^\circ \text{Δ}_{1/3}^\circ (\text{Li}_{0.98} \square_{0.02})_{2/3}^\circ \text{Δ}_{1/3}^\circ][\text{Li}_{2/3}^\circ \text{Al}_{2/3}^\circ \text{Δ}_{2/3}^\circ][\text{S}_{1.95}]$$

with $\square$ and Δ being the disordered and ordered vacancies respectively. The family of quaternary materials, using the same convention, can be written as:

$$[(\text{Li}_{0.44} \square_{0.56})_{1.5}^\circ \text{Δ}_{0.5}^\circ (\text{Li}_{0.25} \square_{0.75})_{1.5}^\circ \text{Δ}_{0.5}^\circ][((\text{Li}_{0.73} \square_{0.27})_{1.5}^\circ \text{Δ}_{0.5}^\circ (\text{M}_{0.2} \text{M'}_{0.3})_{1.5}^\circ][\text{S}_2]$$

Overall, this structure shows fewer ordered vacant sites, but the content of disordered vacancies is considerably higher, which underlines the importance of this feature in order to improve conductivity.

It is interesting to note that in the Na$_3$FeS$_3$ structure, only one type of layer, in which all the sodium is located in octahedral sites, is present. Because the mobile species are believed to be the octahedral lithium in these types of structure,$^{46}$ it would be of high interest to stabilize the Na$_3$FeS$_3$ structure in lithium containing compounds while creating a large number of disordered vacancies.
3.5. Influence of the Al$_2$S$_6$ dimers on the structure and Li ion conductivity

The strong differences between Li$_5$AlS$_4$ or Li$_{4.4}M_{0.4}M'_0.6S_4$ ($M = \text{Al}^{3+}$, Ga$^{3+}$, $M' = \text{Ge}^{4+}$, Sn$^{4+}$) structures and Li$_3$AlS$_3$ comes from the ordering of the tetrahedral cations and the presence of edge-shared AlS$_4$ tetrahedra pairs which form Al$_2$S$_6$ dimers. The three structures have the same anion sublattice with tetrahedral Li and Al layers alternated with Li only layers (= mixed polyhedral layer). In the three
structures, Al atoms must spread over the tetrahedral interstices of the tetrahedral layer, and when this is done in an ordered manner, the $M/S$ ratio imposes the arrangement pattern. Indeed, in Li$_3$AlS$_3$, $M/S = 1/3$ means that there is one Al atom for three tetrahedral interstices (one tetrahedra contains four sulphur atoms, and each tetrahedra is connected to four other tetrahedra in a layer consisting of $T^+$ and $T^-$ interstices, cf. Figure 4). Therefore the $M/S = 1/3$ imposes a 1:2 ordering the Al tetrahedra by optimizing the distance between each AlS$_4$ unit (Figure 9-1). In the same way, $M/S = 1/4$ in Li$_5$AlS$_4$, Li$_{4.4}M_{0.4}M'_{0.6}S_4$ leads to a 1:3 arrangement of the $M$ (or $M'$) tetrahedra in the layer (Figure S6). The interconnection of both $T^+$ and $T^-$ networks presenting this arrangement type inevitably leads to the presence of the Al$_2$S$_6$ dimers in Li$_3$AlS$_3$ on the contrary to the other two phases.

