With a Little Help from \(^{31}\text{P}\) NMR: The Complete Picture on Localized and Long-Range \(\text{Li}^+\) Diffusion in \(\text{Li}_6\text{PS}_5\text{I}\)

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**ABSTRACT:** \(\text{Li}_6\text{PS}_5\text{I}\) acts as a perfect model substance to study length scale-dependent diffusion parameters in an ordered matrix. It provides \(\text{Li}\)-rich cages which offer rapid but localized \(\text{Li}^+\) translational jump processes. As jumps between these cages are assumed to be much less frequent, long-range ion transport is sluggish, resulting in ionic conductivities in the order of \(10^{-6}\) S cm\(^{-1}\) at room temperature. In contrast, the site disordered analogues \(\text{Li}_6\text{PS}_5\text{X}\) (X = Br, Cl) are known as fast ion conductors because structural disorder facilities intercage dynamics. As yet, the two extremely distinct jump processes in \(\text{Li}_6\text{PS}_5\text{I}\) have not been visualized separately. Here, we used a combination of \(^{31}\text{P}\) and \(^{7}\text{Li}\) NMR relaxation measurements to probe this bimodal dynamic behavior, that is, ultrafast *intracage* \(\text{Li}^+\) hopping and the much slower \(\text{Li}^+\) *intercage* exchange process. While the first is to be characterized by an activation energy of ca. 0.2 eV as directly measured by \(^{7}\text{Li}\) NMR, the latter is best observed by \(^{31}\text{P}\) NMR and follows the Arrhenius law determined by 0.44 eV. This activation energy perfectly agrees with that seen by direct current conductivity spectroscopy being sensitive to long-range ion transport for which the intercage jumps are the rate limiting step. Moreover, quantitative agreement in terms of diffusion coefficients is also observed. The solid-state diffusion coefficient \(D_s\) obtained from conductivity spectroscopy agrees very well with that from \(^{31}\text{P}\) NMR \((D_{\text{NMR}} \approx 4.6 \times 10^{-15}\) cm\(^2\) s\(^{-1}\)). \(D_{\text{NMR}}\) was directly extracted from the pronounced diffusion-controlled \(^{31}\text{P}\) NMR spin-lock spin–lattice relaxation peak appearing at 366 K.

### 1. INTRODUCTION

The search for powerful solid electrolytes that can be used in sustainable Li-ion and Na-ion energy storage systems has reached an unprecedented level.\(^*\) To identify and understand the origins behind fast ion transport in crystalline and amorphous solids, model substances are needed that allow the characterization of the distinct dynamic processes in detail, without any interfering effects from other diffusion processes taking place at the same time.

\(\text{Li}_6\text{PS}_5\text{I}\) belongs to the well-known group of argyrodite-type solid electrolytes\(^6–21\) that is assumed to host two dynamically distinct \(\text{Li}^+\) diffusion processes.\(^22,23\) In the anion-ordered \(\text{Li}_6\text{PS}_5\text{I}\), whose structure is depicted in **Figure 1**, \(\text{Li}\)-rich cages are present that provide the opportunity of rapid localized \(\text{Li}^+\) hopping processes.\(^22,23\) Intercage jumps are, however, assumed to be much less frequent.\(^22,23\) This assumption was used to explain the poor long-range ion transport properties of \(\text{Li}_6\text{PS}_5\text{I}\) that shows ionic conductivities in the order of only \(10^{-6}\) S cm\(^{-1}\) at room temperature.\(^22\) In contrast, site disorder, involving \(\text{X}^–(\text{X} = \text{S}^2–, \text{Se}^2–, \text{and Li}^+\), as is present in \(\text{Li}_6\text{PS}_5\text{X}\) (X = Br and Cl),\(^12\) switches on rapid intercage ion dynamics, turning these analogues into extremely fast ion conductors\(^9,11,14–17,19–22\) with specific conductivity values reaching \(3.8 \times 10^{-3}\) S cm\(^{-1}\) (\(\text{Li}_6\text{PS}_5\text{Br}\)) and \(2.2 \times 10^{-3}\) S cm\(^{-1}\) (\(\text{Li}_6\text{PS}_5\text{Cl}\)).\(^22\) As yet, the bimodal diffusion behavior suggested for \(\text{Li}_6\text{PS}_5\text{I}\) has, however, not been experimentally verified or even quantified with methods that are able to directly probe \(\text{Li}^+\) at the atomic scale. Here, we used a combination of \(^{7}\text{Li}\) and \(^{31}\text{P}\) nuclear magnetic resonance (NMR) spin–lattice relaxation techniques\(^14–28\) to conclusively characterize this unique dynamic property in \(\text{Li}_6\text{PS}_5\text{I}\).

