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# Substitutional disorder: structure and ion dynamics of the argyrodites $\text{Li}_6\text{PS}_5\text{Cl}$ , $\text{Li}_6\text{PS}_5\text{Br}$ and $\text{Li}_6\text{PS}_5\text{I}^\dagger$

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For the development of safe and long-lasting lithium-ion batteries we need electrolytes with excellent ionic transport properties. Argyrodite-type  $\text{Li}_6\text{PS}_5\text{X}$  (X: Cl, Br, I) belongs to a family of such a class of materials offering ionic conductivities, at least if  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{Cl}$  are considered, in the  $\text{mS cm}^{-1}$  range at room temperature. Although already tested as ceramic electrolytes in battery cells, a comprehensive picture about the ion dynamics is still missing. While  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{Cl}$  show an exceptionally high Li ion conductivity, that of  $\text{Li}_6\text{PS}_5\text{I}$  with its polarizable I anions is by some orders of magnitude lower. This astonishing effect has not been satisfactorily understood so far. Studying the ion dynamics over a broad time and length scale is expected to help shed light on this aspect. Here, we used broadband impedance spectroscopy and  $^7\text{Li}$  NMR relaxation measurements and show that very fast local Li ion exchange processes are taking place in all three compounds. Most importantly, the diffusion-induced NMR spin-lattice relaxation in  $\text{Li}_6\text{PS}_5\text{I}$  is almost identical to that of its relatives. Considering the substitutional disorder effects in  $\text{Li}_6\text{PS}_5\text{X}$  (X = Br, Cl), we conclude that in structurally ordered  $\text{Li}_6\text{PS}_5\text{I}$  the important inter-cage jump processes are switched off, hindering the ions from taking part in long-range ion transport.

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## 1 Introduction

Energy from renewable sources can be stored in various ways. Considering electrochemical storage, Li-based batteries offer high energy densities combined with a high degree of design flexibility.<sup>1–3</sup> In particular, batteries using  $\text{Li}^+$  as an ionic charge carrier are an emerging option to power electric vehicles.<sup>1–7</sup> Such batteries may, however, suffer from flammable fluorinated liquid electrolytes conventionally used in these energy storage systems. Next-generation Li batteries with, e.g., metallic Li anodes and equipped with solid electrolytes have aroused great interest.<sup>8–12</sup> Devices with non-flammable ceramic electrolytes are anticipated to benefit from increased safety as they easily withstand higher temperatures. Thus, such systems are less sensitive to thermal runaway.

To take full advantage of all-solid-state Li (or Na) batteries, electrolytes with exceptionally high ionic conductivities are needed.<sup>8–15</sup> In the past, only a few ceramics were available fulfilling this requirement.<sup>16,17</sup> This lack of suitable materials prevented any commercialization on a large scale.<sup>18,19</sup> Ideal candidates should (i) show room-temperature ionic conductivities with values comparable to those of liquids, (ii) be chemically stable over a sufficiently wide temperature range and (iii) possess a sufficiently high electrochemical stability over a large potential window.<sup>10,11</sup> For battery applications, the conductivity of a ceramic material should reach a value of  $10^{-3} \text{ S cm}^{-1}$  at room temperature.<sup>10,14</sup>

Over the last years several classes of materials have been presented whose members show very high conductivities. These materials include sulfides, such as  $\text{Li}_7\text{P}_3\text{S}_{11}$  and  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ , oxides including garnets, such as  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ , or phosphates based on the NASICON structure.<sup>8–15,20–26</sup> Although the ionic bulk conductivities of oxides and phosphates can reach very high values, the materials may suffer from high grain boundary (g.b.) resistances.<sup>27</sup> For the softer sulfides the difference between the bulk and g.b. conductivities<sup>28</sup> is expected to be much lower. Of course, Li-bearing sulfides or thiophosphates are sensitive to air and moisture, thus requiring careful handling and adequate processing. As an example, the Ge-containing thiophosphate  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  (LGPS),<sup>13</sup> which initiated the renaissance to consider

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sulfide-based systems as candidates for solid electrolytes, is characterised by an ionic conductivity of  $12 \text{ mS cm}^{-1}$ . Meanwhile the expensive element Ge has been replaced by cheaper and naturally abundant materials.<sup>29</sup> The electrochemical stability of LGPS-based systems needs, however, to be improved.<sup>30</sup>

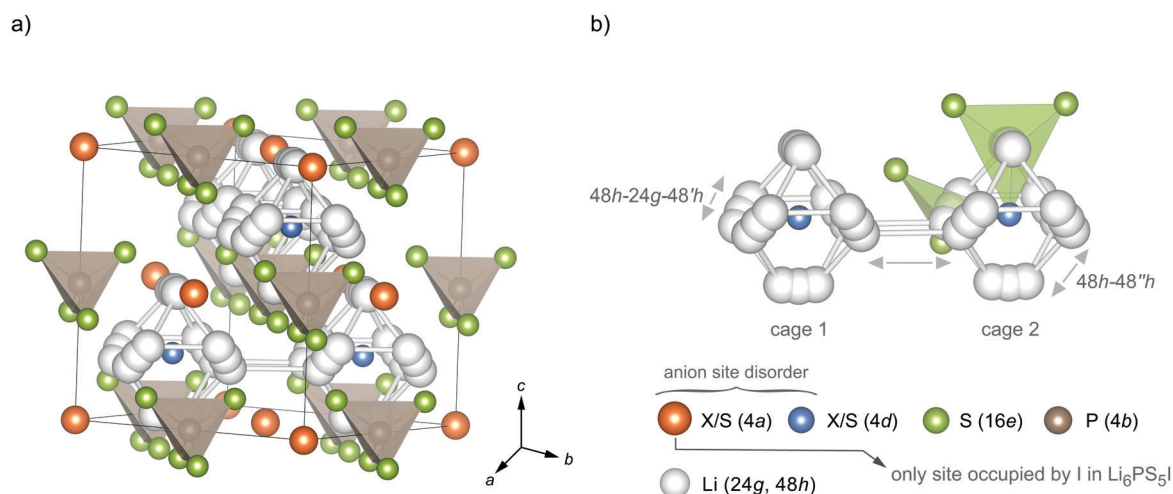
Besides LGPS, Deiseroth and co-workers introduced Li-containing argyrodite-type  $\text{Li}_6\text{PS}_5\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ).<sup>31</sup> The crystal structure is shown in Fig. 1; the possible Li exchange processes are illustrated as well. As an example, the ionic conductivity of  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{Cl}$  is reported to range from  $10^{-3} \text{ S cm}^{-1}$  to  $10^{-2} \text{ S cm}^{-1}$  depending on the preparation technique, which influences the type and number of defects as well as the overall morphology.<sup>32,33</sup> Thus, the ionic conductivity of Li-argyrodites is only slightly smaller than that of the LGPS family. Lower costs make this family of electrolytes highly attractive for application in all-solid-state batteries.<sup>31,34</sup>

In 2008 Deiseroth *et al.* reported the solid-state synthesis of  $\text{Li}_6\text{PS}_5\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and characterised the local and long-range structure by X-ray diffraction and NMR.<sup>31</sup> Three years later Rao *et al.* discussed the synthesis of the lithium argyrodite *via* ball milling.<sup>35</sup> Rayavarapu *et al.* showed that the disorder in both the lithium distribution over the available cation sites and the disorder in the  $\text{S}^{2-}/\text{Cl}^-$  and  $\text{S}^{2-}/\text{Br}^-$  sublattices promotes lithium ion conductivity.<sup>36</sup> This view has further been supported by bond-valence calculations.<sup>37</sup>

Over the last years a number of studies have been carried out to measure the ionic conductivities of the  $\text{Li}_6\text{PS}_5\text{X}$  family by using standard impedance measurements.<sup>31–40</sup> The overall goal, not only for  $\text{Li}_6\text{PS}_5\text{X}$ , is to relate macroscopic application relevant properties to crystal chemical and morphological properties. So far, the results reported have rarely been related to the length-scale specific properties of the measuring technique applied. The ionic conductivities for  $\text{Li}_6\text{PS}_5\text{X}$  vary from  $10^{-7} \text{ S cm}^{-1}$  to  $10^{-2} \text{ S cm}^{-1}$ ,

while the highest values are found for  $\text{X} = \text{Cl}, \text{Br}$ . The corresponding activation energies reported, either experimentally probed or calculated, take values from 0.11 eV to 0.57 eV.<sup>31–40</sup> Astonishingly, the I-compound  $\text{Li}_6\text{PS}_5\text{I}$  shows the lowest conductivity. According to the strategy of substitutional disorder, size mismatch and polarizability of the halogen anion one could have expected the opposite trend. Replacing S by a larger and more polarizable anion such as I, as compared to the small and unpolarizable Li cation, is expected to cause lattice distortions which on their part lead to a broader distribution of slightly inequivalent Li sites in the Li sublattice. Without any strong site preference of the Li ions they are expected to jump quickly between the local minima of such a heterogeneous, *i.e.*, non-uniformly shaped, potential landscape. Such a situation, sometimes also connected to geometric frustration, is very similar to F diffusion in the recently investigated system  $(\text{Ba}, \text{Ca})\text{F}_2$ ,<sup>41,42</sup> Li diffusion in  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  oxides<sup>43</sup> and Na diffusion in some *closo*-borates.<sup>44</sup> While this situation might be the origin for the high conductivity in  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{Cl}$ , for the I analogue it seems to incompletely describe the real situation as for  $\text{Li}_6\text{PS}_5\text{I}$  relatively low ion conductivities are reported.

In an elegant way, Kraft *et al.*<sup>34</sup> tried to establish a connection between the stiffness (or polarizability) of the anion sublattice in  $\text{Li}_6\text{PS}_5\text{X}$  and the macroscopic ionic transport properties. They used impedance spectroscopy and ultrasonic speed of sound measurements to collect information on activation energies and the pre-factors governing the underlying Arrhenius equation. They reported that soft lattices, as is the case for  $\text{Li}_6\text{PS}_5\text{I}$ , lead to smaller Arrhenius pre-factors than obtained for  $\text{Li}_6\text{PS}_5\text{Cl}$  and  $\text{Li}_6\text{PS}_5\text{Br}$ . This decrease in pre-factor, which might originate from a change of the migration entropy or attempt frequencies, has been used to explain the low (overall) ion conductivity in  $\text{Li}_6\text{PS}_5\text{I}$ .



**Fig. 1** (a) Crystal structure of argyrodite-type  $\text{Li}_6\text{PS}_5\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ). In a perfect ordered structure, a cubic lattice is formed with  $\text{PS}_4^{3-}$  tetrahedra and Li ions being arranged octahedrally. Some of the  $\text{S}^{2-}$  (4d) anions are placed in the middle of the Li octahedra; the anions on 4a form a face centred cubic lattice. (b) The two different lithium positions (24g, 48h) form an octahedral arrangement in which three different jump processes can occur: (i) strictly localised jumps between the Li positions  $48\text{h}-24\text{g}-48\text{h}'$ ; (ii) intracage jumps ( $48\text{h}-48\text{h}''$ ) and (iii) so-called intercage jumps  $48\text{h}_1-48\text{h}_2$  between two neighbouring cages 1 and 2. The latter jump process forms interconnected diffusion pathways being responsible for 3D long-range ion transport. Site disorder on the anion positions 4a and 4d, which is absent for  $\text{Li}_6\text{PS}_5\text{I}$ , is expected to influence the Li ion diffusivity significantly.



Here, we employed impedance and NMR spectroscopy to shed more light on the effect seen for  $\text{Li}_6\text{PS}_5\text{I}$ . The important structural differences between the three argyrodites have to be taken into account to explain the significant changes in ionic conductivities, pre-factors and activation energies. For this purpose we have not only looked at the monosubstituted compounds like  $\text{Li}_6\text{PS}_5\text{X}$ , but also at samples with two or three different anions such as  $\text{Li}_6\text{PS}_5\text{Cl}_{0.5}\text{Br}_{0.5}$  or  $\text{Li}_6\text{PS}_5\text{Cl}_{1/3}\text{Br}_{1/3}\text{I}_{1/3}$ . The non-substituted compound  $\text{Li}_7\text{PS}_6$  served as a reference material. Importantly, complementary techniques which are sensitive to ion dynamics on different length-scales and time-scales are used to fully characterise the transport properties. We will show that, on a short-range length scale, the Li ions in  $\text{Li}_6\text{PS}_5\text{I}$  are as rapid as in the Br and Cl analogues. Obviously, the ordered  $\text{S}^{2-}/\text{I}^-$  sublattice, as compared to the disordered situation for  $\text{Li}_6\text{PS}_5\text{Cl}$  and  $\text{Li}_6\text{PS}_5\text{Br}$ , is responsible for a more regular potential landscape with a higher degree of site preference for the Li ions. As a consequence, we assume that intercalation jump processes in  $\text{Li}_6\text{PS}_5\text{I}$  occur less frequently. These processes are, however, needed to establish rapid long-range ion dynamics in the iodide.

## 2 Experimental

### 2.1 Sample preparation through a solid state reaction

The Li argyrodites  $\text{Li}_6\text{PS}_5\text{X}$ , with the compositions shown in Fig. 2b, have been prepared by mixing stoichiometric amounts of  $\text{Li}_2\text{S}$  (Sigma-Aldrich  $\geq 99.98\%$ ),  $\text{P}_2\text{S}_5$  (Honeywell Fluka  $\leq 99\%$ ) and  $\text{LiCl}$  (Sigma-Aldrich, anhydrous, 99%),  $\text{LiBr}$  (Sigma-Aldrich, anhydrous, 99.98%) and  $\text{LiI}$  (Sigma-Aldrich, 99.9%). The starting compounds were mechanically milled using a high-energy planetary ball mill (Fritsch Pulverisette 7 Premium line) at a rotation speed of 400 rpm for 4 hours (15 min milling; 15 min pause). Milling was carried out using  $\text{ZrO}_2$  beakers (45 ml) filled with 180 balls ( $\text{ZrO}_2$ , 5 mm in diameter). Afterwards the mixtures were uniaxially pressed (0.4 tons) into pellets with a diameter of 5 mm, filled into quartz ampoules and sealed under a vacuum. The ampoules were preheated at 573 K under a dynamic vacuum to remove traces of water. The reaction was carried out at 823 K (heating rate: 5 K  $\text{min}^{-1}$ , duration 7 days; cooling rate 10 K  $\text{min}^{-1}$ ). All preparation steps were strictly carried out in an Ar gas atmosphere ( $\text{H}_2\text{O} < 1$  ppm,  $\text{O}_2 < 1$  ppm).

### 2.2 X-ray powder diffraction (XRPD)

The samples were analyzed by X-ray diffraction using a Bruker D8 Advance diffractometer (Bragg Brentano geometry, Cu  $\text{K}_\alpha$  radiation). The patterns, shown in Fig. 2, were recorded with a step size of  $0.02^\circ$  (measuring time 2 s) in the  $2\theta$ -range  $20^\circ$  to  $100^\circ$ . Rietveld refinement, see Fig. 3 and the ESI† (Fig. S1 and S2), was carried out by using X'PertHighScorePlus (Panalytical).

### 2.3 Impedance spectroscopy

To measure the impedance responses of the pellets, Au electrodes were applied. We used a LEICA EM SCD 050 sputter coater to equip the samples with a thin Au layer of 100 nm thickness.

