

# Slow Li Exchange in a $\text{Li}_3\text{N}$ Single Crystal Measured by $^{6,7}\text{Li}$ NMR Selective Quadrupole Satellite Inversion

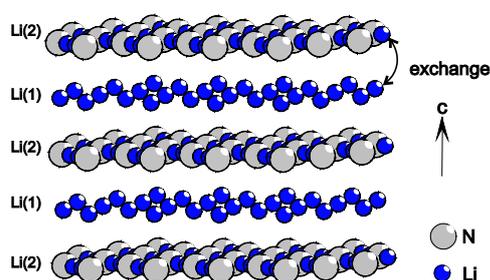
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Lithium nitride,  $\text{Li}_3\text{N}$ , is one of the best Li conductors at room temperature. Unfortunately, its application as electrolyte in batteries is limited due to the low decomposition potential of only 0.45 V. Nevertheless, diffusion in  $\text{Li}_3\text{N}$  was studied by many groups and various techniques (see [1-3] and references therein) which predestines it to act as a model system for the establishment of new techniques.  $\text{Li}_3\text{N}$  crystallizes in a layered structure of the hexagonal space group  $P6/mmm$  [3,4] (see Fig. 1). There are two alternating types of layers, one with the stoichiometry  $\text{Li}_2\text{N}$ , the other containing only Li. As a result, there are two different Li positions, Li(2) in the  $\text{Li}_2\text{N}$  layer and Li(1) in the Li layer. Li diffusion in the  $\text{Li}_2\text{N}$  layer ( $ab$ -plane, intralayer diffusion) is fast, while the Li diffusion parallel to the  $c$ -axis is moderate. The mechanism of this interlayer diffusion process is directly associated with a Li exchange between the two Li positions (see Fig. 1) since the Li ions cannot jump from one Li(2) site to the other but transitionally reside on a Li(1) site [5]. This makes it possible to measure the interlayer diffusion process by exchange NMR techniques.



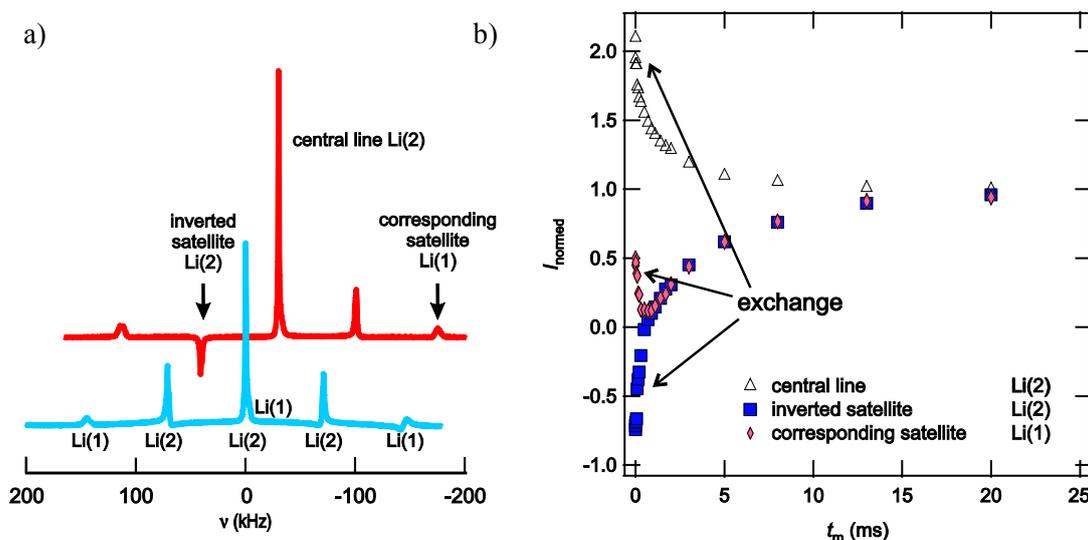
**Fig. 1** The layered structure of  $\text{Li}_3\text{N}$  [2] with the two different Li positions Li(1) and Li(2). The interlayer diffusion process consists of an exchange process between Li(1) and Li(2).

