Structural Disorder in Li$_6$PS$_5$I Speeds $^7$Li Nuclear Spin Recovery and Slows Down $^{31}$P Relaxation—Implications for Translational and Rotational Jumps as Seen by Nuclear Magnetic Resonance

M. Brinek, C. Hiebl, K. Hogrefe, I. Hanghofer, and H. M. R. Wilkening*

ABSTRACT: Lithium-thiophosphates have attracted great attention as they offer a rich playground to develop tailor-made solid electrolytes for clean energy storage systems. Here, we used poorly conducting Li$_6$PS$_5$I, which can be converted into a fast ion conductor by high-energy ball-milling to understand the fundamental guidelines that enable the Li$^+$ ions to quickly diffuse through a polarizable but distorted matrix. In stark contrast to well-crystalline Li$_6$PS$_5$I ($10^{-6}$ S cm$^{-1}$), the ionic conductivity of its defect-rich nanostructured analog touches almost the mS cm$^{-1}$ regime. Most likely, this immense enhancement originates from site disorder and polyhedral distortions introduced during mechanical treatment. We used the spin probes $^7$Li and $^{31}$P to monitor nuclear spin relaxation that is directly induced by Li$^+$ translational and/or PS$_4^{3-}$ rotational motions. Compared to the ordered form, $^7$Li spin–lattice relaxation (SLR) in nano-Li$_6$PS$_5$I reveals an additional ultrafast process that is governed by activation energy as low as 160 meV. Presumably, this new relaxation peak, "rotational jumps as seen by nuclear magnetic resonance"

INTRODUCTION

The enigmatic interplay between cation translational processes and rotational dynamics of complex anions$^{1-3}$ propelled the (re-)investigation of a range of Li-containing and Na-bearing thiophosphates.$^{1-7}$ The interest in fast ionic conductors$^8$ is spurred by the demand to develop high-performance energy storage systems relying on ceramic electrolytes.$^9$ Early examples for which the so-called "paddlewheel"$^{11,13}$ (or "cogwheel" or "revolving door")$^{10}$ mechanism is used to describe the cation–anion coupled transport, include the rotator phases Li$_2$SO$_4$,$^{1,11,14}$ LiMSO$_4$ ($M = Na$ and Ag)$^{3,15,16}$ Na$_2$P$_2$O$_7$,$^{1,14}$ and several borohydrides$^{17-21}$ and a range of closo-boranes$^{22-28}$ including the dynamics of cluster ions in Li$_2$S(BF$_4$)$_{3.5}$Cl$_{0.5}$ and Na$_2$OBH$_4$. As is impressively seen for the low-T modification orthorhombic LiBH$_4$, $^7$Li and $^{11}$B (and even $^1$H) nuclear magnetic resonance (NMR) is suited to directly probe local BH$_4^{-}$ rotational motions in the borohydride.$^{32-35}$

In its narrower sense, the paddlewheel mechanism$^{1,8,36}$ explains rapid cation translational dynamics by opening (or even closing) low-energy passageways through rotational (or librational) jumps of the polyanions that form the polarizable matrix of the electrolyte.$^1$ The cog-wheel mechanism requires significant dynamic coupling of neighboring anions, whereas the revolving door mechanism suggests that the anion reacts with an evasive motion to let the cation pass by.$^1$ Hence, it is still unclear which of the teammates act as the driving force.$^7$ Also, uncoupled fast rotational motions have been proposed to increase cation mobility through the generation of Coulombic fluctuations to affect the cation attempt frequencies.$^1$ The validity of such mechanisms has also been questioned in the past as the larger free transport volume for the rotational phases might play a role too.$^3,10$ Conversely, an increase in lattice volume, e.g., also by the introduction of larger lattice units, will facilitate anion rotation.