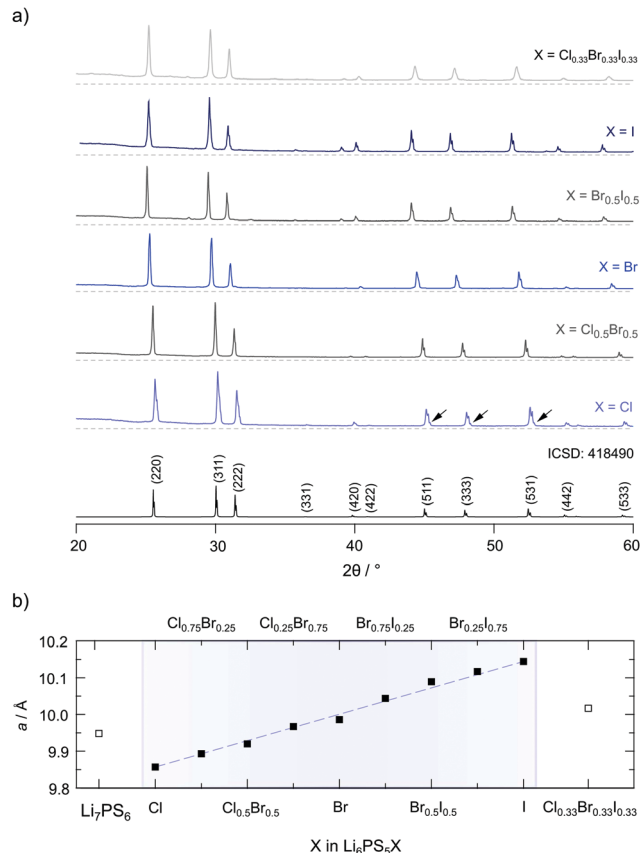


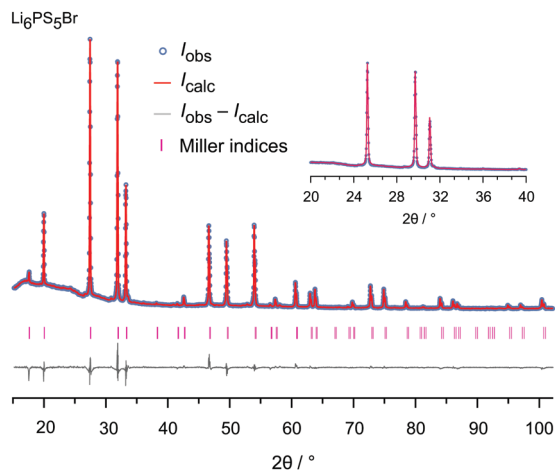
Fig. 2 (a) X-ray powder diffraction patterns of the  $\text{Li}_6\text{PS}_5\text{X}$  series investigated within this study ( $\text{X} = \text{Cl}$ ,  $\text{Cl}_{0.5}\text{Br}_{0.5}$ ,  $\text{Br}$ ,  $\text{Br}_{0.5}\text{I}_{0.5}$ ,  $\text{I}$  and  $\text{Cl}_{0.33}\text{Br}_{0.33}\text{I}_{0.33}$ ). The XRPD patterns were recorded after the final annealing step at room temperature. In some cases, little, almost negligible, amounts of  $\text{Li}_3\text{PO}_4$  and  $\text{LiX}$  are visible; the amount of  $\text{LiX}$  does not exceed 1.5 wt%. Only for  $\text{Li}_6\text{PS}_5\text{Cl}$  ca. 3.3 wt%  $\text{Li}_3\text{PO}_4$  is seen, see the arrows; in all other cases its amount is negligible or less than 1.5 wt%, see the ESI† for Rietveld refinements (Fig. S1 and S2). (b) Lattice parameter of  $\text{Li}_6\text{PS}_5\text{X}$  obtained from Rietveld refinements of the patterns shown in (a). The lattice parameter increases continuously with the radius of X.

Impedance spectra were recorded with a Novocontrol Concept 80 broadband dielectric spectrometer; the frequency range covered ranged from  $\nu = 10$  mHz to 10 MHz. The temperature  $T$  was varied from 173 K to 453 K in steps of 20 K; the temperature in the sample holder was controlled by a QUATRO cryosystem (Novocontrol) that uses freshly evaporated nitrogen and a heater to adjust the temperature with an accuracy of  $\pm 0.5$  K. The measurements were carried out in a dry nitrogen atmosphere to avoid any contamination with water and oxygen.

### 2.4 $^7\text{Li}$ static NMR measurements

For the time-domain NMR measurements the samples  $\text{Li}_6\text{PS}_5\text{Cl}$ ,  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{I}$  were sealed in Duran® glass tubes (ca. 4 cm in length and 3 mm in diameter). They were kept under a vacuum to protect them from any reaction with humidity or traces of oxygen. We used  $^7\text{Li}$  NMR line shape measurements and spin-lattice relaxation (SLR) experiments to collect information about Li activation energies and jump rates. Longitudinal NMR SLR rates ( $1/T_1$ ) as well as spin-lock rates ( $1/T_{1\rho}$ )





**Fig. 3** Rietveld analysis of the XRPD pattern of  $\text{Li}_6\text{PS}_5\text{Br}$  recorded at 293 K ( $R_{\text{Bragg}} = 4.633\%$ ). In this plot the Bragg positions as well as calculated and observed profiles are depicted. The analysis reveals a phase pure sample. The  $R_w$  profile is 10.84% and the GoF amounts to 4.82; see the ESI† for further explanations.

were measured by employing a Bruker Avance III spectrometer connected to a shimmed cryomagnet with a nominal magnetic field of 7 T. This field corresponds to a  $^7\text{Li}$  Larmor frequency of  $\omega_0/2\pi = 116$  MHz. For the measurements at temperatures  $T$  ranging from 173 K to 433 K a ceramic high-temperature probe (Bruker Biospin) was used. At a power level of 200 W the  $\pi/2$  pulse length ranged from 2.7 to 3.2  $\mu\text{s}$  slightly depending on temperature. A Eurotherm temperature controller in combination with a type T thermocouple was used to control and to monitor the temperature in the sample chamber. Low temperature measurements down to  $T = 124$  K were performed with a cryo probe (Bruker) that uses freshly evaporated nitrogen to reach temperatures below ambient. The  $\pi/2$  pulse length of the cryo probe ranged from 3.0 to 4.3  $\mu\text{s}$  at a power level of 95 W. It is equipped with a LakeShore 331 element equipped with two Cernox temperature sensors.

$^7\text{Li}$  NMR SLR rates  $1/T_1 \equiv R_1$  in the laboratory frame were acquired with the well-known saturation recovery pulse sequence.<sup>45,46</sup> This sequence uses a comb of closely spaced  $\pi/2$  pulses to destroy any longitudinal magnetization  $M_z$ . The subsequent recovery of  $M_z$  was detected as a function of waiting time  $t_d$  with a  $\pi/2$  reading pulse:  $10 \times \pi/2 - t_d - \pi/2$  – acquisition.<sup>15</sup> To construct the magnetization transients  $M_z(t_d)$ , we plotted the area under the free induction decays (FIDs) vs.  $t_d$ . Up to 16 FIDs were accumulated for each waiting time.

The transients  $M_z(t_d)$  were parameterised with stretched exponentials,  $M_z(t_d) \propto 1 - \exp(-(t_d/T_1)^\gamma)$ , to extract the SLR rates  $R_1$ . Additionally, rotating-frame  $^7\text{Li}$  NMR SLR rates  $1/T_{1\rho} \equiv R_1$  were measured by means of the spin-lock technique:  $\pi/2 - p_{\text{lock}}$  acquisition. We used a locking frequency  $\omega_1/2\pi$  of 20 kHz.<sup>47,48</sup> The duration  $t_{\text{lock}}$  of the locking pulse  $p_{\text{lock}}$  was varied between 22  $\mu\text{s}$  and 460 ms. To ensure full longitudinal relaxation between each spin-lock scan the recycle delay was set to at least  $5 \times T_1$ . Again, the  $R_{1\rho}$  rates were obtained by analysing the resulting transients  $M_\rho(t_{\text{lock}})$  with stretched

exponentials of the form  $M_\rho(t_{\text{lock}}) \propto \exp(-(t_{\text{lock}}/T_{1\rho})^\kappa)$ . While the stretching exponents  $\gamma$  varied from 1 to 0.9, the exponents  $\kappa$  range from 0.4 to 1, depending on the temperature. Some of the  $T_{1\rho}$  transients showed bi-exponential behaviour and were analyzed with a sum of two stretched exponential functions.

## 2.5 Magic angle spinning (MAS) NMR

$^6\text{Li}$  (73.6 MHz),  $^{31}\text{P}$  (202.4 MHz),  $^{127}\text{I}$  (100.1 MHz),  $^{79}\text{Br}$  (125.3 MHz) and  $^{35}\text{Cl}$  (49.0 MHz) NMR spectra under magic angle spinning (MAS) conditions were recorded with a 500 MHz Avance spectrometer (Bruker). The high-resolution MAS NMR spectra were measured at a rotation speed of 25 kHz using 2.5 mm rotors with an ambient bearing gas temperature. Spectra were recorded with a single pulse sequence. We accumulated up to 128 scans for one spectrum.  $\text{LiCl}$ ,  $\text{KBr}$ ,  $\text{LiI}$  and 85%  $\text{H}_3\text{PO}_4$  served as ref. 31 to determine chemical shifts  $\delta_{\text{iso}}$ . In order to detect also very slow diffusion processes and to obtain quantitative MAS NMR spectra we varied the recycle delay from 1 s to 180 s. Sufficiently long relaxation delays guarantee full longitudinal relaxation of all spectral components. Further information on pulse lengths, temperature effects and delay times are given in the ESI† see Table S1.

## 3 Results and characterization

### 3.1 Sample characterization by X-ray powder diffraction

To study the ion dynamics in argyrodite-type  $\text{Li}_6\text{PS}_5\text{X}$  we used a solid-state synthesis approach to prepare samples with the following compositions:  $\text{X} = \text{Cl}$ ,  $\text{Cl}_{0.75}\text{Br}_{0.25}$ ,  $\text{Cl}_{0.5}\text{Br}_{0.5}$ ,  $\text{Cl}_{0.25}\text{Br}_{0.75}$ ,  $\text{Br}$ ,  $\text{Br}_{0.75}\text{I}_{0.25}$ ,  $\text{Br}_{0.5}\text{I}_{0.5}$ ,  $\text{Br}_{0.25}\text{I}_{0.75}$ ,  $\text{I}$  and  $\text{X} = \text{Cl}_{0.33}\text{Br}_{0.33}\text{I}_{0.33}$ , respectively. Through replacing  $\text{S}^{2-}$  with  $\text{X}^-$  we change the average lattice constant of the crystal structure, the polarisability of the anion lattice and the degree of anion disorder. The relative density of our samples, estimated from the sintered pellets used for impedance spectroscopy, reached values ranging from 92% to 98%. Argyrodite-type  $\text{Li}_6\text{PS}_5\text{X}$  is expected to crystallise with cubic  $F43m$  face centered (fc) symmetry; the crystal structure is depicted in Fig. 1.

In Fig. 2a the XRPD patterns of all samples are shown including a reference pattern taken from the literature (entry no. 418490 in the inorganic crystal structure database (ICSD)). The positions and intensities of the reflections obtained for the different patterns of  $\text{Li}_6\text{PS}_5\text{X}$  including  $\text{Li}_7\text{PS}_6$  match very well with what is expected from the literature. Humps at low diffraction angles originate from the mercapto foil used to protect the samples from reaction with air during the measurements.

To characterise the samples in detail, Rietveld refinements were carried out. As an example, the result of the analysis is shown for  $\text{Li}_6\text{PS}_5\text{Br}$  in Fig. 3. The  $\text{Li}_6\text{PS}_5\text{Br}$  sample is phase pure and crystallises with cubic symmetry (space group  $F43m$ ); the lattice parameter turned out to be  $a = 9.986$  Å. The same symmetry is found for the other samples; the amount of side phases or impurities turned out to be extremely low, see the ESI† When going from  $\text{Li}_6\text{PS}_5\text{Cl}$  to  $\text{Li}_6\text{PS}_5\text{I}$  the lattice parameter  $a$  increases from  $a = 9.857$  Å to  $a = 10.145$  Å. Lattice expansion of





the unit cell is expected because the radius  $r$  of the anion increases in the order  $r_{\text{Cl}} < r_{\text{Br}} < r_{\text{I}}$ . Here, an increasing unit cell volume stabilises the lithium ions in the transition state 24g; the change in lattice constant  $a$  seems to also affect the Li occupancies in the  $\text{Li}_6\text{PS}_5\text{X}$  series as has been shown by neutron diffraction.<sup>34</sup>

Recent neutron and X-ray synchrotron diffraction studies have shown that in *fc* cubic argyrodite-type  $\text{Li}_6\text{PS}_5\text{Cl}$  and  $\text{Li}_6\text{PS}_5\text{Br}$  the  $\text{S}^{2-}$  and X anions can occupy three different crystallographic positions. Whereas the 16e site is fully occupied by  $\text{S}^{2-}$  anions, the sites 4a and 4d are shared by the  $\text{S}^{2-}$  and X anions. For  $\text{Li}_6\text{PS}_5\text{Cl}$  Kraft *et al.* found that 38.5% of the 4a site and 61.5% of the 4d site is occupied by  $\text{Cl}^-$ .<sup>34</sup> The rest is filled by  $\text{S}^{2-}$  anions;  $\text{Li}^+$  only occupies the 48h sites. For  $\text{Li}_6\text{PS}_5\text{Br}$  Rietveld analysis yielded occupancies of 77.9% (4a) and 22.1% (4d) with  $\text{Li}^+$  distributed over the 48h (44.1%) and 24g (11.9%) sites. Thus, the highest degree of anion disorder is found for  $\text{Li}_6\text{PS}_5\text{Cl}$ , while cation disorder for the samples rich in Br. This finding is in contrast to what Rietveld refinement resulted in for  $\text{Li}_6\text{PS}_5\text{I}$ . While Li disorder is also present for the split-site (48h (39.1%) and 24g (21.9%)), in  $\text{Li}_6\text{PS}_5\text{I}$  the I anions solely occupy the 4a sites. The 4d sites are fully occupied by  $\text{S}^{2-}$ . Deiseroth and co-workers also reported on the same order/disorder effects earlier.<sup>31,40,49</sup>

The larger difference in ionic radii between  $\text{I}^-$  and  $\text{S}^{2-}$  ( $r_{\text{I}^-} = 216$  pm vs.  $r_{\text{S}^{2-}} = 184$  pm, as compared to  $r_{\text{Cl}^-} = 181$  pm and  $r_{\text{Br}^-} = 195$  pm) might lead to this site preference for the anions. The anion sublattice in  $\text{Li}_6\text{PS}_5\text{I}$  is, thus, structurally ordered as compared to  $\text{Li}_6\text{PS}_5\text{Cl}$  (and  $\text{Li}_6\text{PS}_5\text{Br}$ ); simultaneously, cation disorder shows up for  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{I}$ .<sup>36,37,50</sup> The compounds with mixed halogen compositions agree well with the trend

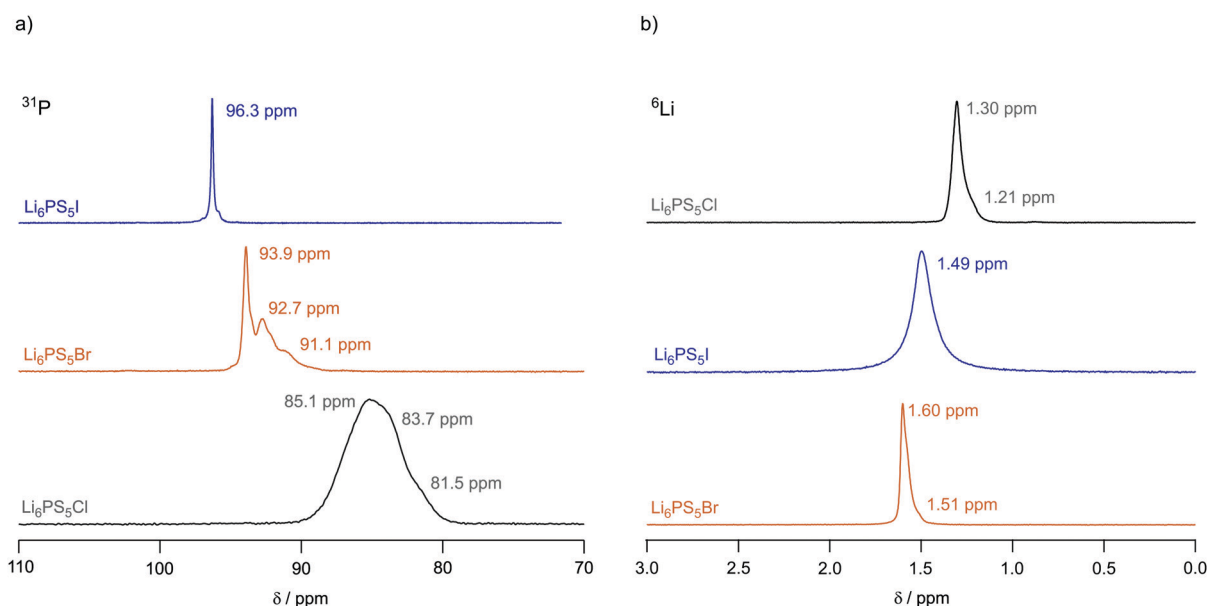
in  $\text{S}^{2-}/\text{X}$  occupancy and cation disorder.<sup>34</sup> As will be discussed below, anion ordering seems to have an important impact on long-range ion diffusion in the I compound.