It turned out that, also based on earlier experiments in our group,\(^22\) the localized intracage dynamic process is to be characterized by an activation energy of only 0.2 eV. Jump rates at ambient conditions reach values in the order of \(10^9\) s\(^{-1}\). This process is best seen by using \(^{7}\text{Li}\) NMR spectroscopy.\(^22,29\) Spin-lock \(^{31}\text{P}\) NMR relaxometry is, however, highly suitable to detect much slower \(\text{Li}^+\) diffusion process.\(^17,18,24\) Thereby, the \(^{31}\text{P}\) nuclei indirectly sense the \(\text{Li}\) spin fluctuations caused by the \(\text{Li}\) translational motions. Thus, we use an immobile nucleus
from the framework to probe the irregular movement of the mobile Li+ ions, which is, for example, similar to that reported in the study of Kim et al., who studied Li ion dynamics in borate glasses via both 7Li and 11B NMR relaxation measurements. Here, we were able to quantify the dynamic parameters from diffusion-induced 31P NMR measurements and to compare them with results from direct current (dc) conductivity spectroscopy being sensitive to macroscopic, long-range ion transport. While classical laboratory-frame NMR spin–lattice relaxation measurements are sensitive to dynamic processes with 1/τNMR rates in the MHz to GHz range, spin-lock NMR is sensitive to atomic motions with jump rates 1/τlock in the kHz range.

In earlier studies of our group, we were able to identify two types of motional processes in Li6PS5I, viz., the fast Li+ intracage process and rotational dynamics of the polyanions. However, the origin of a shallow diffusion-induced peak in spin-lock 7Li NMR appearing at 360 K remained unclear. With the help of spin-lock 31P NMR, we are now able to explain this feature. The current study provides a full picture of Li+ ion diffusion in the high-temperature modification of Li6PS5I and reveals three different types of motional processes. Spin-lock 31P NMR is able to characterize the important intercage Li+ exchange process that is directly related to long-range ion transport in Li6PS5I. In general, the provision of such information is highly desirable if we want to understand length-scale dependent dynamic properties of even more complex materials that are currently being developed for their use as electrolytes in all-solid-state battery systems.

2. METHODS

For the present study, we used a Li6PS5I sample of the same synthesis batch that has been investigated by our group recently. Thus, we refer to the literature for details on sample preparation and structural characterization.

The procedures to record variable-temperature 7Li (spin–quantum number I = 3/2) and 31P (I = 1/2) NMR (spin-lock) spin–lattice relaxation rates are identical to those described elsewhere by our group. We used a Bruker 300 MHz NMR spectrometer in combination with a Bruker broadband probe to record the laboratory-frame rates 1/T1 with the saturation recovery pulse sequence at magnetic fields B0 corresponding to Larmor frequencies ω0/2π in the MHz range. In this sequence, a train of 10 π/2 pulses destroys any longitudinal magnetization M0. The diffusion-induced recovery of M0 is immediately recorded as a function of waiting (or delay) time t and temperature T with a single π/2 detection pulse. Here, we analyzed the area under the free induction decays (FIDs) to construct M0(t, T). The transients M0(t) can be very well parameterized with stretched exponentials to extract the rate 1/T1 at Larmor frequencies of 116 MHz (7Li) and 121 MHz (31P). Here, the 31P NMR curves follow simple exponential behavior. Usually 4 to 16 scans (quadrature detection) were accumulated to obtain a single FID per waiting time; a complete curve M0(t), containing 1/T1(T), consisted of 16 to 30 data points.