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From an experimental point of view, it is striking that the onset of rotational disorder seen in the high-temperature modifications of the sulfate or phosphate compounds is accompanied by an increase in cation diffusivity and a decrease in activation energy.\textsuperscript{1,10} Such a relationship, which may be regarded as a design tool to develop tailor-made, fast Li\textsuperscript+ ion conductors, has also been proposed by Adams and Rao\textsuperscript{37} to explain the overall dynamic situation in the famous ion conductor Li\textsubscript{10}GeP\textsubscript{2}S\textsubscript{11}.\textsuperscript{38} Quite recently, Nazar and coworkers have used the paddlewheel concept to explain enhanced Na\textsuperscript+ ion transport in Na\textsubscript{13}Sn\textsubscript{3}P\textsubscript{12} and provided supporting evidence for this cooperative interplay in β-Li\textsubscript{2}PS\textsubscript{4} as well as its Si-substituted analog Li\textsubscript{12}Si\textsubscript{2}S\textsubscript{3}P\textsubscript{3}S\textsubscript{4}.\textsuperscript{4,5,39} As the latter materials are expected to play decisive roles in all-solid-state batteries equipped with polycrystalline electrolytes or glassy compounds,\textsuperscript{9,40,41} a deeper understanding of the dynamic processes from an atomic-scale point of view is desirable. Quite recently, Smith and Siegel have used ab initio molecular dynamics simulations to characterize translational-rotational coupling in glassy 25Li\textsubscript{2}S-75P\textsubscript{2}S\textsubscript{5}.\textsuperscript{4} Their recent study\textsuperscript{9} and the timeless report of Jansen\textsuperscript{42} include precise and very helpful introductions into the topic, we recommend reading.

In our own group, we interpreted the low-temperature \textsuperscript{31}P NMR response in coarse-grained Li\textsubscript{6}PS\textsubscript{5}I as a signature of fast PS\textsubscript{4}\textsuperscript{3−} rotational jump processes.\textsuperscript{7} In contrast to site-disordered Li\textsubscript{6}PS\textsubscript{5}Br and Li\textsubscript{6}PS\textsubscript{5}Cl in the iodine compound with its expanded volume and ordered sublattices,\textsuperscript{42,43} containing also polarizable I anions, the PS\textsubscript{4}\textsuperscript{3−} units seem to be able to freely perform rotational (and librational) dynamics. At least for Li\textsubscript{6}PS\textsubscript{5}I, this uncoupled rotational motion, even if generating periodically fluctuating electric potentials at the cation sites,\textsuperscript{4} does not favor long-range Li\textsuperscript+ transport.\textsuperscript{46} Interestingly, site disorder and lattice contraction clearly disturb the effectiveness of the underlying \textsuperscript{31}P NMR spin−lattice relaxation processes and lead to a shift in the corresponding rate peaks toward higher temperatures when going from Li\textsubscript{6}PS\textsubscript{5}I to Li\textsubscript{6}PS\textsubscript{5}X (X = Br and Cl).\textsuperscript{7} To underscore our hypothesis that structural disorder hampers rotational motions in Li\textsubscript{6}PS\textsubscript{5}X, we used Li\textsubscript{6}PS\textsubscript{5}I as a model substance\textsuperscript{46} and introduced (site) disorder by soft high-energy ball-milling.\textsuperscript{47} Soft milling takes advantage of a low sample-to-ball ratio in conjunction with low rotational speeds. This approach does not change the overall chemical composition of the nanocrystalline sample but leads to anion, and presumably, also to extensive cation disorder, polyhedral distortions, and strain. These structural changes were revealed by the broadening of the corresponding X-ray reflections and broadened \textsuperscript{31}P (magic angle spinning, MAS) NMR spectra.\textsuperscript{47} The dynamic features of the coarse-grained Li\textsubscript{6}PS\textsubscript{5}I were investigated in detail in three earlier studies\textsuperscript{46,47,48} by our group; the present study is based on these results.