The 24g site represents an intermediate state used by the Li ions on 48h to diffuse through. As a result of these two lithium positions three different jump processes can occur; they are explicitly shown in Fig. 1b. (i) A strongly localised process is given by 48h–24h–48h' jumps. Intracage jumps are possible within the octahedral cage when the Li ions jump between the 48h sites: (ii) 48h–48h''. (iii) Long-range ion dynamics needs 48h<sub>1</sub>–48h<sub>2</sub> intercage jump processes between two different cages 1 and 2. The latter jump process is expected to be strongly affected by the anion site disorder of X and  $\text{S}^{2-}$ . We expect that a high degree of substitutional disorder will have a significant impact on the associated jump rate, which characterises exchange processes between the cages.

### 3.2 Magic angle spinning NMR

To investigate local structures of the argyrodites, we recorded  $^{31}\text{P}$  (spin-quantum number  $I = 1/2$ ) MAS NMR spectra of  $\text{Li}_6\text{PS}_5\text{X}$  (X = Cl, Br, I) at a spinning speed of 25 kHz. The spectra are shown in Fig. 4a. In line with the report of Deiseroth and co-workers,<sup>31</sup> the  $^{31}\text{P}$  MAS NMR resonance of  $\text{Li}_6\text{PS}_5\text{I}$  shows a very sharp line centered at  $\delta_{\text{iso}} = 96.3$  ppm pointing to an ordered anion framework with the I anions non-randomly occupying selected crystal sites. Small shoulders near the main signal might point to defect sites in  $\text{Li}_6\text{PS}_5\text{I}$ .

The  $^{31}\text{P}$  MAS NMR spectrum of  $\text{Li}_6\text{PS}_5\text{I}$  is in stark contrast to the situation that is met for  $\text{Li}_6\text{PS}_5\text{Cl}$ , for which we expect the influence of strong S/Cl disorder on the line shape, see above. Indeed, its very broad line, which can hardly be resolved,



**Fig. 4** (a)  $^{31}\text{P}$  MAS NMR spectra of  $\text{Li}_6\text{PS}_5\text{I}$ ,  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{Cl}$  recorded at 202.4 MHz and a spinning frequency of 25 kHz. The spectra have been referenced to 85%  $\text{H}_3\text{PO}_4$  and were recorded at an ambient bearing gas temperature.<sup>31</sup> (b)  $^6\text{Li}$  MAS NMR spectra of  $\text{Li}_6\text{PS}_5\text{Cl}$ ,  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{I}$  recorded at 73.6 MHz and a spinning speed of 25 kHz. All spectra have been referenced to solid  $\text{LiCH}_3\text{COO}$ . Values given in ppm indicate the isotropic chemical shifts.



reveals a wide distribution of chemical shifts and strong spin-spin interactions. Chemical shifts of lines constituting the overall line range from 85 to 81 ppm. Therefore,  $^{31}\text{P}$  MAS NMR clearly reveals anion disorder in  $\text{Li}_6\text{PS}_5\text{Cl}$ . The  $^{31}\text{P}$  MAS NMR line of  $\text{Li}_6\text{PS}_5\text{Br}$  takes an intermediate position. It is composed of narrower lines than those seen for  $\text{Li}_6\text{PS}_5\text{Cl}$ ; nevertheless, line broadening, as compared to  $\text{Li}_6\text{PS}_5\text{I}$ , reveals disorder in the S/Br sublattice. At least the spectrum is composed of three distinct lines located at 93.9 ppm, 92.7 ppm and 91.1 ppm, respectively. The same increase in substitutional disorder might be seen if we consider the corresponding  $^{127}\text{I}$ ,  $^{79}\text{Br}$  and  $^{35}\text{Cl}$  MAS NMR spectra of the three compounds; the corresponding spectra of the three quadrupole nuclei are shown in the ESI,† Fig. S3. Clearly, because of the large quadrupole moment of I ( $|Q(^{127}\text{I})| = 0.721b$ ) the full spectrum including its spinning side bands is rather broad. The isotropic signal, however, is much smaller than that for  $\text{Li}_6\text{PS}_5\text{Cl}$  and  $\text{Li}_6\text{PS}_5\text{Br}$  with  $|Q(^{35}\text{Cl})| = 0.855b$  and  $|Q(^{79}\text{Br})| = 0.330b$ . Although exposed to less second order quadrupole effects, the line of  $\text{Li}_6\text{PS}_5\text{Cl}$  is as broad as that of the Br compound. Site disorder in  $\text{Li}_6\text{PS}_5\text{Cl}$  might explain this additional broadening.

The ordered anion framework seen for  $\text{Li}_6\text{PS}_5\text{I}$  by  $^{31}\text{P}$  MAS NMR, synchrotron X-ray diffraction and neutron diffraction<sup>34</sup> is fully consistent with results from  $^7\text{Li}$  SLR NMR on the ion dynamics in the I compound. As we will show and discuss below, an almost symmetric diffusion-induced  $^7\text{Li}$  NMR rate peak describes longitudinal spin-lattice relaxation in  $\text{Li}_6\text{PS}_5\text{I}$ ;  $\text{Li}^+$  disorder on the split-site does not influence this symmetry. This observation mainly points to the absence of pronounced site disorder in the anion sublattice. Structural anion disorder is, thus, expected to have a significant impact on both the Li ion diffusion and ionic conductivity in  $\text{Li}_6\text{PS}_5\text{X}$ .

For the sake of completeness, we also recorded  $^6\text{Li}$  ( $I = 1$ ) MAS NMR spectra at an ambient bearing gas temperature, these spectra are shown in Fig. 4b. They have been referenced to  $\text{LiCH}_3\text{COO}$ . For  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{Cl}$  we observe a slightly asymmetric line with chemical shifts of  $\delta_{\text{iso}} = 1.6$  ppm and  $\delta_{\text{iso}} = 1.3$  ppm, respectively. The line of  $\text{Li}_6\text{PS}_5\text{I}$  turned out to be more symmetric in shape and is broader than the other lines. As  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{Cl}$  show rapid Li ion long-range translational dynamics their lines represent already coalesced spectra at the measurement temperature of 307 K, see the ESI.† This observation is in perfect agreement with  $^7\text{Li}$  NMR motional line narrowing (see below), which has reached its extreme limit already well below ambient temperature.

In contrast, complete line narrowing of the static  $^7\text{Li}$  NMR line of  $\text{Li}_6\text{PS}_5\text{I}$  is shifted toward much higher temperature, revealing significantly slower long-range ion dynamics (*vide infra*). In addition, the absence of effective Li ion dynamics in  $\text{Li}_6\text{PS}_5\text{I}$ , which would be able to also average (small) second order quadrupolar interactions that the spin-1 nucleus  $^6\text{Li}$  is exposed to, might further increase the width of the NMR line of  $\text{Li}_6\text{PS}_5\text{I}$  as compared to the samples with  $\text{X} = \text{Cl}$  or  $\text{Br}$ . The increased anisotropy seen for  $\text{Li}_6\text{PS}_5\text{Cl}$  is in line with the degree of site disorder in  $\text{Li}_6\text{PS}_5\text{Cl}$  and  $\text{Li}_6\text{PS}_5\text{Br}$ .

Interestingly, according to the halogen anion introduced into the argyrodite structure the isotropic chemical shift values

$\delta_{\text{iso}}$  of the  $^6\text{Li}$  MAS NMR spectra increase from  $\text{Li}_6\text{PS}_5\text{Br}$  to  $\text{Li}_6\text{PS}_5\text{I}$  and further to  $\text{Li}_6\text{PS}_5\text{Cl}$ . Thus, the paramagnetic component of the NMR line decreases; obviously, the different halogen anions change the electron density distribution in the direct neighborhood of the Li spins with  $\text{Li}_6\text{PS}_5\text{Br}$  having the highest density.

### 3.3 Ion dynamics as seen by conductivity spectroscopy

We used broadband impedance spectroscopy<sup>51–53</sup> covering frequencies from the mHz to the MHz region to study the ion dynamics in  $\text{Li}_6\text{PS}_5\text{X}$  to see the change in the overall ionic transport properties with the X substitution. As an example, in Fig. 5a the real part  $\sigma'$  of the complex conductivity  $\hat{\sigma}$  of  $\text{Li}_6\text{PS}_5\text{Br}$  is plotted vs. the frequency  $\nu$ .

At low frequencies and high temperatures  $T$  the isotherms  $\sigma'(\nu)$  reveal electrode polarization, which results from the accumulation of ions at the surface of the ion blocking electrodes applied.<sup>52–54</sup> Towards higher frequencies or at sufficiently low  $T$ , distinct direct current (DC) plateaus show up, which reflect long-range ion transport. The corresponding  $\sigma_{\text{DC}}$  value is governed by both bulk and grain boundary contributions. For the bromide sample,  $\text{Li}_6\text{PS}_5\text{Br}$ ,  $\log_{10}(\sigma_{\text{DC}})T$  follows Arrhenius behaviour

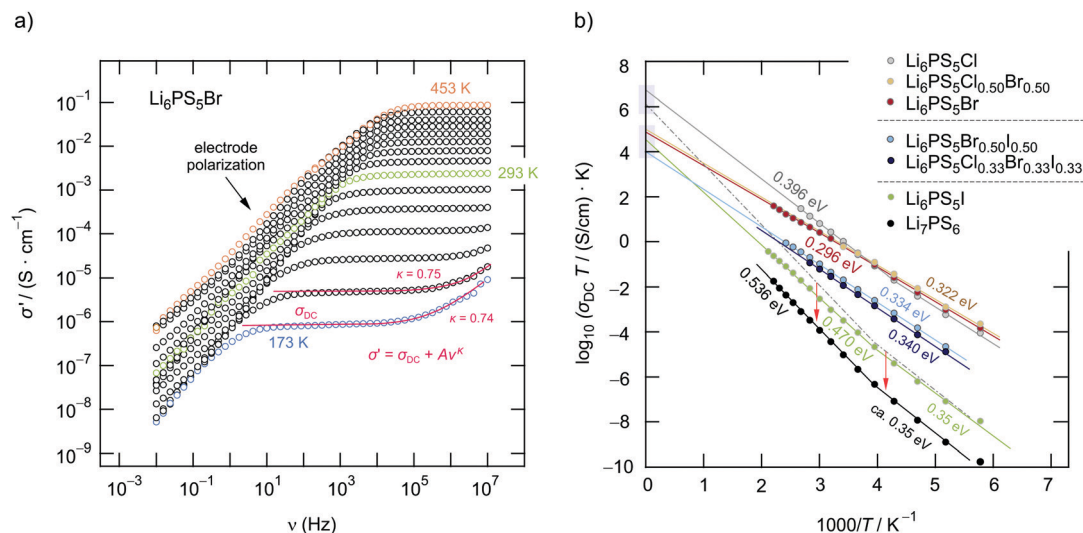
$$\sigma_{\text{DC}}T = \sigma_0 \exp(-E_{\text{a,DC}}/(k_{\text{B}}T)) \quad (1)$$

with an activation energy,  $E_{\text{a,DC}}$ , as low as 0.296 eV. The corresponding Arrhenius line is shown in Fig. 5b. Almost the same behaviour is seen for  $\text{Li}_6\text{PS}_5\text{Cl}_{0.5}\text{Br}_{0.5}$ . Going back to the underlying isotherms  $\sigma'(\nu)$  we clearly observe dispersive regions at very low  $T$  and high frequencies  $\nu$ . These regions can be approximated by a Jonscher-type power law,  $\sigma' = \sigma_{\text{DC}} + A\nu^p$ , where  $A$  is the alternating current coefficient and  $p$  represents the power law exponent. Because of the very high ionic conductivity of  $\text{Li}_6\text{PS}_5\text{Br}$ , this behaviour, influenced by short-range ion dynamics including forward-backward jump processes, is only seen at temperatures below 193 K.<sup>52,54</sup> Here,  $p$  turned out to be *ca.* 0.75; such a value is expected for 3D correlated motion.<sup>55</sup> Similar isotherms were observed for the other compositions investigated.

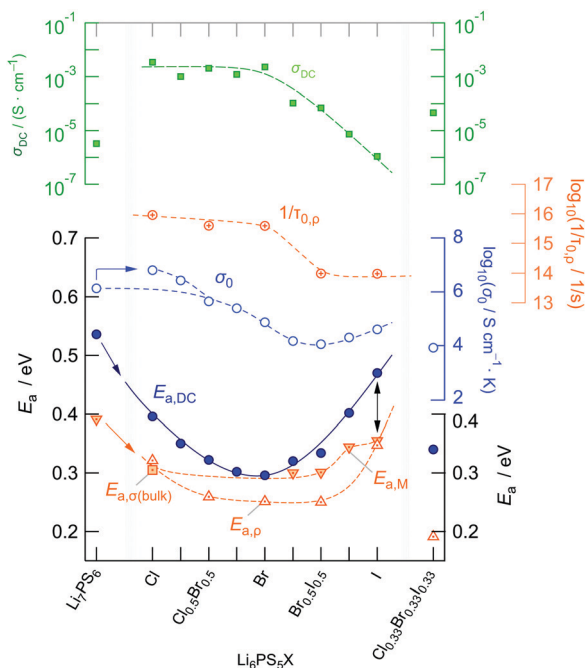
For comparison, in Fig. 5b the temperature dependence of  $\log_{10}(\sigma_{\text{DC}})T$  of the other samples is presented.  $\text{Li}_6\text{PS}_5\text{I}$  and  $\text{Li}_7\text{PS}_6$  are characterised by the lowest conductivities and the highest activation energies  $E_{\text{a,DC}}$  of 0.47 eV and 0.37 eV. At approximately 250 K we notice a slight deviation from the Arrhenius line determining  $\log_{10}(\sigma_{\text{DC}})T$  at higher  $T$ . This behaviour cannot be related to the phase transition of  $\text{Li}_6\text{PS}_5\text{I}$ ;<sup>31,39,40,49</sup> the I compound transforms into a low- $T$  phase at  $T \approx 160$  K, see below. Such a slight deviation is also seen for  $\text{Li}_6\text{PS}_5\text{Cl}$ .

In Fig. 6a the changes in activation energies, ionic conductivities and Arrhenius pre-factors ( $\sigma_0$ , see eqn (1)) are illustrated. In all cases, the replacement of sulfur anions in  $\text{Li}_7\text{PS}_6$  by heavier halide anions leads to a decrease in activation energies. Except for  $\text{Li}_6\text{PS}_5\text{Cl}$  and  $\text{Li}_6\text{PS}_5\text{Cl}_{0.75}\text{Br}_{0.25}$  the Arrhenius pre-factor  $\sigma_0$  also decreases. This feature, which is seen when  $\text{Li}_6\text{PS}_5\text{Br}$  is compared with  $\text{Li}_7\text{PS}_6$  (or  $\text{Li}_6\text{PS}_5\text{Cl}$ ), has been interpreted in terms of the Meyer-Neldel<sup>56</sup> rule and related to a reduction in





**Fig. 5** (a) Conductivity isotherms (10 mHz to 10 MHz) of  $\text{Li}_6\text{PS}_5\text{Br}$  at temperatures ranging from 173 K to 453 K; isotherms have been recorded in steps of 20 K. (b) Change of the DC conductivity of  $\text{Li}_6\text{PS}_5\text{X}$  as a function of inverse temperature. The highest conductivity is found for  $\text{Li}_6\text{PS}_5\text{Cl}$  and the lowest for  $\text{Li}_6\text{PS}_5\text{I}$ . Data points and the Arrhenius line referring to  $\text{Li}_7\text{PS}_6$  have an offset of  $-2$  on the log scale for the sake of clarity.



**Fig. 6** Activation energies  $E_{a,\text{DC}}$  of the argyrodite samples prepared.  $E_{a,\text{DC}}$ , determined with the help of conductivity isotherms, characterises the overall ion transport, which is affected by both bulk and g.b. contributions. A minimum is found for  $\text{Li}_6\text{PS}_5\text{Br}$ . The dependence of the corresponding Arrhenius pre-factor on anion substitution is also shown. For the sake of completeness, we also included activation energies that, most likely, describe bulk ion dynamics. These have been extracted either (i) from conductivity isotherms ( $\text{Li}_6\text{PS}_5\text{Cl}$ ), (ii) from modulus spectra or (iii) from variable-temperature resistivity measurements carried out at fixed frequencies (see below). In the upper graph overall ionic conductivities at room temperature are shown. The highest conductivity of  $3 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$  has been observed for  $\text{Li}_6\text{PS}_5\text{Cl}$ , whereas  $\text{Li}_6\text{PS}_5\text{I}$  reveals the lowest overall conductivity of only  $10^{-6}$ .