The corresponding NMR relaxation rates in the rotating (ρ) frame of reference 1/T1ρ were acquired at a spin-lock frequency of 20 kHz by taking advantage of the two-pulse spin-lock technique. An initial π/2 pulse flips the longitudinal magnetization into the (xy) plane; immediately after that, the locking pulse with varying duration tlock fixes the transversal magnetization M0(ρ, tlock) (ρ in Fig. 2a), containing 1/τlock, with values in the kHz range results in magnetization transients following a stretched exponential decay from which the diffusion-induced rate 1/T1ρ was extracted. The corresponding NMR relaxation rates in the rotating (ρ) frame of reference 1/T1ρ were acquired at a spin-lock frequency of 20 kHz by taking advantage of the two-pulse spin-lock technique. An initial π/2 pulse flips the longitudinal magnetization into the (xy) plane; immediately after that, the locking pulse with varying duration tlock fixes the transversal magnetization M0(ρ, tlock) (ρ in Fig. 2a), containing 1/τlock, with values in the kHz range results in magnetization transients following a stretched exponential decay from which the diffusion-induced rate 1/T1ρ was extracted. The corresponding NMR relaxation rates in the rotating (ρ) frame of reference 1/T1ρ were acquired at a spin-lock frequency of 20 kHz by taking advantage of the two-pulse spin-lock technique. An initial π/2 pulse flips the longitudinal magnetization into the (xy) plane; immediately after that, the locking pulse with varying duration tlock fixes the transversal magnetization M0(ρ, tlock) (ρ in Fig. 2a), containing 1/τlock, with values in the kHz range results in magnetization transients following a stretched exponential decay from which the diffusion-induced rate 1/T1ρ was extracted.

3. RESULTS AND DISCUSSION

Figure 2 gives an overview of the 7Li and 31P (spin-lock) NMR spin–lattice rates of polycrystalline Li6PS5I. In Figure 2a, the 7Li NMR rates 1/T1 and 1/T1ρ of Li6PS5I are shown using an Arrhenius representation. As discussed earlier, 1/T1 passes through a prominent diffusion-induced rate peak (labeled peak A) that is located at T ≈ 330 K. At this temperature, the mean jump rate 1/τNMR is in the order of the angular Larmor frequency ω0 (ω0τNMR ≈ 1), which is given by 2πω0 = 7.3 × 107 s−1, thus reaching values in the GHz regime. Such fast exchange processes would result in ion conductivities in the mS range at 329 K. As this is not the case for Li6PS5I, the NMR peak was interpreted to mirror ultrafast but localized intracage jump processes. These are thermally activated by 0.18–0.20 eV, as it can be deduced from analyzing the flanks

![Figure 1](https://doi.org/10.1021/acs.jpcc.1c06242)