Here, we used \textsuperscript{31}P NMR spin−lattice relaxation experiments to describe any possible influence of structural disorder on \textsuperscript{31}P nuclear spin recovery in nanostructured Li\textsubscript{6}PS\textsubscript{5}I. The results were compared with those obtained for the \textsuperscript{7}Li nucleus recently.\textsuperscript{46,47} In general, the spin recovery is directly driven by the thermally activated jump processes taking place in the crystal structure of the thiophosphate. Most importantly, while Li\textsuperscript+ self-diffusivity is enhanced in disordered Li\textsubscript{6}PS\textsubscript{5}I,\textsuperscript{48} the effective source governing \textsuperscript{31}P nuclear spin relaxation in ordered Li\textsubscript{6}PS\textsubscript{5}I is indeed noticeably weakened in the ball-milled material. In nano-Li\textsubscript{6}PS\textsubscript{5}I, the distinct \textsuperscript{31}P NMR spin−lattice relaxation peak is no longer seen as a separate signal; its disappearance indicates that the disorder has a drastic influence on the temporal \textsuperscript{31}P−\textsuperscript{31}P(\textsuperscript{7}Li) magnetic interactions controlling nuclear spin recovery.

### MATERIALS AND METHODS

The preparation of Li\textsubscript{6}PS\textsubscript{5}I is described elsewhere;\textsuperscript{46} for the present study, we used the material of the same synthesis batch that has been recently investigated by X-ray diffraction, \textsuperscript{31}P MAS NMR, and also by impedance measurements and NMR spectroscopy.\textsuperscript{46} To prepare nanocrystalline Li\textsubscript{6}PS\textsubscript{5}I, 0.5 g of the starting powder was added to ZrO\textsubscript{2} milling vials (45 mL) under an Ar atmosphere (H\textsubscript{2}O < 1 ppm, O\textsubscript{2} < 1 ppm). The milling jars were filled with 60 milling balls (5 mm in diameter). Nano-Li\textsubscript{6}PS\textsubscript{5}I was treated in a Premium line 7 planetary mill (Fritsch) that was operated at a rotation speed of 400 rpm.\textsuperscript{47} The milling time was set to 120 min. For NMR measurements, the powder was sealed in Duran ampoules.

The acquisition of \textsuperscript{7}Li (116 MHz Larmor frequency) and \textsuperscript{31}P (121 MHz) NMR spin−lattice relaxation rates (1/T\textsubscript{1}) was carried out using a Bruker 300-MHz NMR spectrometer; the procedures are identical to those described already elsewhere.\textsuperscript{46} We used the well-known saturation recovery sequence to monitor the recovery of longitudinal magnetization after a comb of closely spaced 90° perturbation pulses. The curves were parametrized with appropriate exponential functions to extract the rate 1/T\textsubscript{1} as a function of temperature, see the Supporting Information.

### RESULTS AND DISCUSSION

Li\textsubscript{6}PS\textsubscript{5}I crystallizes with cubic symmetry (space group F\textit{4}3\textit{m}, see Figure 1a).\textsuperscript{42,46} The Li ions occupy various lattice sites within the structure forming Li-rich cages. While fast Li\textsuperscript+ exchange, with rates on the MHz rage, occurs within these cages for Li\textsubscript{6}PS\textsubscript{5}I, intercage jump processes are much less frequent, that is, reduced by 2–3 orders of magnitude.\textsuperscript{48,49} As these processes are important to guarantee long-range ionic transport, highly crystalline Li\textsubscript{6}PS\textsubscript{5}I turned out to be a poor ionic conductor with an ionic conductivity in the order of 10\textsuperscript{−6} S cm\textsuperscript{−1} at room temperature.\textsuperscript{46}

In contrast, the sibling compounds Li\textsubscript{6}PS\textsubscript{5}X (X = Br and Cl) benefit from both anion and cation site disorder resulting in ionic conductivities in the mS cm\textsuperscript{−1} range.\textsuperscript{46,49} Hence, besides other effects such as the influence of anion polarizability, anion site disorder, i.e., the occupation of 4d sites within the Li-rich cages by X\textsuperscript{−}, and, as has been shown quite recently,\textsuperscript{43} the partial filling of the originally empty Li\textsuperscript{+} sites (see the 48 h and 16e voids shown in Figure 1b) guarantee rapid Li\textsuperscript+ exchange. In addition to strain and polyhedra distortions generated, high-energy ball-milling is, thus, also expected to affect both the Γ/S\textsuperscript{5}− and Li\textsuperscript{+} site distribution in Li\textsubscript{6}PS\textsubscript{5}I. Indeed, as has been shown earlier, soft mechanical treatment can enhance ionic conductivity by several orders of magnitude.\textsuperscript{47,50} The sample milled for 120 min in a planetary mill shows an ionic conductivity almost reaching the mS cm\textsuperscript{−1} regime at ambient conditions.\textsuperscript{47}