Debye frequencies for soft lattices created by substitution of Br and I for S.<sup>34</sup> If we compare our results for  $\text{Li}_6\text{PS}_5\text{Cl}$  with respect

to the conductivity behaviour of  $\text{Li}_7\text{PS}_6$  we witness both a decrease in  $E_{a,\text{DC}}$  from 0.536 eV to 0.396 eV and an increase in  $\sigma_0$  by one order of magnitude. This favorable combination of  $E_{a,\text{DC}}$  and  $\sigma_0$  results in a room temperature ionic conductivity of  $\sigma_{\text{DC}} = 3.8 \text{ mS} \cdot \text{cm}^{-1}$ . For  $\text{Li}_6\text{PS}_5\text{Br}$ , with its more polarisable anions on the other hand, the low activation energy is compensated by a pre-factor two orders of magnitude lower than that for  $\text{Li}_6\text{PS}_5\text{Cl}$ . Considering high temperatures this feature causes  $\sigma_{\text{DC}}$  to adopt values lower than those of  $\text{Li}_6\text{PS}_5\text{Cl}$ .

Interestingly, the ionic conductivity of ordered  $\text{Li}_6\text{PS}_5\text{I}$  is even lower than that of the non-substituted compound  $\text{Li}_7\text{PS}_6$ ; this decrease, despite the higher activation energy found for  $\text{Li}_7\text{PS}_6$ , can also be explained by the relatively low value for  $\sigma_0$ . The pre-factor is proportional to the attempt frequencies  $\nu_a$ , the number of effective charge carriers  $n_{\text{Li}}$  and an entropy term.<sup>42</sup> Besides the effect of  $\nu_a$ , trapping effects in  $\text{Li}_6\text{PS}_5\text{I}$ , because of a very low intercalation jump rate, might reduce  $N$  for this sample. If we assume similar  $\nu_a$  values for  $\text{Li}_6\text{PS}_5\text{Cl}$  and  $\text{Li}_6\text{PS}_5\text{Br}$ , entropy effects could serve as an explanation for the change in  $\sigma_0$ . Especially for the highly disordered  $\text{Li}_6\text{PS}_5\text{Cl}$  sample<sup>50</sup> the migration entropy might take a decisive role in influencing the ion dynamics. For the ordered  $\text{Li}_6\text{PS}_5\text{I}$  compound this contribution might be absent.

When going from  $\text{Li}_6\text{PS}_5\text{Br}$  to  $\text{Li}_6\text{PS}_5\text{I}$  we see that, despite the introduction of polarisable iodine anions, the pre-factor remains almost the same,  $A = \log(\sigma_0 / (\text{S} \cdot \text{cm}^{-1} \cdot \text{K})) = 4.9$  for  $\text{Li}_6\text{PS}_5\text{Br}$  and  $A = 4.6$  for  $\text{Li}_6\text{PS}_5\text{I}$ , but  $E_{a,\text{DC}}$  increases from 0.296 eV to 0.47 eV. From this point of view, although the lattice gets softer in the case of I, Kraft *et al.* mentioned<sup>34</sup> that Meyer Neldel seems to be not fully applicable to describe the situation in  $\text{Li}_6\text{PS}_5\text{I}$ . One could have expected the more polarisable I anions to allow the Li ions to squeeze through smaller voids.<sup>50</sup> Obviously, this concept does not work for  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{I}$ , at least if we regard the (overall) averaged long-range ion transport process as probed by  $\sigma_{\text{DC}}$  measurements.

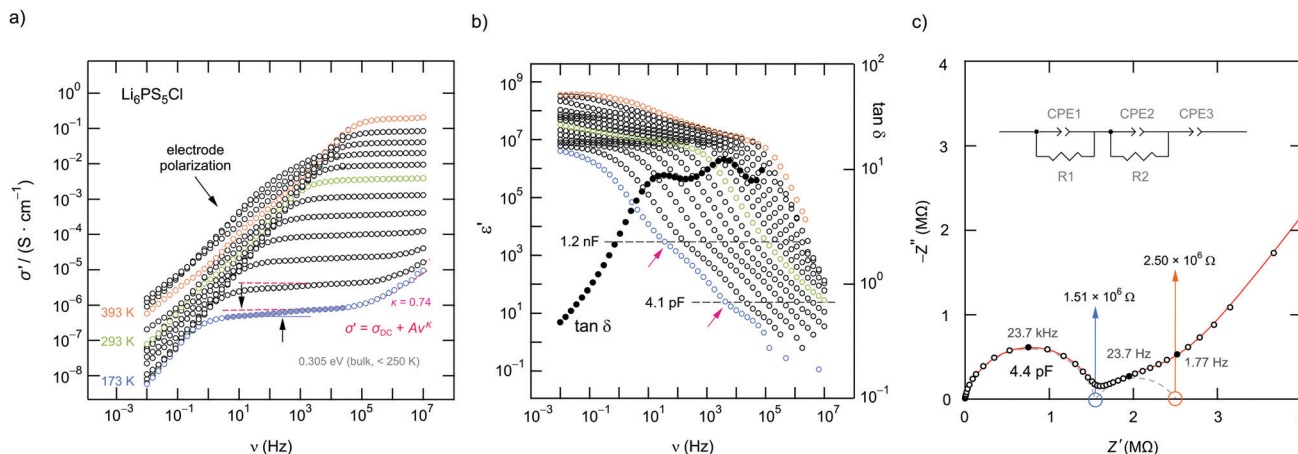


Fig. 7 (a) Conductivity isotherms of  $Li_6PS_5Cl$  recorded at temperatures ranging from 173 K up to 393 K. Jonscher-type power laws are used to parameterise the dispersive regions seen at the lowest temperatures. At sufficiently low  $T$  we notice a step in the DC plateaus that is attributed to contributions from grain boundaries and the bulk regions. (b) Real part of the permittivity (and loss factor (173 K)) plotted as a function of frequency. Disregarding the polarisation regime,  $\epsilon'$  also reveals a two-step frequency decay characterised by the following capacitances:  $4.1 \times 10^{-12}$  F and  $1.2 \times 10^{-9}$  F. Dots show the change of the loss factor  $\tan \delta$  passing through two maxima. (c) Complex plane plot (Nyquist plot) of the real part  $Z'$  vs. the imaginary part  $Z''$  of the complex impedance  $\bar{Z}$  of a  $Li_6PS_5Cl$  pellet (173 K). Two depressed semicircles are seen reflecting the bulk ( $4.4 \times 10^{-12}$  F) and grain boundary response ( $6.8 \times 10^{-9}$  F).

The ionic conductivities of the mixed compounds containing I anions, *viz.*  $Li_6PS_5Br_{0.5}I_{0.5}$  and  $Li_6PS_5Cl_{1/3}Br_{1/3}I_{1/3}$ , do not vary much. Obviously, the introduction of I plays the crucial role to lower  $\sigma_{DC}$ . The Cl anions do not affect the ionic transport in these high-entropy compounds in a positive way, at least for compounds containing two anions greatly differing in ionic radius (181 pm *vs.* 216 pm). To take a closer look at the exceptional behaviour of  $Li_6PS_5Cl$  with its high degree of anion disorder we tried to separate the bulk and grain boundary contributions of this sample. Moreover, we used complex resistivity measurements to further characterise the ion dynamics.

The  $\sigma'(\nu)$  isotherms of  $Li_6PS_5Cl$  are shown in Fig. 7a. A careful look at the DC plateau region shows that it contains a small step. Thus, it is composed of actually two plateaus. Below 250 K, the corresponding activation energies turned out to be 0.310 eV and 0.305 eV, see Fig. 7b. The two-step behaviour of the  $\sigma'(\nu)$  isotherms of  $Li_6PS_5Cl$  are also seen if we plot the real part  $\epsilon'$  of the complex permittivity *vs.*  $\nu$  (Fig. 7b). We used the equation for a parallel-plate capacitor to estimate the corresponding capacitance  $C$  of the two steps:

$$C = \epsilon_0 \epsilon_r \cdot \frac{A}{d} \quad (2)$$

Here  $\epsilon_0$  represents the electric field constant ( $8.854 \times 10^{-12}$  F m $^{-1}$ ), and  $A$  is the area and  $d$  the thickness of the sample. While the first DC plateau at high frequencies is characterised by  $C_1 = 4.1$  pF, for the one at lower  $\nu$  we found  $C_2 = 1.2$  nF. Therefore, the plateau associated with  $C_1$  in the pF range represents the bulk response, whereas the response at lower frequencies is governed by grain boundary contributions for which capacitances typically in the nF regime are expected.<sup>57</sup> The estimated capacitances are in good agreement with those that can be inferred from complex plane plots (Fig. 7c). At 173 K the corresponding Nyquist plot is dominated by two depressed semicircles; electrode polarization

shows up at low frequencies. If we calculate  $C$  *via*  $\omega_{el} = 1/RC$ , where  $\omega_{el} = 2\pi\nu_{el}$  is the electric relaxation frequency and  $R$  the resistance at the intercept of the curve with the  $Z'$  axis,<sup>57</sup> we obtain  $C_1 = 4.4$  pF and  $C_2 = 6.8$  nF, being in good agreement with the estimation presented above. Only for  $Li_6PS_5Cl$  we managed to separate the small difference between the bulk and g.b. contributions. Also for  $Li_6PS_5I$  this difference is expected to be very small.

For comparison, the two contributions in the electrical relaxation of  $Li_6PS_5Cl$  are also seen in the loss factor  $\tan \delta = \epsilon''/\epsilon'$  when plotted as a function of frequency  $\nu$  (see also Fig. 7b). The maxima in  $\tan \delta$ , showing up at 15.36 Hz (g.b.) and 4.21 kHz (bulk), correspond to the plateaus or inflection points of  $\epsilon'/\nu$ , see also Fig. 8. According to  $\hat{\sigma} = i\omega\epsilon_0\hat{\epsilon} = i\omega\epsilon_0\epsilon' + \omega\epsilon_0\epsilon''$  the maxima in  $\tan \delta$  produce two minima if the frequency dependence of the imaginary part  $\sigma''(\propto \epsilon'')$  is analyzed (Fig. 8).

To further characterise ion hopping in  $Li_6PS_5X$ , especially if we consider samples with lower conductivity than  $Li_6PS_5Cl$  and

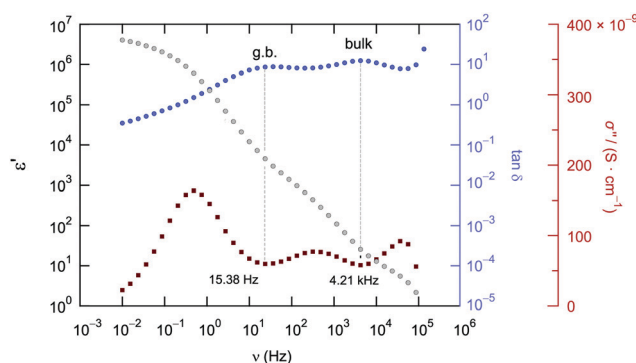


Fig. 8 Comparison of the frequency dependence of  $\tan \delta$ ,  $\epsilon'$  and  $\sigma''$  of  $Li_6PS_5Cl$  measured at 173 K. Plateaus (or inflection points) in  $\epsilon'$  result in minima in  $\sigma''$  and maxima in  $\tan \delta$ , respectively.





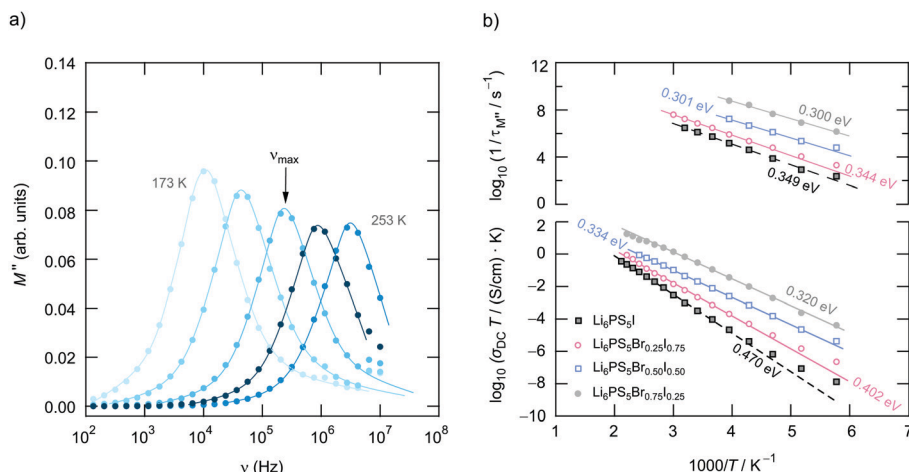


Fig. 9 (a) Frequency dependence of the imaginary part of the modulus,  $M''$ , of  $\text{Li}_6\text{PS}_5\text{Br}_{0.50}\text{I}_{0.50}$  recorded from 173 K to 253 K in steps of 20 K. The lines are to guide the eye. The temperature dependence of the rate  $\tau_M^{-1}$  is shown in (b). For comparison, the results for  $\text{Li}_6\text{PS}_5\text{Br}_{0.25}\text{I}_{0.75}$ ,  $\text{Li}_6\text{PS}_5\text{Br}_{0.75}\text{I}_{0.25}$  and  $\text{Li}_6\text{PS}_5\text{I}$  are also included. The lower part of the graph shows  $\sigma_{\text{DC}}T(1/T)$ ; the values given represent activation energies. For the sake of clarity, data of  $\text{Li}_6\text{PS}_5\text{Br}_{0.75}\text{I}_{0.25}$  (solid line, grey) have been plotted using an offset of +1 on the log scale.

$\text{Li}_6\text{PS}_5\text{Br}$ , we used the electric modulus representation<sup>58,59</sup> to take a look at electrical relaxation frequencies  $\tau_M^{-1} = \nu_{\text{max}}$ . As an example, in Fig. 9 for  $\text{Li}_6\text{PS}_5\text{Br}_{0.5}\text{I}_{0.5}$  the imaginary part  $M''$  of the complex modulus is plotted vs.  $\nu$ . Since the amplitude of  $M''$  is proportional to  $1/C$ , bulk processes are mainly seen. For samples with very high conductivities, such as  $\text{Li}_6\text{PS}_5\text{Cl}$ , the peaks are shifted to too high frequencies and are, thus, no longer fully visible. Activation energies  $E_{a,M''}$  from our  $M''(\nu)$  analysis are also included in Fig. 6. For comparison, the bulk activation energy deduced from Fig. 7 is included, too. They reveal that the activation energies, which we ascribe to bulk properties, do not change much if we consider compounds up to the composition  $\text{Li}_6\text{PS}_5\text{Br}_{0.5}\text{I}_{0.5}$ . This behaviour changes if we increase the I concentration. Importantly, for the compounds rich in I, especially if we consider  $\text{Li}_6\text{PS}_5\text{I}$ , the observation  $E_{a,M''} < E_{a,\text{DC}}$  suggests that the charge carrier concentration increases with temperature. For  $\text{Li}_6\text{PS}_5\text{I}$  the difference  $E_{a,\text{DC}} - E_{a,M''}$  turned out to be relatively high, viz. 0.121 eV (see the vertical arrow in Fig. 6).

Additionally, after we took a look at the overall and bulk ion dynamics in  $\text{Li}_6\text{PS}_5\text{X}$  we used complex resistivity measurements,  $\hat{\rho} = 1/\hat{\sigma} = \hat{M}/(i\omega\epsilon_0)$ , carried out at constant frequency but varying temperature, to answer the question of how the bulk ion dynamics depends on the time-scale and length-scale that the technique applied is sensitive to. In Fig. 10a the temperature dependence of the real part  $\rho' = M''/\omega$  of the complex resistivity  $\hat{\rho}$  is shown for  $\text{Li}_6\text{PS}_5\text{Br}$ . The peaks in Fig. 10a have been recorded for two different frequencies viz. 1 MHz and 10 MHz.

$\rho'$  is given by a Lorentzian-shaped function containing the electrical relaxation time  $\tau_p$ :<sup>60</sup>

$$\rho' \propto \frac{\tau_p}{1 + (\omega\tau_p)^{\beta'}} \quad (3)$$

The quantity  $\log_{10}(M''/\omega)$  when plotted vs.  $1/T$  shows similar features to the diffusion-induced NMR spin-lattice relaxation rate.<sup>15,51,60</sup> The higher the frequency the more the peaks shift

towards higher temperatures. Symmetric peaks are obtained for  $\beta' = 2$ ; if  $\beta' < 2$  the low- $T$  flank becomes lower than that of the high- $T$  side. Indeed, for  $\text{Li}_6\text{PS}_5\text{Br}$  we notice an asymmetric peak that strongly points to correlated motion in disordered ion conductors.<sup>15,61–64</sup> While the high- $T$  flank yields an activation energy  $E_{a,\rho}$  comparable to  $E_{a,\text{DC}}$  when bulk processes are probed, short-range motions are seen on the low- $T$  side. The latter motions are characterised by values as low as 0.15 eV, which are also seen for  $\text{Li}_6\text{PS}_5\text{Cl}$  and  $\text{Li}_6\text{PS}_5\text{Br}_{0.5}\text{I}_{0.5}$  (Fig. 10b).  $E_{a,\rho}$  of  $\text{Li}_6\text{PS}_5\text{Cl}$  is only slightly higher than  $E_{\sigma,\text{bulk}} = 0.305$  eV (see above).