**Figure 1.** (a) Crystal structure of argyrodite-type, anion-ordered Li6PS5I. The I− anions occupy the 4a sites, while the S2− anions reside on the 4d and the 16e sites forming an ordered anion sub-lattice; for the sake of clarity, not all the S2− anions are shown. Li+ ions are arranged such in the iodide compound that they build cages consisting of 48h-24g-48h′ triplets, also called T5a sites. These sites are only partially occupied by Li ions, as illustrated, enabling them to quickly jump within the cages, that is, within the triplets and between them. Jumps within the pocket-like triplets are to be considered as spatially highly confined. (b) Long-range Li+ ion dynamics in Li6PS5I is either possible via direct jumps between the cages or via interstitial sites. Interstitial sites are illustrated as green spheres (labelled T4 and T2 corresponding to the Wyckoff sites 16e (dark green) and 48h (light green)).
of the $1/T_1$ NMR peak. The corresponding spin-lock NMR peak ($A'$) is expected to be seen at much lower temperatures. Indeed, below 200 K, the rates $1/T_{1\rho}$ reveal the high-temperature flank of this peak. Extrapolating this flank toward higher temperatures shows that it will coincide with the corresponding one of the $1/T_1$ peak (0.2 eV, see the dashed line in Figure 2a). The maximum of the $7^\text{Li}$ spin-lock NMR $1/T_1\rho$ peak is expected at ca. 165 K, which is in agreement with the curvature of the dashed line indicated in Figure 2a. However, because of the phase transformation Li$_6$PS$_5$I is undergoing, an abrupt change of the $7^\text{Li}$ NMR rates $1/T_{1\rho}(1/T)$ peak is observed at temperatures lower than 170 K. Below 170 K, the $1/T_{1\rho}$ rates mirror the low-temperature flank (negative slope) of a diffusion-induced peak that reveals much lower Li$^+$ diffusivity in the low-$T$ modification of Li$_6$PS$_5$I.

Most interestingly, the $7^\text{Li}$ NMR rates $1/T_{1\rho}$ of Li$_6$PS$_5$I pass through a shallow maximum at 360 K (peak B), whose origin is still unclear. As we will show below, this peak reflects the rate-limiting Li$^+$ hopping processes connecting the Li-rich cages enabling long-range ion transport in Li$_6$PS$_5$I.

Turning to $31^\text{P}$ NMR spin–lattice relaxation (see Figure 2b), we recognize that the rate $1/T_1$ passes through two different maxima located at approximately 220 K (peak C) and 344 K (again labeled as peak A). As we have shown earlier, peak C, most likely, reflects rotational motions of the polyanions as it is unique to $31^\text{P}$ and is not seen in $7^\text{Li}$ NMR. On the other hand, the $31^\text{P}$ NMR peak located at 330 K (peak A) mirrors the fast Li$^+$ translational intra-cage jumps that also dominate the $1/T_1\rho$ NMR response (see peak A in Figure 2a).

A comparison of the two peaks detected by $7^\text{Li}$ and $31^\text{P}$ NMR is given in Figure 2c. Note that the $7^\text{Li}$ and $31^\text{P}$ rates were recorded at almost the same Larmor frequencies (116 MHz vs 121 MHz), which is important for such a direct comparison, because to fulfill the condition $\omega_0T_{\text{NMR}} \approx 1$ (see above), the
position of the peaks will shift with increasing \( \omega_L \) toward higher temperatures. Here, the \(^{31}\text{P} \) nuclei are used as spies to indirectly sense the \((^{31}\text{P}-^{7}\text{Li})\) spin fluctuations in their direct neighborhood, which are produced by \( ^{7}\text{Li} \) translational motions. Importantly, the \(^{31}\text{P} \) magic angle spinning NMR spectrum\(^ {22} \) shows only a single P-site for which the relaxation occurs.

It has to be mentioned that the two nuclei \((^{7}\text{Li}, I = 3/2; ^{31}\text{P}, I = 1/2)\) are subjected to different interactions; whereas \(^{7}\text{Li} \) senses electric quadrupolar and \((^{7}\text{Li}-^{7}\text{Li}, \text{Li}^{\bullet}-\text{P})\) magnetic dipolar interactions, \(^{31}\text{P} \) NMR relaxation is mainly influenced by the heteronuclear, dipolar \((\text{P}-\text{Li})\) interactions. Naturally, these differences result in distinct motional correlation functions seen by the NMR active spins. Estimating the effect on motional correlation times \( \tau_c \), show that the differences in \( \tau_c \) do not exceed a factor of five, which hardly affects the position of the corresponding rate peaks.