To understand how mechanical treatment affects the various interactions of the \textsuperscript{7}Li (spin quantum number I = 3/2) and \textsuperscript{31}P (I = 1/2) spins, we recorded diffusion-induced 1/T\textsubscript{1} NMR rates as a function of the inverse temperature. The change of variable-temperature \textsuperscript{7}Li NMR lines, clearly pointing to faster Li\textsuperscript+ dynamics in nano-Li\textsubscript{6}PS\textsubscript{5}I, is discussed elsewhere.\textsuperscript{46} In Figure 2, the \textsuperscript{31}P (and \textsuperscript{7}Li) NMR 1/T\textsubscript{1} rates of unmilled
Li₆PS₅I are shown using an Arrhenius representation. In particular, the present paper focusses on the ³¹P NMR relaxation rates peaks (C) and (D) in Figure 2a and the corresponding one in Figure 2b. The values included correspond to the activation energies of either the low-T ($E_{a, \text{high}}$) and high-T flanks ($E_{a, \text{high}}$) of the peaks. The rates were extracted from the full magnetization transients shown in Figure S1. Here, we focus on data obtained for the cubic modification. As indicated in Figure 2, below 160 K the iodide transforms into an orthorhombic phase. Coming from low temperatures, the $^7$Li NMR rates pass into a well-defined relaxation rate peak, which was attributed to intra-cage $^7$Li jump processes.

We parameterized the peak with a modified Lorentzian-shaped spectral density function based on the relaxation model of Bloembergen, Purcell and Pound (BPP), see the Supporting Information and Table S1 for further information. The peak turned out to be rather symmetric which is expected for 3D uncorrelated $^7$Li motions.

The same relaxation source, that is, the $^{31}$P NMR relaxation due to the translational motion of the $^7$Li ions is indirectly sensed by the $^{31}$P nuclei; see peak (C) in Figure 2. In addition, the $^{31}$P NMR data unveil a second, more prominent peak at $T = 220$ K (D), which we assume is mainly driven by the homonuclear $^{31}$P–$^{31}$P dipole–dipole interactions. Presumably, this peak mirrors the fast $\text{PS}_4^{3−}$ rotational motions. Interestingly, both NMR peaks are governed by almost the same activation energy of $E_{a, \text{high}} = 0.20$ eV (Figure 2a). The fact that the $^{31}$P NMR peak (D) is not visible in $^7$Li NMR could have various reasons. Heteronuclear $^{31}$P–$^7$Li coupling, which is generally weaker than the homonuclear interactions, might be too low or the peak might be hidden in the low-temperature region shown as a dashed area in Figure 2a. In this region, the $^7$Li NMR rates are increasingly dominated by the nondiffusive relaxation processes such as the coupling of the $^7$Li spins to lattice vibrations or paramagnetic impurities.

$^7$Li and $^{31}$P NMR experiments on nano-Li₆PS₅I reveal two important differences compared to the unmilled sample. First, the prominent $^{31}$P NMR rate peak seen at 220 K is absent for the nanocrystalline sample. Hence, the relaxation source is either switched off or the original peak (D) is shifted toward higher temperatures as indicated by the curved arrow in Figure 2b. This shift means that the $\text{PS}_4^{3−}$ rotational motion is slowing down in nano-Li₆PS₅I. It also helps interpret the width of the $^{31}$P NMR peak of nano-Li₆PS₅I, which now turned out to be a superposition of several rate peaks. The $^{31}$P spins are sensing, including peaks (A) and (B) seen by $^7$Li NMR, see below. The activation energies calculated from the flanks of the $^{31}$P 1/$T_1(1/T)$ peak are regarded as apparent values that do not represent a single, distinct motional process.

