Brief Reports

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⁷Li diffusion constant in the superionic conductor Li₃N measured by NMR

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The anisotropic diffusion coefficient of ⁷Li in Li₃N has been measured by the pulsed magnetic-field-gradient method of NMR. Activation energy and jump rates obtained for diffusion along the hexagonal c axis are in good agreement with our previous data, thus suggesting that the hopping of Li ions between the inequivalent Li(1) and Li(2) sites dominates the conductivity along the c axis.

The crystal structure of the superionic conductor Li₃N (space group $P6/mmm$) can be considered as a layer structure with alternately Li₂N layers [containing the Li(2) positions] and pure Li layers [with Li(1) positions] perpendicular to the hexagonal c axis. The Li ionic conductivity is anisotropic with room-temperature values $\sigma_\parallel = 10^{-3}$ $(\Omega\,m)^{-1}$ and $\sigma_\perp = 0.12$ $(\Omega\,m)^{-1}$ parallel and perpendicular to the c axis, respectively.[1] Conduction is attributed to a vacancy-induced Li diffusion process: the presence of $(NH)^{--}$ and $(NH_2)^-$ complexes[2-4] creates Li vacancies in the Li₂N layers with a concentration of the order of 1% around 300 K (Ref. 5).

Recently we have reported[6] extensive NMR investigations of the Li diffusion within the Li₂N layers (intralayer process) and perpendicular to the layers (interlayer process). A large body of experimental data provided conclusive evidence that the interlayer diffusion process involves both Li sites. That result was in contrast to x-ray studies[5] which postulate an exchange of Li(2) ions belonging to different layers without involving Li(1) ions. However, a reevaluation of the x-ray data leads to conclusions which agree with the NMR results.[7] In this Brief Report we present further evidence that the Li(1)-Li(2) ion exchange is essential for the conductivity parallel to the c axis and we will argue that the Li(1)-Li(1) and Li(2)-Li(2) processes are of minor importance.

We have measured the self-diffusion coefficient D of the ⁷Li ions by the pulsed magnetic-field-gradient (PMG) technique.[8] This is a nondestructive method which uses the nuclear spin as a label and proceeds as follows. First, in a conventional $\pi/2$-π NMR pulse experiment the amplitude A of the so-called spin-echo signal is measured. Then, the experiment is repeated but now by applying two magnetic-field-gradient pulses (amplitude g, width δ), the first between the rf pulses, the second between the π pulse and the echo. The echo amplitude is now A^* and D is obtained from the relation

$$\ln(A^*/A) = -D\gamma^2\delta^2 g^2(\Delta - \tfrac{1}{3}\delta) \ ,$$

where Δ is the delay time between the two gradient pulses, and γ is the gyromagnetic ratio. Details of our experimental setup are given in Ref. 9.

The results of our measurements for diffusion along the c axis $(D_\parallel)$ and perpendicular to the c axis $(D_\perp)$ are shown in Fig. 1. $D_\perp$ could not be determined below 654 K because of the short spin-spin relaxation time T_2. The diffusion coefficients obey an Arrhenius law $D = D_0\exp(-E/kT)$ where E is an activation energy. A least-squares fit to the data yields

$$D_\parallel = (0.81 \pm 0.1) \times 10^{-5}\exp(-7891/T) \text{ m}^2/\text{s} \ ,$$

$$D_\perp = (3.0 \pm 2) \times 10^{-7}\exp(-4758/T) \text{ m}^2/\text{s} \ , \tag{1}$$

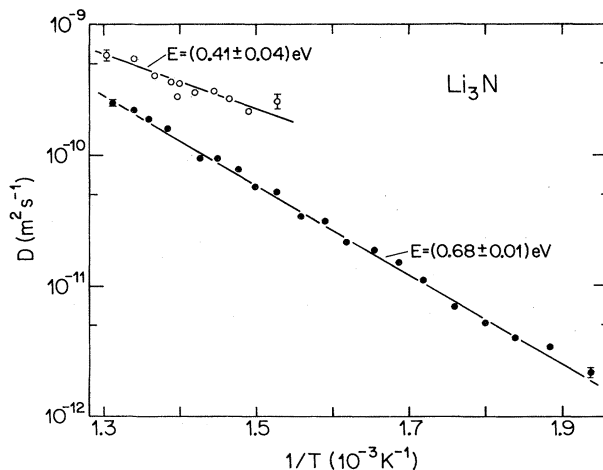where the temperature T is measured in K. The respective

FIG. 1. Diffusion coefficient of ⁷Li in Li₃N as a function of inverse temperature for diffusion along (●) and perpendicular (O) to the c axis as measured by NMR. The straight lines are least-squares fits to the data yielding the activation energies quoted.

activation energies are

$$E_{\parallel} = 0.68 \pm 0.01 \text{ eV}, \quad E_{\perp} = 0.41 \pm 0.04 \text{ eV} .$$

Symmetry requires the diffusion tensor to be axially symmetric with respect to the c axis. In particular, the diffusion coefficient $D(\theta)$ measured along an arbitrary direction which makes an angle θ with the c axis, must obey the equation

$$D(\theta) = D_{\parallel} + \sin^2(\theta)(D_{\perp} - D_{\parallel}) ,$$

which has been confirmed experimentally at 722 K.