We cannot see any strong variation in  $E_{a,\rho}$  when comparing the response of  $\text{Li}_6\text{PS}_5\text{Br}_{0.5}\text{I}_{0.5}$  with that of  $\text{Li}_6\text{PS}_5\text{Br}$ .  $E_{a,\rho}$  values have also been included in Fig. 6; for the sake of clarity, they are separately shown in Fig. 10c. Obviously, a lower pre-factor of the underlying Arrhenius relation is responsible for this shift. The same effect is seen for  $\text{Li}_6\text{PS}_5\text{I}$ . Although the lattice is expected to be much softer in the case of  $\text{Li}_6\text{PS}_5\text{I}$  as compared to the situation in  $\text{Li}_6\text{PS}_5\text{Cl}$ ,  $\rho(\omega)$  tells us that the activation energies  $E_{a,\rho}$  of the two compounds are very similar (0.32 eV vs. 0.35 eV). However, the peak  $\rho'(\omega)$  of  $\text{Li}_6\text{PS}_5\text{I}$  is clearly shifted toward higher  $T$  and shows up at 385 K; the origin of this difference has to be looked for in the bulk ion dynamics, g.b. resistances cannot explain it. As compared to the peak of  $\text{Li}_6\text{PS}_5\text{Cl}$  the peak of the I compound is symmetric in shape ( $\beta \approx 1.95$ ) and points to an ordered structure.

Obviously, as in the case of  $E_{a,\text{DC}}$  the reason for the lower conductivity and, thus, the slower bulk electrical relaxation in  $\text{Li}_6\text{PS}_5\text{I}$  (and in  $\text{Li}_6\text{PS}_5\text{Br}_{0.5}\text{I}_{0.5}$ ) has been looked for in the prefactor of the underlying Arrhenius relationships. Most likely, the anion site disorder in  $\text{Li}_6\text{PS}_5\text{Cl}$  is responsible for this behaviour. Indeed, if we approximate the  $\rho'(\nu)$  peaks with eqn (3) we can extract pre-factor  $\tau_{0,\rho}^{-1}$  assuming  $\tau_p^{-1}$  to be depending on temperature according to Arrhenius.  $\tau_{0,\rho}^{-1}$  values are also included in Fig. 6; indeed, they clearly reveal lower pre-factors for  $\text{Li}_6\text{PS}_5\text{I}$  by approximately two orders of magnitude. If we assume that the attempt frequencies are similar for  $\text{Li}_6\text{PS}_5\text{Cl}$  and

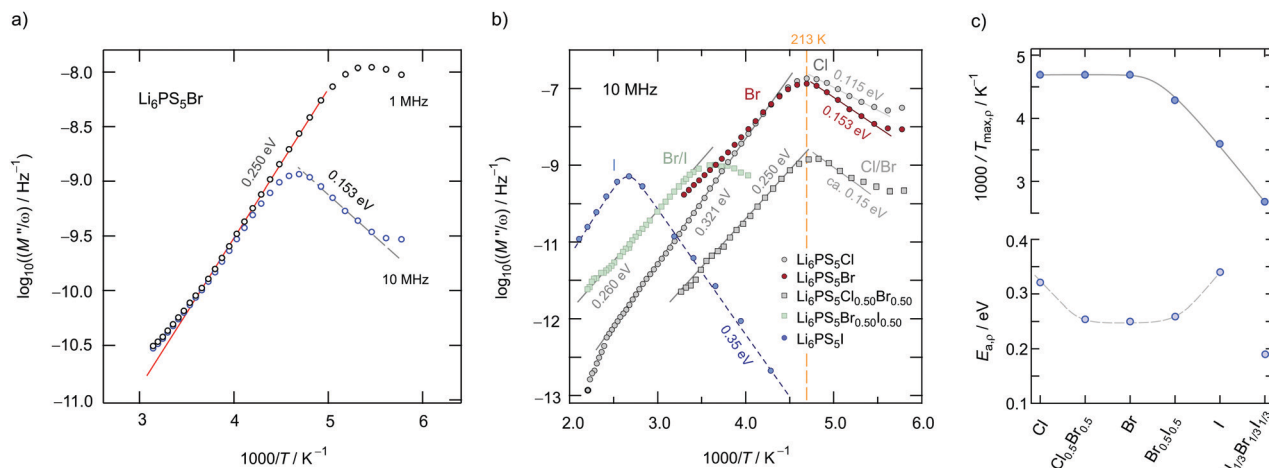


Fig. 10 (a) Real part of the complex resistivity  $\rho'$  of  $\text{Li}_6\text{PS}_5\text{Br}$ , measured at a fixed frequency (1 MHz and 10 MHz), vs.  $1000/T$ . (b)  $\rho'(\omega)$  peaks (10 MHz) of the argyrodites indicated. Asymmetric peaks point to time-scale dependent (heterogeneous) ion dynamics with local jump processes characterised by activation energies as low as 0.115 eV ( $\text{Li}_6\text{PS}_5\text{Cl}$ ). (c) Temperatures (shown as  $1000/T$ ) at which the  $\rho'(\omega)$  peaks show up. For  $\text{Li}_6\text{PS}_5\text{I}$  the peak is clearly shifted toward higher  $T$  indicating much slower ion dynamics. The change in  $E_{a,p}$  is also shown.

$\text{Li}_6\text{PS}_5\text{I}$  a significant change in migration entropy, as mentioned above, might explain the prominent change seen. To check whether this phenomenon is also apparent in SLR NMR, which is in general sensitive to both short-range and long-range ion dynamics, we carried out  $^7\text{Li}$  NMR measurements in both the laboratory and rotating-frame of reference.<sup>64,65</sup> Line shape measurements carried out at temperatures down to the cryogenic region complement our investigation.

### 3.4 $^7\text{Li}$ NMR relaxometry to probe the bulk ion dynamics

In Fig. 11 an overview of the  $^7\text{Li}$  NMR spin-lattice relaxation rates  $1/T_1 \equiv R_1$  and  $1/T_{1\rho} \equiv R_{1\rho}$  measured over a wide temperature

range is given. To identify the thermally activated regions the rates of  $\text{Li}_6\text{PS}_5\text{X}$ , with  $\text{X} = \text{Cl}$ ,  $\text{Br}$ , and  $\text{I}$ , were plotted using an Arrhenius representation, *i.e.*,  $\log(1/T_1)$  is plotted vs.  $1000/T$ . The rates have been recorded at a Larmor frequency of  $\omega_0/2\pi = 116$  MHz; for the locking frequency we used a magnetic  $B_1$  field corresponding to  $\omega_1/2\pi = 20$  kHz. At very low temperatures ( $T < 160$  K) the  $R_1$  rates shown in Fig. 11a reveal a non-diffusive background; in this  $T$  range longitudinal relaxation is primarily induced by lattice vibrations or coupling of the Li spins ( $I = 3/2$ ) with paramagnetic impurities.<sup>61,65–67</sup>

At higher  $T$  we expect spin-lattice relaxation to be increasingly induced by Li self-diffusion.<sup>61</sup> Indeed, the rates sharply increase

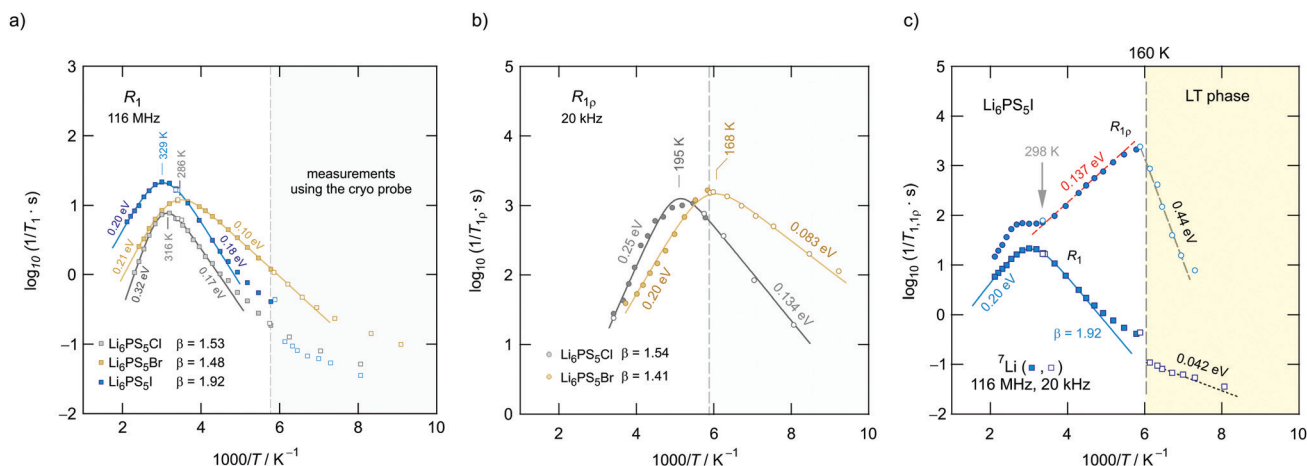


Fig. 11 (a) Temperature dependence of the diffusion-induced  $^7\text{Li}$  NMR spin-lattice relaxation rates  $R_1$  (116 MHz) of  $\text{Li}_6\text{PS}_5\text{X}$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$  and  $\text{I}$ ). Solid lines refer to BPP-type fits to extract activation energies and pre-factors. (b) Arrhenius plot of the corresponding  $^7\text{Li}$  SLR  $\rho$  NMR rates recorded in the rotating frame of reference using a nominal locking frequency of  $\omega_1/2\pi = 20$  kHz. Again, the solid lines represent fits according to a modified BPP relaxation model taking into account the asymmetry of the peaks by parameter  $\beta$ . The further the relaxation peak is shifted to lower  $T$ , the faster the Li exchange process inducing spin-lock spin-lattice relaxation. Therefore, Li diffusion, as seen by NMR, is increasing in the following order:  $\text{Li}_6\text{PS}_5\text{I} < \text{Li}_6\text{PS}_5\text{Br} < \text{Li}_6\text{PS}_5\text{Cl}$  (see also c). (c)  $R_1$  and  $R_{1\rho}$  of  $\text{Li}_6\text{PS}_5\text{I}$ ; at 160 K  $\text{Li}_6\text{PS}_5\text{I}$  reversibly transforms into its low- $T$  phase. At this temperature the rates  $R_1$  show a jump toward lower values; the  $R_{1\rho}$  rates sharply decay with an activation energy of 0.44 eV. The unfilled symbols in (a–c) show rates measured with an NMR probe designed for experiments at cryogenic temperatures; the filled symbols refer to data which were acquired with a standard probe.

with temperature and characteristic diffusion-induced rate peaks show up. We recognise that  $R_1$  passes through well-defined maxima as has been found by some of us in an earlier study on the ion dynamics in  $\text{Li}_6\text{PS}_5\text{Br}$ .<sup>15</sup> At the temperature  $T_{\text{max}}$ , where  $R_1$  reaches its maximum value, the motional correlation rate  $1/\tau_c$  is given by  $\tau_c\omega_0 \approx 1$ .  $1/\tau_c$  is identical within a factor of two to the Li jump rate  $1/\tau$ .<sup>61,65</sup> The same holds for  $R_{1\rho}$ , for which the maximum condition is  $\omega_1\tau \approx 0.5$ .<sup>61,65</sup> As  $\omega_0$  and  $\omega_1$  differ by more than three orders of magnitude, the SLR NMR experiments, when taken together, are able to sense motional processes covering a large time scale.<sup>67,68</sup>

We notice that the rate peak of  $\text{Li}_6\text{PS}_5\text{Br}$  shows up at  $T_{\text{max}} = 286$  K. The peak is asymmetric and we used a Lorentzian-type (BPP-type)<sup>62,69</sup> spectral density function  $J(\omega_0) \propto R_1$  of the form<sup>70</sup>

$$J(\omega_0) \propto \frac{\tau_c}{1 + (\omega\tau_c)^\beta} \quad (4)$$

to approximate its shape. Eqn (4) holds for 3D diffusion;  $J(\omega_0)$  is the Fourier transform of the underlying motional correlation function  $G(t')$ . If  $G(t')$  is a single exponential,  $\beta$  in  $J(\omega_0)$  takes a value of 2. For a 3D diffusion process, at high temperatures, *i.e.*, if  $\tau_c\omega_0 \ll 1$ , eqn (4) yields  $J \propto \tau_c$ ; in the limit  $\tau_c\omega_0 \gg 1$ , that is, on the low- $T$  side of the rate peak, we have  $J \propto \tau^{-1}\omega_0^{-\beta}$  ( $1 < \beta \leq 2$ ). While we expect  $\beta = 2$  for uncorrelated motion,<sup>61,62,69,71</sup> asymmetric peaks are often found for structurally complex ion conductors<sup>15,71–73</sup> whose dynamic processes are affected by correlation effects because of both disorder and strong Coulomb interactions of the moving ions.<sup>71</sup> For such materials the activation energies for short-range and long-range processes might largely differ.<sup>62</sup> In general,  $\beta$  can also be related to a distribution width of motional correlation times; in this sense it has a similar meaning to the exponent in the Cole–Davidson spectral density function used to approximate asymmetric rate peaks.<sup>74–76</sup>

Here, the analysis of the rate peak of  $\text{Li}_6\text{PS}_5\text{Br}$  with eqn (4) yields an activation energy  $E_{\text{a,NMR}}$  of 0.213 eV, which is in perfect agreement with earlier findings for this compound.<sup>15,50</sup> As mentioned above, the parameter  $\beta$  describes the deviation from symmetric behaviour ( $\beta = 2$ ).  $\beta$  turned out to be  $\beta \approx 1.5$ ,<sup>65</sup> which gives rise to a much lower activation energy  $E_{\text{a,low}}$  on the low- $T$  side of the peak. In this regime, characterised by  $\tau_c\omega_0 \ll 1$ , short-range or localised ion dynamics in double-well potentials, including also highly correlated forward-backward jumps, are sensed by  $R_1$ .<sup>61</sup> The activation energy of the low- $T$  flank is given by 0.10 eV, which is in very good agreement with that seen by  $\rho'(\omega)$ . Localised intracage jump processes involving the 48h and 24g sites in  $\text{Li}_6\text{PS}_5\text{Br}$  could be mainly responsible for spin-lattice relaxation in this region, as has been precisely calculated (0.11 eV) by De Klerk *et al.*<sup>50</sup> The higher activation energy  $E_{\text{a,high}} (= E_{\text{a,NMR}})$  seen in the limit  $\tau_c\omega_0 \ll 1$  might, however, additionally be affected by 48h–48h jumps. Usually in this regime, in which many jump processes occur during one Larmor precession of the spin,  $E_{\text{a,NMR}}$  should be comparable with  $E_{\text{a,DC}}$  (0.296 eV) or  $E_{\text{a},\rho}$  (0.250 eV).<sup>61</sup>  $E_{\text{a,DC}}$  could be influenced by g.b. effects; here,  $E_{\text{a,NMR}} < E_{\text{a},\rho}$  shows that the number of jump events sensed by NMR, which should not necessarily include all types of jumps needed for long-range diffusion, is sufficient to generate a full  $R_1$  peak.