Second, the original $^7$Li NMR response of coarse-grained, i.e., structurally ordered Li₆PS₅I, is split into two rate peaks labeled (A) and (B); these peaks appear at $T_{\text{max}} = 373$ K and 281 K, respectively. The shift is mainly due to a reduction in the activation energy from $E_{a, \text{high}} = 0.23$ eV to $E_{a, \text{high}} = 0.16$ eV. The corresponding prefactors $\tau_{0, \text{fl}}$ of the underlying Arrhenius relations, $\tau^{-1} = \tau_{0}^{-1} \exp(-E_{a, \text{high}}/k_B T)$, where $k_B$ denotes Boltzmann’s constant, turned out to be in the same order of magnitude ($10^{12}$ s⁻¹), see Table S1; they simply differ by a factor of two. It is a fundamental question whether this “attempt frequency” $\tau_{0, \text{fl}}$ is related to a vibrational frequency experienced by the mobile ion residing in a potential well between the hops, as suggested by the simple, classical diffusion theory. Phonon frequencies usually take values from 10¹² to 10¹⁴ s⁻¹; thus, the $\tau_{0, \text{fl}}$ values extracted from the NMR data lie at the lower limit of this range.

In the following, we discuss a possible scenario that explains the splitting of the $^7$Li NMR peak, thereby also pointing out the differences between results from NMR relaxation and conductivity spectroscopy. In line with earlier studies, we suppose that the original, almost symmetric BPP-type peak of microcrystalline Li₆PS₅I is mainly mirroring fast intracage jump processes involving the sites 24 $g$ and 48 $h$, whereas the $^7$Li NMR rates are increasingly dominated by the nondiffusive relaxation processes such as the coupling of the $^7$Li spins to lattice vibrations or paramagnetic impurities.
corresponds to conductivity $\sigma$ in the order of 1.6 mS cm$^{-1}$ at 329 K. This value is much too high to explain the experimental value of 10$^{-8}$ S cm$^{-1}$ observed at ambient conditions. Even if we take into account any deviations of the Haven ratio $H_\alpha$ and the correlation factor $f$ from 1, as might be expected for correlated diffusion, the difference between the solid-state diffusion coefficient $D_\alpha$ as extractable from conductivity measurements, and the self-diffusion coefficient $D = (H_\alpha/f)$ $D_\alpha$, as probed by NMR, is several orders of magnitude. Hence, we are confident that the symmetric rate peak seen at 329 K mirrors the rapid but spatially constrained ion dynamics that do not contribute to long-range ion transport that is probed by $\sigma$. This interpretation has also been underscored by $^7$Li NMR line width measurements performed recently. They reveal only a partial averaging of the Li–Li dipolar interactions as the important intercage jump processes needed to fully average homonuclear broadening take place much less frequently. However, full averaging is seen at higher temperatures.

For the ball-milled sample, this BPP-type peak that does not change much in shape ($E_{\text{high}} = 0.2$ eV, see Figure 2) shifts by approximately 50 K toward higher temperatures, see peak (A). Obviously, the disorder perturbs the Li$^+$ dynamics associated with the Li-rich cages, as pointed out recently. The Arrhenius laws belonging to the original and final peak differ in activation energy; however, the prefactors remain almost unaffected (Table S1). Hence, in contrast to macroscopic bulk electrical relaxation for which a significant change in prefactor was observed, $^7$Li NMR does not reveal a strong influence of the prefactor on this spatially restricted type of Li$^+$ motion.