We start the discussion of our results by comparing $D_{\parallel}$ of Eq. (1) with the diffusion coefficient D_{σ} as defined by the Nernst-Einstein equation and referring to diffusion parallel to the c axis:

$$\sigma(0) = D_{\sigma} \frac{q^2 n_{\sigma}}{kT} , \tag{2}$$

where $\sigma(0)$ is the dc ionic conductivity along the c axis and n_{σ} the number of charge carriers (with charge q) per unit volume. In Li_3N, $\sigma(0)$, n_{σ}, and D_{σ} refer to the migration of Li vacancies while $D_{\parallel}$ as determined by NMR refers to the diffusion of ^7Li ions. $D_{\parallel}$ and D_{σ} can be connected by means of the Einstein relation

$$D_{\sigma} = \frac{1}{g} f_{\sigma} r^2 \Gamma_{\sigma} , \tag{3}$$

$$D_{\parallel} = \frac{1}{g} f r^2 \Gamma . \tag{4}$$

Here, g is a geometrical constant dependent on the dimension, r is the jump distance of the particle or the vacancy, and Γ and Γ_{σ} are the corresponding jump frequencies; f and f_{σ} are correlation factors.[10] Furthermore,

$$\Gamma = \frac{n_{\sigma}}{n} \Gamma_{\sigma} , \tag{5}$$

where n is the total number of Li atoms per unit volume. Combining Eqs. (2)–(5) yields

$$\sigma(0) = D_{\parallel} \frac{f_{\sigma}}{f} \frac{nq^2}{kT} . \tag{6}$$

Since hydrogen impurities considerably enhance the conductivity in Li_3N (Refs. 2–4) we choose for calculating $D_{\parallel}$ from (6) the data

$$\sigma(0) = 7 \times 10^5 \exp(-7800/T)(\Omega \text{m})^{-1} , \tag{7}$$

obtained by Wahl[2] for a Li_3N sample with a low hydrogen impurity concentration of 7.2×10^{25} m^{-3}. That sample and the sample used in the present and our previous[6] NMR studies were grown in a similar way by E. Schönherr of the Max-Planck-Institut für Festkörperforschung at Stuttgart. Equation (7) was determined for temperatures up to about 390 K with a factor 2 uncertainty for the preexponential factor and an activation energy of 0.67 ± 0.03 eV. Assuming that (7) is also valid at temperatures where our $D_{\parallel}$ values were measured one obtains for $T = 625$ K from (7) $\sigma(0) = 2.66 \ (\Omega \text{m})^{-1}$. Then, with $n = 6.72 \times 10^{28}$ m^{-3} and the reasonable assumption that f_{σ}/f is close to 1, Eq. (6) yields $D_{\parallel} = 1.3 \times 10^{-11}$ m^2/s which agrees quite well with our experimental value 2.6×10^{-11} m^2/s. However, what is more important is the agreement between the activation energies determined by conductivity and diffusion experi-

ments. That implies that both methods probe the same transport mechanism and that our sample has indeed a relatively low hydrogen impurity concentration.

Next, we discuss the argument that the hopping of Li ions between the Li(1) and Li(2) sites is the major contribution to the ionic conductivity $\sigma_{\parallel}$. From (4) we can calculate the jump frequency Γ of the diffusing ions. Since the NMR experiment determines the component of the diffusion current along the c axis, the jump distance r must be identified with the projection of the Li(1)-Li(2) distance onto the c axis, that is, $r = c/2 = 1.938$ Å. Taking $g = 2$ (for one-dimensional diffusion) and assuming $f = 1$, Eqs. (1) and (4) yield

$$\Gamma = 4.3 \times 10^{14} \exp(-7891/T) \text{ s}^{-1} .$$

These rates are plotted in Fig. 2 for the temperature range where $D_{\parallel}$ was measured. Also shown are the correlation rates of the fluctuating electric field gradients at the Li sites arising from site-exchange jumps Li(1)-Li(2). We have obtained these rates which we identified with the jump rates of the Li ions, from our previous analysis[6] of three sets of NMR observables in terms of the interlayer process: the second-order quadrupolar shift of the ^7Li central signal and the spin-lattice relaxation times T_1 of both the ^7Li and the ^6Li isotopes. The results for ^7Li are given in Fig. 2 only.