**Table 1** Results of the individual BPP-fits used to analyse the  $^7\text{Li}$  NMR  $R_1$  and  $R_{1\rho}$  peaks of the three argyrodite samples  $\text{Li}_6\text{PS}_5\text{X}$  (X = Cl, Br, I). For comparison, the activation energies obtained from the low- $T$  flank,  $E_{\text{a,low}}$ , are also included

	$\text{Li}_6\text{PS}_5\text{Cl}^a$	$\text{Li}_6\text{PS}_5\text{Br}^a$	$\text{Li}_6\text{PS}_5\text{I}^b$
$\beta$	1.53(2)	1.48(2)	1.92(1)
$E_{\text{a}}$	0.320(1) eV	0.213(1) eV	0.198(1) eV
$E_{\text{a,low}}$	0.170(4) eV	0.102(5) eV	0.182(5) eV
$\tau_0$	$1.3(5) \times 10^{-14}$ s	$2.3(5) \times 10^{-13}$ s	$8.2(5) \times 10^{-13}$ s
$\beta_\rho$	1.54	1.41	—
$E_{\text{a},\rho}$	0.248(9) eV	0.201(9) eV	0.137(3) eV
$E_{\text{a,low},\rho}$	0.134(1) eV	0.083(1) eV	—
$\tau_{0,\rho}$	$9.5(5) \times 10^{-13}$ s	$3.3(1) \times 10^{-12}$ s	—

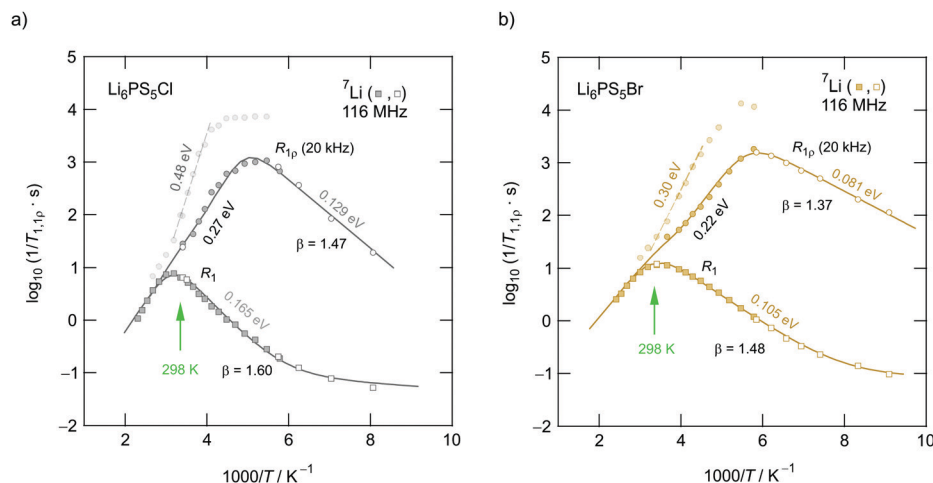
<sup>a</sup> The best  $R_{1\rho}$  fit is obtained if we replace  $\omega_1/2\pi = 20$  kHz by a slightly higher effective locking frequency  $\omega_{\text{eff}}$  that also takes into account local magnetic fields. For  $\text{Li}_6\text{PS}_5\text{Cl}$  several runs of the global fit procedure yields  $\omega_{\text{eff}} = 1.68 \times \omega_1$ ; for  $\text{Li}_6\text{PS}_5\text{Br}$   $\omega_{\text{eff}}$  is given by  $\omega_{\text{eff}} = 1.41 \times \omega_1$ .<sup>b</sup>  $\text{Li}_6\text{PS}_5\text{I}$  undergoes a phase transition at 160 K; thus, no  $\beta_\rho$  can be observed. The symmetric rate peak ( $\beta \approx 2$ ) agrees with the ordered anion sublattice as suggested by XRPD, see above.

A very similar behaviour is found for  $\text{Li}_6\text{PS}_5\text{Cl}$ . The corresponding rate peak is shifted toward higher temperature revealing that faster ion dynamics is present in  $\text{Li}_6\text{PS}_5\text{Br}$ . In agreement with conductivity spectroscopy and our  $\rho'(\omega)$  analysis, for  $\text{Li}_6\text{PS}_5\text{Cl}$  higher activation energies ( $E_{\text{a,high}} = 0.32$  eV,  $E_{\text{a,low}} = 0.17$  eV) than those seen for the Br analogue were found. Although  $E_{\text{a,high}} = 0.32$  eV perfectly agrees with  $E_{\text{a},\rho}$ , see Fig. 10, and calculated values,<sup>35</sup> it is higher than expected from  $R_{1\rho}$  NMR in the limit  $\tau_c\omega_1 \ll 1$  (0.248 eV). Furthermore, the shapes of the  $R_1(1/T)$  peaks of the two compounds are very similar. Obviously, similar (local) jump processes influence the NMR rates. In Table 1 an overview of the parameters is given obtained from the analysis with individual BPP-type spectral densities for each peak.

Exactly the same trend is seen when we look at the  $R_{1\rho}(1/T)$  peaks of the two compounds, which are shown in Fig. 11b. These have been, independently of the  $R_1$  experiments, also parameterised with Lorentzian-shaped spectral density functions. The activation energies of the peak of  $\text{Li}_6\text{PS}_5\text{Br}$  (0.201 eV, 0.083 eV) match with those reported earlier<sup>15</sup> also including calculated values.<sup>50</sup> They also agree with those from the  $R_1$  peak. Here,  $R_{1\rho}(1/T)$  of  $\text{Li}_6\text{PS}_5\text{Br}$  turned out to be much smaller than that reported by Yu *et al.*;<sup>77</sup> most likely, the difference has to be looked for in the preparation conditions such as milling steps and annealing procedures.

In Fig. 12 so-called joint fits<sup>65</sup> of the two types of NMR experiments,  $R_1$  and  $R_{1\rho}$ , are shown. For the joint fits the parameters  $E_{\text{a,NMR}}$  and  $\tau_0^{-1}$ , which is the pre-factor of the Arrhenius equation of  $\tau_c^{-1}$ , have been linked to each other. The best fit is obtained if we use two independent values for  $\beta$  and if we replace  $\omega_1$  by effective frequencies  $\omega_{1,\text{eff}}$ , also taking into account local magnetic fields.<sup>73</sup> To estimate the latter, we did not fix  $\omega_1$  and looked at how the quality of the fit changes if it is a free parameter. Only a slight change of  $\omega_1$  was necessary giving rise to  $\omega_{\text{eff}} \approx 1.5 \times \omega_1$ . A successful joint fit shows that the same overall diffusion processes govern the peaks  $R_1$  and  $R_{1\rho}$ . The results of our joint fits are shown in Table 2.





**Fig. 12** Arrhenius plot of the  $^7\text{Li}$  NMR relaxation rates  $R_1$  and  $R_{1\rho}$  of (a)  $\text{Li}_6\text{PS}_5\text{Cl}$  and (b)  $\text{Li}_6\text{PS}_5\text{Br}$  measured in the laboratory frame of reference (116 MHz) and in the rotating frame of reference (20 kHz, nominal locking frequency). The solid lines represent the global fit based on a modified BPP model that takes into account peak asymmetries by the parameter  $\beta_{(\rho)}$ . The fastest Li diffusion is found for  $\text{Li}_6\text{PS}_5\text{Br}$  with the peak maxima showing up at 286 K and 168 K, respectively. The second  $R_{1\rho}$  relaxation process, most likely also influenced by spin–spin relaxation to a certain degree, is indicated, too. As mentioned before (see Fig. 11), the open symbols represent rates that were measured with an NMR probe designed for experiments at cryogenic temperatures; the filled symbols show rates which were acquired with the standard probe.

**Table 2** Results of the overall fit used to jointly parameterise the  $^7\text{Li}$  NMR  $R_1$  and  $R_{1\rho}$  peaks of  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{Cl}$ .  $E_a$  agrees well with the results if we analyse the peaks individually. For comparison, results for  $\text{Li}_6\text{PS}_5\text{I}$  taken from Table 1 are also included

	$E_{a,\text{NMR}}$	$C$	$\beta_{(\rho)}$	$\tau_0$
$\text{Li}_6\text{PS}_5\text{Cl}$				
$R_1$	0.273(5) eV	$3.5(5) \times 10^9 \text{ s}^{-2}$	1.60(1)	$4.9(4) \times 10^{-14} \text{ s}$
$R_{1\rho}$		$3.1(5) \times 10^{10} \text{ s}^{-2}$	1.47(1)	
$\text{Li}_6\text{PS}_5\text{Br}$				
$R_1$	0.218(1) eV	$5.6(7) \times 10^9 \text{ s}^{-2}$	1.48(1)	$2.0(2) \times 10^{-13} \text{ s}$
$R_{1\rho}$		$3.3(9) \times 10^{10} \text{ s}^{-2}$	1.47(1)	
$\text{Li}_6\text{PS}_5\text{I}^a$				
$R_1$	0.198(1) eV	$1.1(4) \times 10^{10} \text{ s}^{-2}$	1.92(1)	$8.2(9) \times 10^{-13} \text{ s}$
$R_{1\rho}$	0.137(3) eV	—	—	—

<sup>a</sup> The best global fits are obtained if we replace  $\omega_1$  by the effective locking frequencies  $\omega_{\text{eff}} = 1.68 \times \omega_1$  ( $\text{Li}_6\text{PS}_5\text{Cl}$ ) and  $\omega_{\text{eff}} = 1.41 \times \omega_1$  ( $\text{Li}_6\text{PS}_5\text{Br}$ ). The coupling constant  $C$ , which is the amplitude of the rate peak,  $J(\omega_0) = C\tau_c/(1 + (\omega\tau_c)^\beta)$ , turns out to be on the order of  $10^9$  to  $10^{10} \text{ s}^{-2}$ .

The activation energies  $E_{a,\text{NMR}}$  ( $=E_{a,\text{high}}$ ) obtained fulfill the relationship

$$E_{a,\text{low}} = (\beta_{(\rho)} - 1)E_{a,\text{high}}. \quad (5)$$

$\beta_{(\rho)} < 2$  points to correlated  $\text{Li}^+$  motion and indicates a sub-quadratic dependence of the diffusion-induced SLR NMR rates in the low- $T$  limit  $\tau_c\omega_{0(1)} \gg 1$ . Our results are in good agreement with those of Epp *et al.* as well as Rao *et al.*<sup>15,35</sup> We clearly see that correlation effects such as structural disorder and Coulomb interactions<sup>71</sup> have a larger effect on the cation dynamics in  $\text{Li}_6\text{PS}_5\text{Br}$  than in  $\text{Li}_6\text{PS}_5\text{Cl}$ .

Considering the overall constants  $C$  obtained from the joint fits, they reveal that both dipolar and electric quadrupolar interactions govern the diffusion-induced SLR NMR rates. Estimating  $C_{\text{dipolar}}$  with the help of the rigid lattice line width

for  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{Cl}$  would underestimate  $C$  to be on the order of  $10^{10} \text{ s}^{-2}$ .<sup>46</sup> As we will discuss below, for  $\text{Li}_6\text{PS}_5\text{Br}$  quadrupolar interactions have been identified to greatly influence longitudinal relaxation.<sup>15</sup>

Interestingly, a very close look at the  $R_{1\rho}$  magnetization transients revealed that they contain a minor magnetization component that leads to activation energies of 0.484 eV ( $\text{Li}_6\text{PS}_5\text{Cl}$ ) and 0.298 eV ( $\text{Li}_6\text{PS}_5\text{Br}$ ); the corresponding  $R_{1\rho}$  rates are included in Fig. 12. We cannot exclude that these rates are to a certain degree also influenced by spin–spin relaxation. Obviously, the rates sense long-range Li jump processes characterised by higher activation energies. The interstage jumps might contribute to this type of magnetic relaxation, too.

For  $X = \text{Cl}$  and  $\text{Br}$ , if we consider activation energies,  $T_{\text{max}}$ ,  $\beta$  and  $\beta_{(\rho)}$ , the  $^7\text{Li}$  SLR NMR data reveal the same trend for the ion dynamics as seen by the conductivity and  $\rho'(\omega)$ .  $\text{Li}_6\text{PS}_5\text{Br}$  shows fast ion dynamics and the lowest activation energies. For  $\text{Li}_6\text{PS}_5\text{Cl}$  we witness slightly higher activation energies; simultaneously, the peaks shift toward higher temperature. For  $\text{Li}_6\text{PS}_5\text{I}$ , on the other hand, significant differences show up (see the next section).

The NMR rate peaks of  $\text{Li}_6\text{PS}_5\text{I}$ , remembering its low  $\sigma_{\text{DC}}$  conductivity of  $10^{-6} \text{ S cm}^{-1}$  at ambient temperature, are expected to show up at temperatures much higher than 320 K. We would expect much higher activation energies, at least similar to or higher than those found for  $\text{Li}_6\text{PS}_5\text{Cl}$ . Surprisingly, the  $R_1$  rate peak of  $\text{Li}_6\text{PS}_5\text{I}$  shows up at a temperature highly comparable to that of  $\text{Li}_6\text{PS}_5\text{Cl}$  *viz.* at  $T_{\text{max}} = 329 \text{ K}$ , see Fig. 11a. In stark contrast to our expectation, NMR does not point to slower  $\text{Li}^+$  diffusion. Hence, in  $\text{Li}_6\text{PS}_5\text{I}$  the same fast (local) jump processes are present as in their parent compounds.<sup>35,40,50</sup> Here, we anticipate that the Li ions in  $\text{Li}_6\text{PS}_5\text{I}$ , with its ordered anion sublattice, have access to the same rapid intracage jump processes. According to NMR the barriers have to be characterised by an





activation energy of 0.2 eV. Obviously, only intracage jump processes in  $\text{Li}_6\text{PS}_5\text{I}$  are sufficient to produce a full  $R_1(1/T)$  peak, see the discussion above.

As expected for a material with an ordered anion lattice such as  $\text{Li}_6\text{PS}_5\text{I}$  and without severe influences of motional correlation effects, an almost symmetric rate peak  $R_1(1/T)$  ( $\beta = 1.92(\approx \beta')$ ) is obtained for  $\text{Li}_6\text{PS}_5\text{I}$ . The same shape was seen in  $\rho'(\omega)$ . Interestingly, an even lower activation energy determines  $R_{1\rho}(1/T)$ , see Fig. 11c: in the limit  $\tau_c\omega_1 \ll 1$  the rates follow an Arrhenius line whose activation energy  $E_{a,\text{high}}$  is given by only 0.137 eV. This value is remarkably similar to a cage-like local pathway studied by Rao and Adams (0.15 eV) who used a bond valence approach to investigate the Li ion dynamics in  $\text{Li}_6\text{PS}_5\text{I}$ . Our experimental value also coincides with that of Pecher *et al.*<sup>40</sup> (0.14 eV) who studied the local ion dynamics by molecular dynamics simulations.

The amplitude  $(R_1)_{\text{max}}$  of the  $R_1(1/T)$  rate of  $\text{Li}_6\text{PS}_5\text{I}$  turned out to be higher than that of the peaks belonging to  $\text{Li}_6\text{PS}_5\text{Cl}$  and  $\text{Li}_6\text{PS}_5\text{Br}$ . This could be because of stronger heteronuclear Li–X interactions and the fact that Li ions on the distorted 24g sites give rise to stronger dipolar and electric quadrupolar couplings constants. These are lowest for the  $\text{Li}_6\text{PS}_5\text{Cl}$  compound. In general,  $(R_1)_{\text{max}}$  is proportional to the square of the magnetic dipolar or electric quadrupolar coupling constant.<sup>75,78,79</sup> If we use an electric quadrupole constant of at least 50 kHz, as has been estimated for  $\text{Li}_7\text{PS}_6$ ,<sup>46</sup> we obtain  $(R_1)_{\text{max}} \approx 2 \text{ s}^{-1}$  yielding  $\log_{10}((R_1)_{\text{max}}/\text{s}) \approx 0.3$ , showing that for  $\text{Li}_6\text{PS}_5\text{Cl}$  both dipolar and electric quadrupolar interactions play a role in determining the relaxation mechanism. For  $\text{Li}_6\text{PS}_5\text{Br}$  we showed *via* comparative  $^7\text{Li}$  and  $^6\text{Li}$  SLR NMR measurements that quadrupole fluctuations greatly affect the overall spin–lattice relaxation.<sup>15</sup>

Coming back to the temperature dependence of the SLR NMR rates of  $\text{Li}_6\text{PS}_5\text{I}$ , we see that at higher temperatures than ambient the rates  $R_{1\rho}$  are increasingly governed by  $R_1$ , which produces an apparent maximum at *ca.* 330 K. Unfortunately, the peak maximum of  $R_{1\rho}(1/T)$  cannot be detected as  $\text{Li}_6\text{PS}_5\text{I}$  undergoes a phase transition at 160 K;<sup>31,39,40,49</sup> see the abrupt change in  $R_{1\rho}$  in Fig. 11c. The ion dynamics in the low- $T$  (LT) phase is characterised by a much higher activation energy of 0.44 eV. Below 160 K the rates  $R_1$  are no longer induced by diffusive Li jump processes.