In the present case, \(^{31}\text{P} \) \( 1/T_1 \) NMR is able to probe different motional processes, \( viz., \) \( i \) the fast translational \textit{intracage} dynamics \((\text{seen by} \ ^{7}\text{Li} \ {\ \text{and} \ ^{31}\text{P} \ NMR}) \) and \( ii \) the even faster rotational motions of the \( \text{PS}_4^{3\text{−}} \) polyanions \((\text{seen by} ^{31}\text{P} \ NMR)\). The two corresponding peaks in spin-lock \( 1/T_{1p} \) \(^{31}\text{P} \) NMR measurements are expected to appear at much lower temperatures, that is, lower than \( 160 \text{ K} \) to satisfy the condition \( \omega_{1,T_{1\text{p}}} \approx 1 \). Here, when coming from high temperatures, we do only see the beginning of a mutual high-temperature flank of these peaks that is activated by approximately \( 0.08 \text{ eV} \); see Figure 2b.

Most importantly, the spin-lock \(^{31}\text{P} \) NMR rates \( 1/T_{1\text{p}} \) measured in the rotating frame of reference (Figure 2b), reveal a prominent diffusion-induced peak at \( 360 \text{ K} \), which is exactly the temperature at which the shallow peak in spin-lock \(^{7}\text{Li} \) \( 1/T_{1p} \) NMR appears \((360 \text{ K})\); a comparison is shown in Figure 2d. This \(^{31}\text{P} \) NMR peak reflects spin fluctuations pointing to much slower motional processes as those seen by \( 1/T_1 \). The corresponding \( 1/T_1 \) \(^{31}\text{P} \) NMR peak is expected to appear at a higher \( T_1 \); indeed, the \(^{31}\text{P} \) NMR rates \( 1/T_1 \) reveal the beginning of a new low-\( T \) flank at temperatures higher than \( 415 \text{ K} \). In contrast to the \(^{7}\text{Li} \) \( 1/T_{1p} \) NMR peak that is seen at \( 360 \text{ K} \), the spin-lock \(^{31}\text{P} \) NMR rates are not affected by the laboratory-frame \(^{31}\text{P} \) \( 1/T_1 \) NMR rates. The rates \( 1/T_{1p} \) \( 1/T_1 \) of the \(^{31}\text{P} \) spins differ by more than \( 2 \) orders of magnitude (Figure 2d), which is not the case for \(^{7}\text{Li}; \) see Figure 2a. Hence, the high-temperature flank of the shallow peak seen in \( 1/T_{1p} \) \(^{7}\text{Li} \) NMR underestimates the activation energy on the high-\( T \) side of this peak. This comparison reveals the advantages of using the \(^{31}\text{P} \) spin to indirectly sense the \( ^{7}\text{Li} \) dynamics.

In the following, we will analyze the properties and origins of the spin-lock \( 1/T_{1p}(1/T) \) \(^{31}\text{P} \) NMR peak in more detail. First of all, it turned out to be asymmetric in shape. The solid line shows a parameterization of the spin-lock NMR response with a spectral density function \( J \) commonly used to describe correlated 3D motion in solids.\(^ {28} \) \( J^{3\text{D}} \) relies on the well-known Lorentzian-shaped function \( \rho_{J_{\text{FF}}} \) introduced by Bloembergen, Purcell, and Pound\(^ {34,35} \) and is, in general, given by \( J^{3\text{D}}(\omega_0, T) \approx \tau_c/[1 + (\omega_0(1)\tau_c)] \).\(^ {23} \) For \( \beta = 2 \), this function is a special case of the more general Cole–Cole distribution function \( J_{\text{CC}} \) that also contains a width parameter \( \delta \) to take into account a distribution of Debye spectral densities.\(^ {36} \) For \( \delta = 1 \), the Cole–Cole spectral density function \( J_{\text{CC}} \) yields \( J_{\text{FF}} = (J^{3\text{D}}) \) with \( \beta = 2 \). In general, the motional correlation rate \( 1/\tau_c \) is expected to be identical with the jump rate \( 1/T_{1\text{NMR}} \) within a factor of two. The asymmetry parameter \( \beta \) describes the deviation from symmetric behavior of the peak.\(^ {29,37,38} \) A symmetric peak is expected for uncorrelated 3D motion \((\beta = 2)\) which produces a quadratic dependence of \( 1/T_1 \) on the Larmor frequency \( \omega_0/\pi \) on the low temperature side \((\omega_0\tau_c \gg 1)\).\(^ {29,37} \) Here, the peak is characterized by \( \beta = 1.65 \) (see Table 1). Such asymmetric peaks are described by a high-\( T \) \((E_a, \text{high} \equiv E_{a,NMR}) \) and a low-\( T \) activation energy linked to each other via \( E_{a,\text{low}} = (\beta - 1)E_a, \text{high} \), whereby \( E_{a,\text{low}} \) is affected by motional correlation effects.\(^ {28} \) For \( 1/\tau_c, \) Arrhenius behavior is assumed, \( 1/\tau_c = 1/\tau_c^0 \exp(-E_{a,NMR}/k_BT) \), where \( k_B \) denotes Boltzmann’s constant. \( \beta \) values smaller than 2 might also be interpreted in terms of a distribution of relaxation times. \( \beta \) measurement analysis could be beyond the scope of the present study.