As may be seen in Fig. 2 there is good agreement between the three sets of jump rates as obtained from the second-order quadrupolar shift, the spin-lattice relaxation, and the diffusion of the ^7Li ions. In particular, all three sets of measurements yield the same activation energy. This is taken as strong evidence that the jumping between the inequivalent Li(1) and Li(2) sites is the major contribution to the diffusion and hence to the conductivity along the c axis. While jumping between equivalent sites Li(1)-Li(1) and Li(2)-Li(2) would not contribute to the quadrupolar shift and the relaxation time as analyzed in Ref. 6, the diffusion
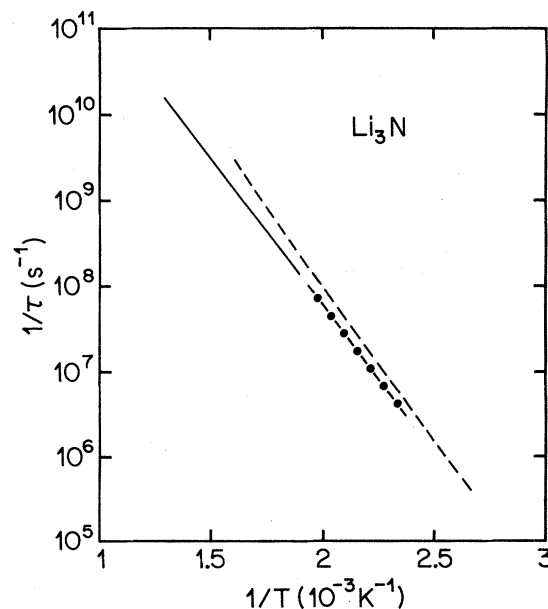

FIG. 2. Temperature dependence of the correlation rate $1/\tau$ of the Li(1)-Li(2) site exchange motion in Li_3N calculated from diffusion (——), second-order quadrupolar shift ($-\bullet-\bullet-$), and spin-lattice relaxation ($- - -$) data of ^7Li.

coefficient $D_{\parallel}$ comprises any translational movement along the c axis. However, it is highly unlikely that Li(1)-Li(2) jumps taking place between inequivalent layers are thermally activated with the same activation energy as jumps between equivalent layers. We thus conclude that diffusion along the c axis predominantly arises from jumps between inequivalent sites; this process is essential for the conductivity $\sigma_{\parallel}$ in relatively pure Li_3N samples.

For the Li diffusion perpendicular to the c axis $(D_\perp)$ we obtained an activation energy $E_\perp = 0.41 \pm 0.04$ eV which is smaller than the value 0.56 eV found by Wahl from conductivity measurements in his "pure" sample and larger than the values of the doped samples; it is also larger than the value 0.25 eV deduced from NMR line-narrowing data.[11] However, when comparing these energies one has to keep in mind that the $D_\perp$ values we have measured contain a contribution from the interlayer Li(1)-Li(2) diffusion and thus the $D_\perp$ data of Fig. 2 have to be analyzed in terms of two exponential functions. The limited range of the present data do not justify such an analysis.

Finally, we want to comment briefly on a paper by Nishida, Asai, and Kawai[12] about NMR-T_1, T_2, and σ measurements in Li_3N crystals doped with oxygen impurities up to 11 at.%. The authors assert that the "site exchange motion of the Li(1) and Li(2) ions does not contribute to the ionic conduction of Li_3N" because the activation energy found in the $\sigma_{\parallel}$ data (0.49 eV) does not show up in the T_2 data. We object to this conclusion for the following reasons. (i) As long as the nature of the defect formed by the 0 impurities is not known a direct comparison with H-doped samples is questionable. (ii) Rather than 0.6 eV as stated by Nishida et al.,[12] the fit to their high-temperature data yields 0.42 eV which comes close to the 0.49 eV value of $\sigma_{\parallel}$. So the 0.6 eV of the site exchange effect does *not* show up in the T_2 data. (iii) The "unexpected minimum" of their $1/T_2$ data probably arises from experimental limitations; i.e., only the larger component of the two T_2 times which one would expect could be measured hence causing a decrease of the $1/T_2$ rate. Thus the T_2 data are less reliable for drawing conclusions concerning the site exchange motion.

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