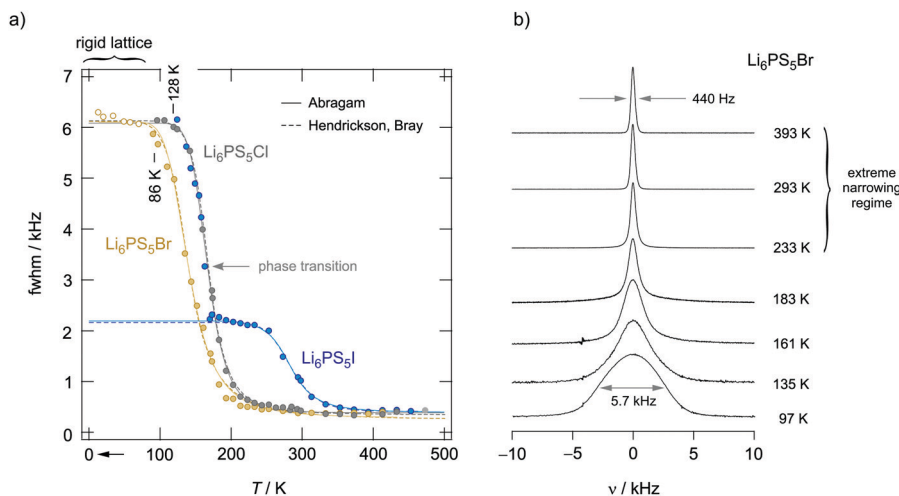
To explain the evident differences between the results from conductivity measurements and nuclear spin relaxation in  $\text{Li}_6\text{PS}_5\text{I}$  we anticipate that the fast diffusion Li processes in the I compound are not interconnected to give rise to long-range, through-going ion transport. As has been pointed out in detail by Wagemaker and co-workers, and first mentioned by Rao and Adams,<sup>35</sup> the jump probability between two rings in  $\text{Li}_6\text{PS}_5\text{I}$  is very low.<sup>50</sup> Inter-cage jump processes with higher activation energies lead to poor ion transport in  $\text{Li}_6\text{PS}_5\text{I}$ . On a shorter length scale, however, the same structural motifs in  $\text{Li}_6\text{PS}_5\text{X}$  cause very similar NMR rate peaks. Anion disorder, taking advantage of anions with radii that do not differ much to that of  $\text{S}^{2-}$ , switches on the inter-cage exchange processes, making  $\text{Li}_6\text{PS}_5\text{Br}$  a fast ion conductor. This design principle causes the overall activation energy to increase in the following order:  $\text{Li}_6\text{PS}_5\text{Br} < \text{Li}_6\text{PS}_5\text{Cl} < \text{Li}_6\text{PS}_5\text{I}$ .

To verify whether some intragrain translational processes needed for long-range diffusion in  $\text{Li}_6\text{PS}_5\text{I}$  are indeed missing or governed by higher activation energies we carefully looked at the  $R_{1\rho}$  transients and recorded  $^7\text{Li}$  NMR line shapes over a broad temperature range (Fig. 13). Interestingly, the above-mentioned slow magnetization component seen for  $\text{Li}_6\text{PS}_5\text{Cl}$  and  $\text{Li}_6\text{PS}_5\text{Br}$  (Fig. 12) is missing for the I compound. Furthermore, the inter-cage jumps are expected to contribute to the averaging of homonuclear (Li–Li) dipole–dipole interactions. If missing at low temperatures, for  $\text{Li}_6\text{PS}_5\text{I}$  the change in line width  $\Delta\nu$  should occur in two steps. Full averaging is expected at temperatures for which the inter-cage exchange rate reaches sufficiently high values on the order of some kHz. Indeed, whereas for  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{Cl}$  the  $^7\text{Li}$  NMR line width continuously decreases with temperature revealing typical narrowing curves (Fig. 13a), that of  $\text{Li}_6\text{PS}_5\text{I}$  is different.

For  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{Cl}$  the extreme narrowing regime is already reached at 250 K ( $\nu_\infty \approx 300 \text{ Hz}$ ); the final line width is caused by external field inhomogeneities. In contrast to the situation observed for  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{Cl}$ , at 250 K the  $^7\text{Li}$  NMR line of  $\text{Li}_6\text{PS}_5\text{I}$  is still relatively broad and shows a width of  $\nu = 2.2 \text{ kHz}$ . At 350 K it finally reaches  $\nu_\infty$ . Thus, for  $\text{Li}_6\text{PS}_5\text{I}$  full averaging of the NMR line width is shifted by  $\Delta T = 100 \text{ K}$  toward higher  $T$ . Most likely, the latter step corresponds to inter-cage ion dynamics which are governed by a larger activation barrier. Hence, it is clear from NMR motional narrowing data that in  $\text{Li}_6\text{PS}_5\text{I}$  a much slower process kicks in only at higher  $T$ . The fact that  $\Delta\nu$  of  $\text{Li}_6\text{PS}_5\text{I}$  and  $\text{Li}_6\text{PS}_5\text{Cl}$  is very similar, at least at temperatures just above the phase transition, shows that mainly fast intracage jump processes are responsible for the narrowing seen in this  $T$  range. Differences show up, however, if we consider the rotating-frame spin–lattice relaxation rates, see above. The activation energies of the two samples differ by *ca.* 0.11 eV. Interestingly, the  $R_{1\rho}(1/T)$  peak of  $\text{Li}_6\text{PS}_5\text{I}$  is expected at a similar temperature to that of  $\text{Li}_6\text{PS}_5\text{Br}$  (0.20 eV), again pointing to very fast intracage jump processes in the iodide compound. Most likely, so-called doublet-jump processes<sup>50</sup> have to be considered to explain this feature, see below.

Unfortunately, we cannot probe the rigid-lattice line width  $\nu_0$  of the  $\text{Li}_6\text{PS}_5\text{I}$  compound because of the phase transition that occurs at 160 K.<sup>31,39,40,49</sup> For both  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{Cl}$  the value of  $\nu_0$  is very similar;  $\nu_0$  turned out to be *ca.* 6.1 kHz. Therefore, the magnetic dipolar Li–Li interactions, which are determined by the Li–Li distances, are almost the same in the two compounds. The inflexion point of the motional narrowing curve of  $\text{Li}_6\text{PS}_5\text{Br}$  is located at  $T = 150 \text{ K}$  (Fig. 13a).  $R_{1\rho}(1/T)$  tells us that at this temperature the motional correlation rate  $\tau_c^{-1} (\approx 2\omega_1)$  should be on the order of  $2.51 \times 10^5 \text{ s}^{-1}$ . This value clearly exceeds  $\nu_0$  and causes full averaging of the spin–spin interactions in this  $T$  range. The changes of the corresponding  $^7\text{Li}$  NMR lines are shown in Fig. 13b.  $\text{Li}_6\text{PS}_5\text{Br}$  shows one of the lowest onset temperatures seen by NMR motional line narrowing; already at 86 K the shape of the NMR line starts to change as a result of rapid  $\text{Li}^+$  self-diffusion.<sup>15</sup> This observation excellently agrees with results from density functional theory molecular dynamics simulations.<sup>50</sup>





**Fig. 13** (a) Temperature dependence of the  ${}^7\text{Li}$  NMR line widths (FWHM = full width at half maximum) of the aryrodites  $\text{Li}_6\text{PS}_5\text{X}$  (X: Cl, Br and I). Some of the data points referring to  $\text{Li}_6\text{PS}_5\text{Br}$  and measured at temperatures lower than 80 K were taken from Epp *et al.*,<sup>15</sup> they perfectly complement the results of the sample studied here. Line widths  $\Delta\nu_r(T)$  of  $\text{Li}_6\text{PS}_5\text{Br}$  start to narrow at temperatures as low as 86 K indicating ultrafast hopping processes that average homonuclear dipole–dipole interactions being responsible for the rigid lattice line width  $\Delta\nu_r \approx 6.1$  kHz. Li diffusion in the compound with Cl is slightly slower as the onset of line narrowing is shifted toward higher  $T$ . The line of  $\Delta\nu_r(T)$  of  $\text{Li}_6\text{PS}_5\text{I}$  narrows in steps of two. At  $T < 160$  K it indicates dipole averaging in the low- $T$  phase. Because inter-ring jump processes are absent, the line does not reach its extreme value at a temperature comparable to that of  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{Cl}$ . Higher temperatures are necessary to obtain a fully narrowed  ${}^7\text{NMR}$  line. Lines represent fits according to the models of Hendrickson and Bray (dashed lines) and Abragam (solid lines). (b)  ${}^7\text{Li}$  NMR line shapes of  $\text{Li}_6\text{PS}_5\text{Br}$  recorded at the temperatures indicated; the line transforms from a Gaussian shape at low  $T$  to a Lorentzian one at elevated temperatures.

Extracting quantitative information from NMR motional line narrowing is always fraught with difficulties.<sup>80</sup> Abragam<sup>81</sup> and Hendrickson and Bray<sup>82,83</sup> introduced models to use the change in line widths to deduce activation energies for the hopping process behind. There is still debate over whether these models are accurate enough for this purpose. Hence, we should not over-interpret the results but regard them as estimates. The dashed lines in Fig. 13 refer to the following relationships<sup>82</sup>

$$\Delta\nu(T) = \Delta\nu_0 \left\{ 1 + [(\Delta\nu_0/B) - 1] \exp\left(-\frac{E_{a,\text{HB}}}{k_B T}\right) \right\}^{-1} + \nu_\infty \quad (6)$$

$\Delta\nu(T)$  is the line width of the central transition at a given temperature and  $B$  is a parameter that is related to the number of thermally activated ions.<sup>82</sup> The final line width  $\nu_\infty$  is determined by the inhomogeneities of the external magnetic field  $B_0$ . Another possibility to deduce activation energies is given by the formalism of Abragam<sup>81</sup> (see the solid line in Fig. 13):

$$\Delta\nu^2(T) = \Delta\nu_0^2 \frac{2}{\pi} \arctan \left[ \alpha \Delta\nu(T) \tau_\infty \exp\left(\frac{E_{a,\text{A}}}{k_B T}\right) \right] + \Delta\nu_\infty^2 \quad (7)$$

$\alpha$  is a fitting parameter, here chosen to be 1.  $\tau_\infty$  is the pre-factor of the underlying Arrhenius law of the correlation time  $\tau_c$ . With the Abragam fit we obtained activation energies  $E_{a,\text{A}}$  of 0.06 eV ( $\text{Li}_6\text{PS}_5\text{Br}$ ), 0.11 eV ( $\text{Li}_6\text{PS}_5\text{Cl}$ ) and 0.23 eV ( $\text{Li}_6\text{PS}_5\text{I}$ ), respectively. Typically, the formalism of Hendrickson and Bray yields somewhat higher activation energies; here, we found  $E_{a,\text{HB}} = 1.6 \times E_{a,\text{A}}$ , see Table 3. Interestingly, although line narrowing is expected to be sensitive to long-range ion dynamics which can fully average all dipolar interactions, the activation energies  $E_{a,\text{A}}$  and  $E_{a,\text{HB}}$  are remarkably similar to those governing the low- $T$  flank of the  $R_1(1/T)$  peaks, see also Table 3.

**Table 3** Activation energies obtained when analysing the motional narrowing curves shown in Fig. 13. We used the Abragam (A) and Hendrickson–Bray (HB) formalism to extract activation energies; the error is in the last digit. For comparison, activation energies describing the slopes of the  $R_1(1/T)$  peaks in the limit  $\tau_c \omega_0 \gg 1$  are also shown

	$E_{a,\text{A}}$ (eV)	$E_{a,\text{HB}}$ (eV)	$E_a$ (low- $T$ flank) (eV)
$\text{Li}_6\text{PS}_5\text{Cl}$	0.11(1)	0.18(2)	0.17(4)
$\text{Li}_6\text{PS}_5\text{Br}$	0.06(1)	0.09(1)	0.10(4)
$\text{Li}_6\text{PS}_5\text{I}$	0.23(1)	0.38(2)	0.18(5)

Finally, we will quantitatively compare jump rates  $\tau^{-1}$  from NMR with electrical relaxation rates from impedance and conductivity spectroscopy. Using the Nernst–Einstein equation<sup>84</sup> we can convert  $\sigma'$  into diffusion coefficients and, thus, jump rates. The easiest way, being also independent of any relaxation model, is to determine jump rates  $\tau^{-1}$  at the temperatures where the NMR relaxation rate peaks show up. With the conditions  $\tau_c \omega_{1(\rho)} = 1(0.5)$ , valid at  $T_{\text{max}}$ , and the jump distances  $\ell$  obtained from XRD we estimated diffusion coefficients according to the Einstein–Smoluchowski relation<sup>84</sup> for 3D diffusion

$$D_{\text{NMR}} = \frac{\ell^2}{6\tau} \quad (8)$$

For  $\ell$  we used the jump distance of the 48h–48h jump process, which is assumed to be the slowest one. The results are listed in Table 4. At  $T_{\text{max}}$  the jump rate turned out to be on the order of  $1.36 \times 10^{-9} \text{ s}^{-1}$ . As an example, the mean residence time of the Li ions in  $\text{Li}_6\text{PS}_5\text{Br}$  at 286 K is on the order of 1 ns only. Such a short residence time, which is already reached below room temperature, corresponds to ionic conductivities on the order of  $10^{-3}$  to  $10^{-2} \text{ S cm}^{-1}$ .



**Table 4** Results of the diffusion coefficient  $D$ .  $\tau$  was calculated from the  $R_1(1/T)$  rate peak measurements performed at 116 MHz

	$\ell/\text{\AA}$	$T_{\max}(R_1)/\text{K}$	$D_{\text{NMR}}/\text{cm}^2 \text{ s}^{-1}$	$n_{\text{Li}}/\text{m}^{-3}$
$\text{Li}_6\text{PS}_5\text{Cl}$	2.34	316	$6.7 \times 10^{-8}$	$6.3 \times 10^{27}$
$\text{Li}_6\text{PS}_5\text{Br}$	2.41	286	$7.1 \times 10^{-8}$	$6.0 \times 10^{27}$
$\text{Li}_6\text{PS}_5\text{I}$	2.66	329	$8.6 \times 10^{-8}$	$5.8 \times 10^{27}$

For  $\ell$  we used the 48h–48h distance, which is the longest jump distance in  $\text{Li}_6\text{PS}_5\text{Br}$ , when we consider cation hopping processes near the regularly occupied Li sites.

Using structural data from our Rietveld analysis we also estimated the charge carrier density  $n_{\text{Li}}$  in  $\text{Li}_6\text{PS}_5\text{Br}$ .  $n_{\text{Li}}$ , which is on the order of  $10^{27} \text{ m}^{-3}$ , is needed to convert  $D_{\text{NMR}}$  into conductivities expected at or near  $T_{\max}$ . Disregarding any correlation effects for our estimation of  $\sigma_{\text{NMR}}$ , the following relation holds<sup>11</sup>

$$\sigma_{\text{NMR}} = \frac{e^2 \cdot n}{k_{\text{B}} T} D_{\text{NMR}} = \frac{e^2 \cdot n_{\text{Li}} \cdot \ell^2}{6k_{\text{B}} T} \cdot \frac{1}{\tau} \quad (9)$$

where  $e$  denotes the elementary charge. Here, a residence time  $\tau$  of 1 ns results in conductivities of the order of  $2 \text{ mS cm}^{-1}$ . In Table 5 the estimated results from NMR are compared with those measured by conductivity spectroscopy. Assuming no correlation effects or other influences for this estimation means that  $H_{\text{R}}/f$  in  $D_{\text{NMR}} = (H_{\text{R}}/f)D_{\sigma}$  is approximated by  $H_{\text{R}}/f = 1$ ; while  $H_{\text{R}}$  denotes the Haven ratio connecting the tracer diffusion coefficient  $D_{\text{tr}}$  with  $D_{\sigma}$ , the correlation factor  $f$  links  $D_{\text{NMR}}$  with  $D_{\text{tr}}$ .<sup>11</sup>

While good agreement is seen for  $\sigma_{\text{NMR}}$  and  $\sigma_{\text{DC}}$  of  $\text{Li}_6\text{PS}_5\text{Br}$ , we have to notice a somewhat larger difference for the Cl compound. In general, conductivities indirectly deduced from NMR should be regarded as estimates because relaxation NMR and conductivity spectroscopy sense different kinds of motional correlation functions. Agreement over a large temperature is only obtained if both techniques are sensitive to the same diffusion process and the same correlation function.<sup>51</sup>

As expected, for  $\text{Li}_6\text{PS}_5\text{I}$  the values listed in Table 5 differ by three orders of magnitude. Whereas  $\sigma_{\text{DC}}$  is mainly governed by successful jump processes resulting in long-range ion transport,  $\sigma_{\text{NMR}}$  reflects short-range ion dynamics. The difference can easily be explained by the fact that in  $\text{Li}_6\text{PS}_5\text{I}$  the interstage jump processes are less probable; these processes hinder the ions in long-range diffusion. Note that the comparison in Table 5 only refers to  $T \approx T_{\max}$  at which the NMR peaks show up. Comparing dynamic parameters over the full temperature range will show deviations between nuclear spin relaxation and conductivity spectroscopy as the techniques deliver different activation energies in the present case. Such a comparison is presented in Fig. 14. Squares represent jump rates obtained at the NMR

rate peaks; at  $T \rightarrow 0$  we have indicated the pre-factors of the Arrhenius lines.