Most importantly, a careful evaluation of the rates below 330 K reveals a second 1/$T_1(1/T)$ peak, labeled (B) in Figure 2b, that is located at $T_{\text{max}} = 281$ K. For comparison, the corresponding and prominent $^7$Li NMR rate peaks of the fast Li$^+$ ion conductor Li$_6$PS$_5$Br appear at almost the same temperature, $T_{\text{max}} = 286$ K. Hence, nanocrystalline Li$_6$PS$_5$I increasingly start to resemble the nuclear spin behavior of the site-disordered bromide analog. As mentioned above, neutron diffraction revealed that the Li$^+$ ions in Li$_6$PS$_5$Br do also populate the so far unexplored intercage voids (48 h sites) that are empty in structurally ordered Li$_6$PS$_5$I. The interplay between the anion disorder and Li$^+$ charge distribution seems to play the decisive role in explaining the facile Li$^+$ transport observed. This finding can also be used to explain the highly asymmetric shape of the 1/$T_1$ peak of Li$_6$PS$_5$Br being produced by a superposition of elementary jump processes including localized ones and those enabling long-range ion transport. Frustration effects introduced by the anion disorder and concerted motions have been considered to explain the overall dynamic situation in Li$_6$PS$_5$X ($X = \text{Br and Cl}$), which also seems to be triggered by the Li-Li Coulombic interactions.

Assuming that mechanical treatment forces the Li ions in Li$_6$PS$_5$I also to considerably occupy the additional sites outside the cages, we could interpret peak (B) as being controlled by...
fast intercage jump processes. Indeed, $^7$Li NMR linewidth measurements unveiled that almost fully hopping-controlled dipole–dipole averaging takes place in nano-Li$_6$PS$_5$I. In addition, to underpin this scenario from a quantitative point of view, we calculated the ionic conductivity expected for the $T_{\text{max}}$ of peak (B). Anticipating that 10% of the total number of ions have access to the fast intercage jump processes yields $\sigma_{\text{calc}} = 0.19$ mS cm$^{-1}$. This value is in good agreement with the experimental one ($\sigma_{\text{exp}} = 0.14$ mS cm$^{-1}$). Increasing the effective number density $N^2$ to 20% of the total number of available Li$^+$ ions per unit cell$^{41}$ increases $\sigma_{\text{calc}}$ to 0.37 mS cm$^{-1}$. Again, the deviations of $H$ and especially $f$ from 1 will further influence $\sigma_{\text{calc}}$. In the latter case, a correlation factor of $f \approx 0.4$ will immediately result in $\sigma_{\text{calc}} = \sigma_{\text{exp}}$ at 281 K. Altogether, we found evidence that the boost in ionic conductivity seen for Li$_6$PS$_5$I is represented by the $^7$Li NMR relaxation peak appearing at 281 K. Its presence helps explain the colossal increase in Li$^+$ dynamics when going from microcrystalline to nanocrystalline Li$_6$PS$_5$I. In addition, further dynamic processes were also probed by spin-lock $^7$Li NMR, recently. As an example, at locking frequencies in the kHz range, a spin-lock relaxation peak at a temperature as low as 190 K shows up for nano-Li$_6$PS$_5$I.\(^{47}\)

In contrast to conductivity spectroscopy being sensitive to long-range ion transport, the flanks of $^7$Li NMR relaxation rate peaks, unlike stimulated echo techniques,\(^{41,62}\) capture the barriers of the elementary steps of ion hopping. In addition, in the low-$T$ regime, the slopes of these flanks are influenced by correlation effects. Thus, the activation energies calculated from NMR, here ranging from 0.23 to 0.16 eV (Figure 2b), do not agree with the macroscopic activation energy seen by conductivity spectroscopy (0.36 eV) and electric modulus measurements (0.33 eV).\(^{47}\) Such discrepancies are well known in the literature\(^{63}\) and leave room for ideas that, for example, Li$^+$ ions have to surmount even larger barriers of a macroscopic length scale or the underlying motional correlation functions, probed by the different methods, simply differ.