These dimers have a crucial influence on the displacement of atoms within the structure. Because of the strong electronic repulsive forces between the two Al$^{3+}$ cations in the dimer, the Al position is driven off the centre of the tetrahedron and the S3-S3 distance are successively compressed and stretched among the layers (Figure 9-2). In Li$_5$AlS$_4$ and Li$_{4.4}M_{0.4}M'_{0.6}S_4$, on the other hand, the S-S edges are not as compressed. This is reflected in the values of the standard deviations for the S-S distances: 0.13 (Li$_5$AlS$_4$), 0.20 (Li$_{4.4}Al_{0.4}Ge_{0.6}S_4$) and 0.24 (Li$_3$AlS$_3$) and in the maximum/minimum S-S distances (in Å): 4.1564/3.6805 (Li$_5$AlS$_4$), 4.3176/3.6016 (Li$_{4.4}Al_{0.4}Ge_{0.6}S_4$) and 4.4206/3.4631 (Li$_3$AlS$_3$). This strongly impacts the geometry and the volume of the polyhedral sites in adjacent layer, ie. the Li only layer (Figure 9-3). In Li$_3$AlS$_3$, the volumes of the three different octahedral interstices are 26.7227, 27.1162 and 30.4551 Å$^3$. The latter is considerably bigger than the other two and is not favourable to host a small Li atoms. This explains why only 2/3 of the octahedral sites are occupied in the Li-only layer (Li2, Li2b and Li3). In the same way, in Li$_{4.4}Al_{0.4}Ge_{0.6}S_4$, 3/4 of the octahedral sites are occupied, and the volume of the ordered vacant site is 31.5654 Å$^3$. In Li$_5$AlS$_4$, all of the octahedral sites have the adequate geometry to host lithium, therefore leading to a full occupation of the octahedral sites within this layer. In Li$_3$AlS$_3$, it will be preferable for the remaining Li atoms to occupy a tetrahedral site. Li4 thus occupies the tetrahedral interstices which are away from the already occupied octahedra as well as away from the above (or below) occupied Al tetrahedra (Figure 9-3). The positions of the Li4 atoms are driven towards the above (or below) S-S slab to minimize repulsion with the
other edge shared Li4 tetrahedra creating a pseudo bipyramid trigonal environment. The displacement of the Li4 atoms is then detrimental to the occupation by another cation of the above or below tetrahedra in the tetrahedral layer. The latter would then more preferably be left vacant. This explains why among the two other tetrahedral sites not occupied by Al, only one is occupied by Li, and a 1:1:1 arrangement of Al, Li and ordered vacancies is stabilized (Figure 9-4). In Li4.4Al0.4Ge0.6S4, apart from the tetrahedral site that lies just below the MS4 tetrahedra of the above tetrahedral layer, all the other tetrahedral sites of the Li-only are equivalent and Li atoms therefore randomly occupy these positions. The motivation for the ordering of vacancies in the tetrahedral layer is therefore suppressed and the remaining Li are delocalized among all tetrahedral sites in this layer. The ordered vacancy sites, unfavourable to host lithium atoms, are likely to act as a barrier for Li diffusion, and result in lower lithium ionic conductivity in Li3AlS3 than in Li4.4M0.4M’0.6S4. A complete study of the Li energy landscape to elucidate Li diffusion pathways will be undertaken to yield further insight into the role of these structural features.

In this structure type, the M/S ratio imposes the arrangement pattern of the Al tetrahedra in dimers or isolated tetrahedra and triggers the stabilization of ordered or disordered vacancies within both the tetrahedral and the Li-only layer. The lithium conductivity properties of each of the compounds can then directly be related to the structure through the amount of disordered Li vacancies, which itself can be explained by the composition through the M/S ratio. This work illustrates that, in this structure type, an M/S ratio that is too large causes structural arrangements that inhibit the diffusion of Li.
Figure 9. Representation of the influence of the $M/S=1/3$ ratio on the structure and arrangement of Li polyhedra in Li$_3$AlS$_3$ having the “Li$_5$AlS$_4$ type” structure leading to the presence of ordered vacancies in the tetrahedral layer.
4. Conclusion

We have investigated the Li-Al-O-S phase diagram through a probe structure approach, which combined experimental and computational studies to yield a new phase while ruling out others. Indeed, this study revealed that no oxysulphide phases could be successfully obtained, but led to the discovery of the new sulphide \( \text{Li}_3\text{AlS}_3 \). The structure and properties of this compound were determined by means of high-resolution X-ray and neutron diffraction, multinuclear NMR spectroscopy and electrochemical impedance spectroscopy. The stability of the new phase is believed to rely on the presence of \( \text{AlS}_4 \) dimers, a peculiar feature not observed before in other Li-ion conducting phases. The structure was described by comparing the cation polyhedral arrangements with those of other related phases with similar composition, such as \( \text{Na}_3\text{MCh}_3 \) \((M = \text{Al, Ga, In}; \text{Ch} = \text{S, Se})\), \( \text{Li}_2\text{FeS}_2 \) and \( \text{Li}_5\text{AlS}_4 \). The study of this new compound in comparison with other similar sodium and lithium chalcogenide phases widens the spectra of possibilities to explore new interesting structures in related phase fields.

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Supporting Information

Experimental synthesis procedure for the preparation of \( \text{LiAlO}_2 \) and the attempted \( \text{Li}_3\text{AlO}_3 \), X-ray diffraction patterns of the samples prepared in the Li-Al-O-S phase fields, comparison of the Le Bail fits of the SXRD data with and without the use of the spherical harmonics, details of the elemental analysis of \( \text{Li}_3\text{AlS}_3 \), structural
information of Li2AlS3 determined by diffraction data refinement (refinement details, atomic positions, Fourier difference map of the Li2 and Li3 positions, bond distances and angles), NMR shift calculations and additional NMR experimental results, analysis of the impedance data.

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