Coming back to the spin-lock \(^{31}\text{P} \) NMR peak of \( \text{Li}_6\text{PS}_5\text{I} \) (peak B in Figure 2b), two important properties help us to identify its origin. First, the corresponding activation energy \( E_{a,NMR} \), of 0.44(4) eV, corresponding to the high-\( T \) flank \((\omega_0\tau_c \ll 1)\), perfectly agrees with that obtained by dc conductivity spectroscopy \((E_a = 0.47 \text{ eV})\). It is, as probed by dc conductivity, sensitive to long-range ion dynamics because many jumps are probed during one Larmor precession. Note that the periodic time of one spin precession is defined by the angular locking frequency \( \omega_L \) that is, in the high temperature limit of a given spin-lock NMR peak, we are dealing with the situation where \( 1/\tau_c \approx \omega_L = (20 \text{ kHz} \times 2\pi = 1.25 \times 10^5 \text{ s}^{-1}) \). Because of the perfect agreement seen in activation energies \((E_{a,NMR} = E_a)\), we interpret the \(^{31}\text{P} \) spin-lock \( 1/T_{1p} \) NMR peak (labeled B in Figure 2b) as that directly mirroring the slow \( \text{Li}^+ \) exchange processes between the \( \text{Li}-\text{rich} \) cages in poorly conducting \( \text{Li}_6\text{PS}_5\text{I} \).

Further evidence of this assignment is provided by quantitatively comparing the diffusion coefficients obtained from dc conductivity measurements and the \(^{31}\text{P} \) spin-lock NMR data. If we use the Einstein–Smoluchowski equation,\(^ {27} \) \( D_{\text{NMR}} = a^2/(6\tau_{1\text{NMR}})^{1.5} \) to convert \( 1/T_{1\text{NMR}} \) estimated from the peak maximum appearing at \( 366 \text{ K} \) into a diffusion coefficient, we obtain \( D_{\text{NMR}} = 4.56 \times 10^{-15} \text{ m}^2 \text{ s}^{-1} \). For \( a = 3.3 \text{ Å} \), \( D_{\text{NMR}} \) corresponds, according to the Nernst–Einstein equation, to an
ionic conductivity of 5.4 × 10−6 S cm−1. Note that the Nernst–Einstein equation is, strictly speaking, only valid for diluted, non-interacting species; here, it serves as a tool to estimate the ionic conductivity. For comparison, the independently measured dc conductivity at 373 K is 5 × 10−6 S cm−1; at 353 K, it turned out to be 2 × 10−6 S cm−1.22,33 These values are in very good agreement with the one probed by diffusion-induced 1/T1 ρ31P NMR spin–lattice relaxation.

In conclusion, while 7Li NMR is sensitive to the fast intercage ion dynamics, which are also indirectly seen by the 31P probes, with the help of spin-lock 31P NMR, it is possible to selectively study a much slower translational Li+ hopping process. We attribute this process to the much less frequent jumps between the Li-rich cages in crystalline Li6PS5I. Table 1 briefly summarizes our findings from both 7Li and 31P NMR.