In the case of nuclei with spin  $I = 1/2$ , an easy and accurate NMR technique to measure slow exchange between two spin reservoirs referring to two non-equivalent sites is the selective inversion technique which uses the pulse sequence  $\pi_{\text{sel}} - t_m - \pi/2_{\text{det}}$ . The first pulse  $\pi_{\text{sel}}$  selectively inverts the population difference of one of the spin reservoirs and thus the peak in the NMR spectrum referring to that coherence. During the variable mixing time  $t_m$  the negative amplitude of the inverted peak is partially transferred to the peak corresponding to the inverted one via the exchange process. The detection pulse  $\pi/2_{\text{det}}$  transfers the longitudinal magnetization into a detectable transversal magnetization. When the

mixing time is varied, the exchange process can be followed directly, unless relaxation or spin diffusion processes are faster than the exchange process to be measured.

However, in the case of Li there are the two natural isotopes <sup>6</sup>Li with  $I = 1$  and <sup>7</sup>Li with  $I = 3/2$ . As well known, nuclei with  $I > 1/2$  have an electrical quadrupole moment in addition to their magnetic dipole moment. Therefore, for both <sup>6</sup>Li and <sup>7</sup>Li, the interaction between a non-vanishing local electric field gradient and the nuclear quadrupole moment has to be taken into account. This interaction causes a shift of the Zeeman energy levels leading to an NMR spectrum of the single crystal with two peaks in the case of <sup>6</sup>Li and with three peaks (central transition and two quadrupolar satellites) in the case of <sup>7</sup>Li.

In the case of Li<sub>3</sub>N, the chemical shifts of Li(1) and Li(2) are nearly identical. Extraordinarily high electrical field gradients with different magnitudes and signs (ratio-2:1) dominate the <sup>7</sup>Li NMR spectrum shown in Fig. 2 a). This makes it impossible to selectively invert one spin reservoir as a whole. But it is indeed possible to selectively invert one of the quadrupolar *satellites* of one spin reservoir. The pulse sequence used is identical to the one given above. The principle of the measurement is absolutely analogous to the one described above: The intensities of the inverted peak and the corresponding peak, *i.e.*, the quadrupolar satellite of the other spin reservoir referring to the same quantum transition, are followed by varying the mixing time (see Fig. 2 b)). It has to be noted that not only the population difference of the inverted peak is touched by the inversion but also that of the neighbouring quantum transitions. Thus, the exchange process can be followed by looking at (i) the inverted peak, (ii) peak corresponding to the inverted one and (iii) the neighbouring quantum transition peaks.



**Fig. 2** a) <sup>7</sup>Li NMR spectrum of a Li<sub>3</sub>N single crystal ( $B \parallel c$ ) before and shortly after the selective inversion. The spectra were recorded at 333 K and 77.7 MHz. b) normalized peak amplitudes of the inverted satellite Li(2), the corresponding satellite Li(1) and the central transition Li(2) as a function of the mixing time  $t_m$ .

The amplitudes depicted in Fig. 2 b) show the expected biexponential behavior: the variation of the peak amplitudes at a shorter time scale is due to exchange. At a longer timescale the amplitudes relax back to equilibrium (<sup>7</sup>Li NMR spin-lattice relaxation). However, below room temperature, relaxation and exchange occur on similar time scales which makes it impossible to separate the two effects. Therefore, at lower temperatures, <sup>6</sup>Li NMR measurements were performed. The NMR spin-lattice relaxation rate of <sup>6</sup>Li is generally smaller than that of <sup>7</sup>Li due to its smaller magnetic dipole moment and electric quadrupole moment while the exchange rate should be nearly identical. Using <sup>6</sup>Li exchange NMR measurements, relaxation and exchange occur on well separated time scales. The ex-

change rates extracted from the <sup>6</sup>Li and <sup>7</sup>Li NMR exchange measurements are consistent with those obtained by SAE NMR [1] and β-NMR techniques [1,2] as well as by conductivity measurements [3].

### References

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