Coming back to $^{31}$P NMR relaxometry, we recognize that the $T_{\text{max}}$ of the $^1$H $T_1/1/(T)$ rate peak (B) agrees very well with the position of the $^{31}$P NMR peak of nano-Li$_6$PS$_5$I (Figure 2b). If we assume that PS$_4^{−3}$ rotational jumps contribute to the overall $^{31}$P response, these processes take place on the same time scale as Li$^+$ hopping does, that is, on the ns scale (300 K). Thus, they are in resonance with Li$^+$ translational dynamics. This situation is in stark contrast to that discussed recently for ordered Li$_6$PS$_5$I.\(^7\) In the structurally ordered counterpart, the translational and any rotational jump processes seem to be, at least, temporarily decoupled;\(^7\) in unmillled Li$_6$PS$_5$I, the rotational motions are much faster than the long-range Li$^+$ ion dynamics. On the other hand, in disordered Li$_6$PS$_5$I, the matching characteristic motional correlation rates $r^{-1}$ point to dynamic cation–anion coupling that affects the overall Li$^+$ translational dynamics, possibly due to the paddle-wheel mechanism. This view is in line with that of Smith and Siegel who presented evidence that this mechanism is relevant for ion dynamics in glassy electrolytes such as 75Li$_2$S–25P$_2$S$_5$.\(^8\)

Certainly, further spectroscopic studies in combination with calculations are needed to support our findings and to unravel the true nature of anion–cation coupling in thiophosphates. We are still at the beginning to understand this important interaction. Such a beginning resembles a dialog of Rowling: “Is this real? Or has this been happening in my head?” Of course it is happening inside your head, Harry, but why on earth should that mean that it is not real.” (J. K. Rowling, Harry Potter and the Deathly Hallows, 2007.)

**Conclusions**

Li$_6$PS$_5$I serves as a highly suitable model system to study the influence of the structural disorder on dynamic properties. Here, the disorder was introduced by a soft mechanical treatment. We assume that the distortions and (anion and cation) site disorders are responsible for the immense increase in the ionic conductivity of the nanocrystalline, ball-milled Li$_6$PS$_5$I. Such disorder is absent for the unmilled samples. Variable-temperature $^{31}$P NMR reveals that an important source for spin–lattice relaxation is significantly changed after ball-milling. For ordered Li$_6$PS$_5$I, the prominent $^{31}$P NMR relaxation peak attributed to the ultrarapid PS$_4^{−3}$ rotational jumps either shifts toward higher $T$ or is missing. We conclude that structural disorder in Li$_6$PS$_5$I sensitively affects such motions. Moreover, it does not only alter the $^{31}$P NMR relaxation response but also reveals the subtle, but important, differences in $^7$Li NMR relaxation. While structural disorder slow down the fast intracage Li$^+$ dynamics, a new rate peak emerges at 281 K pointing to the highly effective source inducing $^7$Li NMR spin–lattice relaxation. We propose that this peak is responsible for the fast jump processes that enable the ions to diffuse over long distances. The mean activation energy for these elementary jump processes turned out to range between 150 and 160 meV. The associated translational jump rate is in the GHz range ($r^{-1}(281 K) = 7.3 \times 10^8$ s$^{-1}$) and would be in resonance with the mean rotational jump rate of the PS$_4^{−3}$ polyanions.

**Associated Content**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c06090.

Magnetization transients and results obtained from analyzing the relaxation rate peaks with modified BPP-type spectral density functions (PDF)

**Author Information**

Corresponding Author

H. M. R. Wilkening — Institute for Chemistry and Technology of Materials, Christian Doppler Laboratory for Lithium Batteries, Graz University of Technology (NAWI Graz), 8010 Graz, Austria; orcid.org/0000-0001-9706-4892; Email: wilkening@tugraz.at

Authors

M. Brinek — Institute for Chemistry and Technology of Materials, Christian Doppler Laboratory for Lithium Batteries, Graz University of Technology (NAWI Graz), 8010 Graz, Austria

C. Hiebl — Institute for Chemistry and Technology of Materials, Christian Doppler Laboratory for Lithium Batteries, Graz University of Technology (NAWI Graz), 8010 Graz, Austria

K. Hogrefe — Institute for Chemistry and Technology of Materials, Christian Doppler Laboratory for Lithium Batteries, Graz University of Technology (NAWI Graz), 8010 Graz, Austria

I. Hanghofer — Institute for Chemistry and Technology of Materials, Christian Doppler Laboratory for Lithium Batteries,
Graz University of Technology (NAWI Graz), 8010 Graz, Austria

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.0c06090

Author Contributions
M.B. and C.H. contributed equally to the work.

Notes
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