Quite recently, we have seen that the introduction of the structural site disorder, by means of high-energy ball milling, leads to an increase of the direct current ion conductivity 7σdc, of Li6PS5I by 2 orders of magnitude.31 This effect has not only been seen by dc conductivity measurements but is also present in electric modulus spectroscopy. Here, the position of the corresponding spin-lock 31P NMR 1/T1 ρ rates of this sample, which has been milled for 120 min in a planetary mill, are shown in the Arrhenius plot of Figure 2d as a dashed line. In agreement with the enhancement of long-range Li+ ion transport, we also recognize that the 31P NMR spin-lock peak, which is mirroring intercage ion dynamics being crucial for long-range ion transport, slightly shifts toward lower temperatures (347 K). However, this slight shift cannot fully explain the increase seen in 7σdc by factor of 100. As it has been revealed by 7Li spin-lock NMR, additional Li+ intercage processes, not necessarily seen by 31P NMR, became activated in disordered nano-Li6PS5I.31 As shown in the literature, the 7Li NMR 1/T1 ρ rates of the nanostructured sample pass through a broad peak located at ca. 265 K,31 which might reflect the source of rapid Li+ movements explaining the increase seen in nano-Li6PS5I.

Apart from this possible explanation provided by 7Li NMR, the current spin-lock 31P NMR peak of nano-Li6PS5I indicated in Figure 2d is to be characterized by an activation energy of 0.32 eV, which is by 0.12 eV lower than that of unmilled Li6PS5I. The same decrease in activation energy is also seen on the low-T flanks of the two corresponding peaks (Figure 2d); for unmilled Li6PS5I, the low-T flank is given by a slope resulting in 0.29 eV also see Table 1, while for nano-Li6PS5I, a value of only 0.18 eV is found, see Figure 2d. This comparison points to a flattening of the energy landscape in nanocrystalline Li6PS5I. At the same time it also indicates a larger distribution of relaxation times in materials with disordered structure as it is the case for nano-Li6PS5I. 7Li and 31P NMR data on nanocrystalline Li6PS5I and Li6PS5Cl are not yet available. As these compounds, particularly the Br one, are to be characterized by extensive site disorder12 resulting in very high conductivities, we do not expect that ball milling has such a strong effect on overall ion transport as it is seen for the poorly conducting and site-ordered Li6PS5I compound.

4. CONCLUSIONS

The combination of 7Li and 31P NMR spin–lattice relaxation measurements helped us in revealing two quite different motional processes in crystalline Li6PS5I. Whereas the ultrafast Li intracage diffusion process is best seen by 7Li NMR, the much less frequent hopping processes connecting the Li cages is revealed by 31P spin-lock NMR spin–lattice relaxation measurements carried out in the so-called rotating frame of reference. This method allows the detection of motional processes with correlation rates in the kHz regime. Here, the 31P nuclei do indirectly sense the Li+ exchange processes that are responsible for long-range ion transport in Li6PS5I. The activation energy associated with this process turned out to be 0.44 eV. It was extracted from a high-temperature flank of the 1/T1 ρ(1/T) 31P spin-lock NMR rate peak. This value is in excellent agreement with that probed by macroscopic dc conductivity measurements (0.46 eV). Moreover, the self-diffusion coefficient determined by NMR at 366 K (D31P = 4.56 × 10−15 m2 s−1) does also agree very well with that dc conductivity spectroscopy is pointing at. Hence, 31P NMR turned out to be a complementary instrument, working at atomic scale, to fully characterize Li+ ion dynamics in thiophosphates. Results from complementary methods being sensitive to ion dynamics on different length scales are needed to entirely understand the complex dynamic processes in solid electrolytes. Considering the large family of lithium-ion conducting thiophosphates, we expect that 31P NMR will be highly useful to identify and characterize even more diffusion processes in this class of materials.

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Notes

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