In Fig. 14a  $\tau_{\text{NMR}}^{-1}$  as deduced from the joint fits of  $\text{Li}_6\text{PS}_5\text{Cl}$  and  $\text{Li}_6\text{PS}_5\text{Br}$  are shown. The line belonging to  $\text{Li}_6\text{PS}_5\text{I}$  refers to the  $R_1$  rates only. First of all, we notice a correlation between  $E_{\text{a,NMR}}$  and the pre-factor  $\tau_0^{-1}$  (see also Table 2). The decrease in  $E_{\text{a,NMR}}$ , which changes from 0.273 eV to 0.218 eV and further to 0.198 eV ( $R_1$  of  $\text{Li}_6\text{PS}_5\text{I}$ ), is accompanied by a decrease in  $\tau_0^{-1}$ . The attempt frequency  $\tau_0^{-1}$  decreases by a factor of 80 when going from  $\text{Li}_6\text{PS}_5\text{Cl}$  to  $\text{Li}_6\text{PS}_5\text{I}$ . This small variation either reflects a decrease in phonon frequencies or a change in migration entropy  $\Delta S$  of the ions as  $\tau_0^{-1} = \nu_{\text{p},0} \exp(\Delta S/k_{\text{B}})$ . Phonon frequencies, to which  $\nu_{\text{p},0}$  is proportional, usually take values on the order of  $10^{12}$  to  $10^{15} \text{ s}^{-1}$ . As discussed above, for  $\text{Li}_6\text{PS}_5\text{I}$  a decrease in migration entropy is reasonable because of the ordered anion sublattice. The decrease in  $E_{\text{a,NMR}}$  reflects the increase in anion polarizability ( $\text{I} > \text{Br} > \text{Cl}$ ), which should, apart from effects due to disorder, also lead to lower hopping barriers. This trend for  $E_{\text{a,NMR}}$  is at least valid for the elementary  $\text{Li}^+$  jumps seen by NMR. If we include  $\tau_{\sigma}^{-1}$  values obtained by transforming  $\sigma_{\text{DC}}$  into hopping rates after eqn (9), we notice that good agreement is only seen at temperatures around  $T_{\max}$ , see Fig. 14a and b. Clearly, the fact that  $E_{\text{a,NMR}} \neq E_{\text{a,DC}}$  leads to deviations at temperatures  $T \leq T_{\max}$ . For comparison, in Fig. 14b hopping rates from  $\rho'(T)$  have also been included.

The pre-factors of the Arrhenius lines referring to  $\tau_{\sigma}^{-1}$  estimated from  $\sigma_{\text{DC}}$  also vary with X. While we cannot see any large difference between  $\tau_{0,\sigma}^{-1}$  from  $\text{Li}_6\text{PS}_5\text{I}$  and  $\text{Li}_6\text{PS}_5\text{Br}$  as mentioned above, we see that  $\tau_{0,\sigma}^{-1}$  of the Cl-compound is much higher than expected. This increase is caused by a change in slope of  $\sigma_{\text{DC}}$  at a temperature slightly below 400 K; it is also seen for  $\text{Li}_6\text{PS}_5\text{I}$ . Below 400 K the ionic conductivity  $\sigma_{\text{DC}}$  (as well as  $\tau_{\sigma}^{-1}$ ) follows an Arrhenius law with an activation energy very similar to that of  $\text{Li}_6\text{PS}_5\text{Br}$  (0.273 eV). As  $\sigma_{\text{DC}}$  of  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{Cl}$  almost coincide in this  $T$  range, also the corresponding pre-factors  $\tau_{0,\sigma}^{-1}$  would be the same. Here, the fact that  $\tau_{0,\sigma}^{-1}$  of  $\text{Li}_6\text{PS}_5\text{Cl}$  is larger than that of  $\text{Li}_6\text{PS}_5\text{Br}$  originates the kink in the Arrhenius line causing  $\sigma_{\text{DC}}T(1/T)$  to be characterised by an activation energy (0.396 eV) much larger than that in the low- $T$  range. Obviously, another  $\text{Li}^+$  diffusion process, being characterised by an activation energy larger than 0.3 eV, contributes to  $\tau_{\sigma}^{-1}$  of  $\text{Li}_6\text{PS}_5\text{Cl}$ .

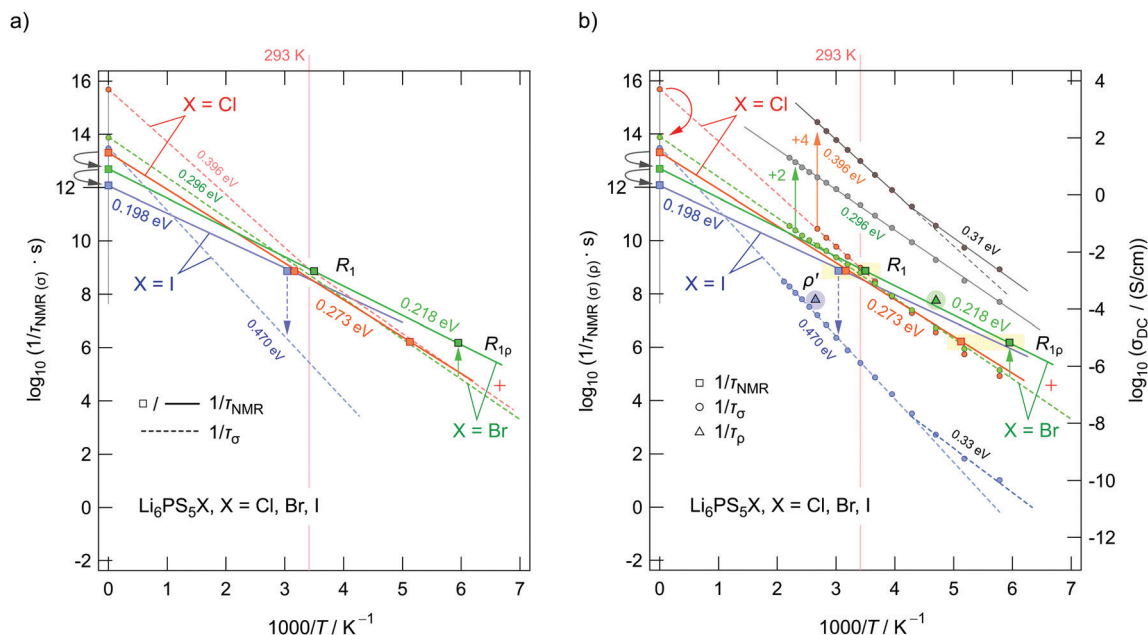
Such an additional process, which we assume could stem from an ordered Li sublattice in  $\text{Li}_6\text{PS}_5\text{Cl}$ , has been seen by  $R_{1\rho}$ , see Fig. 12. The  $R_{1\rho}$  magnetization transients of  $\text{Li}_6\text{PS}_5\text{Cl}$  are characterised by a second decay process that is thermally activated by 0.48 eV. The same feature is also seen for  $\text{Li}_6\text{PS}_5\text{Br}$  with both a disordered anion structure and  $\text{Li}^+$  sublattice. The corresponding activation energy of 0.30 eV (see Fig. 12) is, however, very similar to that of  $\sigma_{\text{DC}}T(1/T)$ . This similarity thus gives rise to no increase in  $\sigma_{\text{DC}}T$  above  $T \approx 400 \text{ K}$ .

The pre-factors seen by conductivity spectroscopy, especially those of  $\text{Li}_6\text{PS}_5\text{Cl}$ , clearly represent mean values. In materials with several diffusion processes taking place in parallel, each process needs to be characterised by its individual pre-factor.

**Table 5** Estimated conductivity values ( $\sigma_{\text{NMR}}$ ) from NMR data. For comparison, the measured values  $\sigma_{\text{DC}}$  are also listed

	$\sigma_{\text{NMR}}/\text{mS cm}^{-1}$	$\sigma_{\text{DC}}/\text{mS cm}^{-1}$
$\text{Li}_6\text{PS}_5\text{Cl}$	2.46 (316 K)	9.00 (313 K)
$\text{Li}_6\text{PS}_5\text{Br}$	2.78 (286 K)	2.20 (293 K)
$\text{Li}_6\text{PS}_5\text{I}$	2.80 (329 K)	$8.60 \times 10^{-3}$ (333 K)





**Fig. 14** Arrhenius plot of the jump rates deduced from the  $^7\text{Li}$  NMR rate peaks shown in Fig. 11c, 12a and (b). (a) Squares represent either pre-factors or jump rates at the maxima of the peaks. Solid lines represent the Arrhenius lines according to the joint fits. Dashed lines indicate the position of  $\tau_{\text{DC}}^{-1}$ , i.e., estimated from  $\sigma_{\text{DC}}$ . (b) The same data points as in (a) but with  $\tau_{\text{DC}}^{-1}$  included as data points. The lines referring to  $\text{Li}_6\text{PS}_5\text{Cl}$  and  $\text{Li}_6\text{PS}_5\text{Br}$  have been shifted by a factor of +4 (+2) (on the log scale) to illustrate the kink seen in  $\tau_{\text{DC}}^{-1}(1/T)$  for  $\text{Li}_6\text{PS}_5\text{Cl}$ . It is absent for  $\text{Li}_6\text{PS}_5\text{Br}$ . Electrical relaxation rates  $\tau_p^{-1}$  from our  $\rho'(1/T)$  analyses have been included as well. The vertical arrow drawn with a dashed line indicates the large difference in jump rates seen for  $\text{Li}_6\text{PS}_5\text{I}$ . The arrows near the ordinate illustrate the change in pre-factors. See the text for further explanation.

**Table 6** Activation energies as deduced from the various methods applied here to investigate the ion dynamics in  $\text{Li}_6\text{PS}_5\text{X}$  by conductivity spectroscopy and NMR relaxometry

	$\text{Li}_6\text{PS}_5\text{Cl}$ (eV)	$\text{Li}_6\text{PS}_5\text{Br}$ (eV)	$\text{Li}_6\text{PS}_5\text{I}$ (eV)
$\sigma_{\text{DC}}$	0.396(3)	0.296(2)	0.470(5)
$\rho'$ , high- $T$ flank <sup>a</sup>	0.321(3)	0.250(3)	0.347(7)
$\rho'$ , low- $T$ flank <sup>a</sup>	0.153(2)	0.115(9)	0.305(2)
$M''$	—	—	0.349(5)
$R_1$ , high- $T$ flank <sup>a</sup>	0.320(1)	0.213(1)	0.198(1)
$R_1$ , low- $T$ flank <sup>a</sup>	0.170(4)	0.102(4)	0.182(5)
$R_{1\rho}$ , high- $T$ flank <sup>a</sup>	0.248(9)	0.201(9)	0.137(3)
$R_{1\rho}$ , low- $T$ flank <sup>a</sup>	0.134(1)	0.083(1)	—
$R_1$ (global fit) <sup>b</sup>	0.273(5)	0.218(1)	—
	(0.165(8))	(0.105(4))	—
$R_{1\rho}$ (global fit) <sup>b</sup>	0.273(5)	0.218(1)	—
	(0.129(7))	(0.081(4))	—

<sup>a</sup> The values referring either to the high- $T$  or to the low- $T$  flank were obtained by a line fit. <sup>b</sup> Results from the global fit analysis are obtained by linking  $E_a$  and  $\tau_0^{-1}$  of the individual relaxation rate peaks. Values in brackets refer to the low- $T$  flanks of the global fit.

In the case of  $^7\text{Li}$  NMR, which is primarily sensitive to the elementary jump processes between 24g and 48h, we see a slight increase in the pre-factor when going from  $X = \text{I}$  to  $X = \text{Cl}$  (see above). The change in  $\tau_0^{-1}$  is, however, small as compared to the drastic decrease in  $\sigma_{\text{DC}}T(1/T)$  seen for  $\text{Li}_6\text{PS}_5\text{I}$ . Hence, the increase in overall migration enthalpy for  $\text{Li}_6\text{PS}_5\text{I}$ , for which the intergate diffusion process is characterised by a high hopping barrier, turned out to be mainly responsible for its poor ionic conductivity. On shorter length scales, Li ion hopping in  $\text{Li}_6\text{PS}_5\text{I}$ , with its

ordered anion sublattice, is as fast as in  $\text{Li}_6\text{PS}_5\text{Br}$ . This result is in perfect agreement with the pioneering calculations by Rao and Adams as well as the in-depth study presented by De Klerk *et al.*<sup>50</sup> They already pointed out, as mentioned above, that for  $\text{Li}_6\text{PS}_5\text{I}$  the intergate jump processes are interrupted and fast localized motions with very low activation energies are present. By  $^7\text{Li}$  NMR relaxometry their observation is now fully supported. The calculations by Pecher *et al.* point in the same direction.<sup>40</sup> As an example, De Klerk *et al.* report an activation energy as low as 0.05 eV for the doublet jump process in  $\text{Li}_6\text{PS}_5\text{I}$ .<sup>50</sup>

Besides these peculiarities for  $\text{Li}_6\text{PS}_5\text{Cl}$  and  $\text{Li}_6\text{PS}_5\text{I}$ , the complex ion dynamics in Li-bearing argyrodites with anion disorder is reflected in the distribution of activation energies. Table 6 summarises the activation energies obtained by the different methods applied. Depending on the length-scale and time-scale to which the specific method is sensitive quite different activation energies can be probed. Such a result is typical for ionic conductors whose charge carriers are exposed to an irregularly shaped energy landscape that gives rise to highly correlated forward and backward motions or fast (local) dynamics on the angstrom length scale.

## 4 Summary and conclusion

We studied the Li ion dynamics in argyrodite-type  $\text{Li}_6\text{PS}_5\text{X}$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) by a wide range of complementary techniques with a special focus on conductivity spectroscopy and nuclear magnetic relaxation. The latter technique is able to probe short-range as





well as long-range bulk ion dynamics. The analysis of electric modulus data also helped us to shed light on the bulk ion dynamics. In all compounds, even in those where two different halogen atoms were used to replace a sulfur anion per formula unit, complex ion dynamics is found. Heterogeneous Li ion transport is traced back to the fact of an irregularly shaped potential landscape that the ions are exposed to during diffusion. The vacancy-rich Li sublattice offers a range of hopping barriers between the Li sites involved in the overall ionic transport. Depending on the method applied to study the hopping processes, Li ion translational motions on quite different time scales and lengths scales are probed. This circumstance results in activation energies ranging from 0.08 eV to values as high as 0.48 eV.

Anion disorder in  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{Cl}$ , as verified by X-ray powder diffraction measurements, boosts the ion dynamics as compared to the parent compound  $\text{Li}_7\text{PS}_6$ . The halogen anions are clearly distributed over the crystallographic sites 4a and 4d.  $\text{Li}_6\text{PS}_5\text{Br}$  reveals the lowest activation energies and the bulk ion conductivities follow a single Arrhenius line. Deviations from this behaviour are seen for  $\text{Li}_6\text{PS}_5\text{Cl}$  and  $\text{Li}_6\text{PS}_5\text{I}$ . For  $\text{Li}_6\text{PS}_5\text{Cl}$  an additional dynamic process shows up at higher  $T$ , which is also seen in  $^7\text{Li}$  spin-lock NMR spectroscopy. This process leads to a relatively high mean activation energy in  $\sigma_{\text{DC}}$  characterising the overall ion transport.

Most importantly, also for the poor ionic conductor  $\text{Li}_6\text{PS}_5\text{I}$  our NMR relaxation measurements reveal very fast Li ion dynamics on a local to medium-range length scale. Obviously, the ions have access to the same, rapid exchange processes as in  $\text{Li}_6\text{PS}_5\text{Br}$  but long-range transport is switched off. In the spirit of De Klerk and co-workers we think that the ordered anion sublattice, combined with the larger lattice constant, is responsible for this peculiarity. It leads to a heterogeneous potential landscape with low and high hopping barriers. High activation barriers seem to characterize the interstage jumps; these jump processes are, however, necessary to transport the ions over long distances.

## Conflicts of interest

There are no conflicts to declare.

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