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# Model for Ionic Hopping in $Li_3N$

Analysis of published NMR relaxation data of $^6Li$ and $^7Li$ in $Li_3N$ leads to a unique model for $Li^+$ hopping along the $c$-axis. It is one in which an ion goes directly from one Li(1) plane to another Li(1) plane by passing through the intermediate Li(2) plane.

## I. Introduction

$Li_3N$ has been one of the most intensively studied superionic conductors in the recent literature (*1*). Its high $Li^+$ ionic conductivity makes it a system of potential interest for solid electrolyte batteries as well as a good subject for basic studies. The structure (*2*) is relatively simple compared with the complexities of several other superionics; so it should be possible to make detailed comparison between experimental data and models of the hopping mechanism and defect structure. We show in this paper that certain aspects of the NMR results (*3, 4*) are consistent with a particular hopping model and seem to be difficult, if not impossible, to explain otherwise.

The model, illustrated in Fig. 1, is one in which the relatively low conductivity parallel to the $c$-axis ($\sigma_{\|}$) takes place by Li(1)–Li(1) as well as Li(2)–Li(2) jumps (labeled $B \to D \to B'$ and $A \to C \to A'$, respectively, in Fig. 1). The time spent in the intermediate layers is very short so that effectively ions jump to the next nearest-neighbour plane.

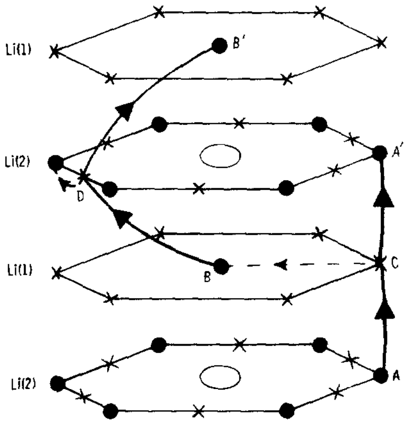

FIG. 1. Schematic arrangement of $Li^+$ ions in $Li_3N$ showing cooccupied A and B sites and unoccupied D and C sites in the Li(2) and Li(1) planes. Proposed hopping paths are shown going through intermediate interstitial sites. Solid BDB′ and ACA′ paths contribute to conductivity but not to fluctuating efg, which requires BDA′ or ACB. (Open circles in Li(2) planes represent N sites.)

## II. Review of NMR Results

Brinkmann and co-workers (*3, 4*) have done a thorough study of the quadrupole splittings and spin–lattice relaxation times, $T_1$, of both $^6Li$ and $^7Li$ nuclei. At room temperature two distinct sites are seen with quadrupole splittings, $\omega_A$ and $\omega_B$, identified with the Li(2) A sites and Li(1) B sites, respectively. At higher temperature only a single splitting is seen which is consistent with an average coupling constant (*5*). This is immediately suggestive of some interchange between A and B sites at a rate faster than $|\omega_A - \omega_B|$; so at least some motion of the Li(1) ions is implied.

We are mainly concerned, however, with the following features of $T_1$. For both $^6Li$ and $^7Li$ there is a pronounced minimum in $T_1$ vs

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temperature $T$ in the vicinity of 500 K. From this, hopping rates and their activation energies were extracted in the usual way by application of the BPP formula (*6*). For $^7$Li with the field $H_0$ perpendicular to $c$ these rates were further identified with the Li(1)–Li(2) interchange which gives rise to a fluctuating electric field gradient (efg). Rapid diffusion in the Li(2) plane (*1*, *8*) was assumed to produce fluctuating efg's at a rate too fast to be an effective $T_1$ mechanism at high temperature. Since $^6$Li has a much smaller quadrupole moment, fluctuating efg's are not of sufficient magnitude to explain its $T_1$ values. Instead its relaxation was suggested to be caused by paramagnetic impurities.

We take the position here that the above interpretations, which are documented in detail in Refs. (*3*) and (*4*), are correct and proceed to consider two striking features:

(i) The activation energy for hopping inferred from the $^7$Li relaxation, $\Delta_7 = 0.83$ eV, is considerably larger than that for $c$-axis conductivity (*1*), $\Delta_\parallel = 0.49$ eV.

(ii) The activation energy for hopping $\Delta_6$ inferred from the $^6$Li relaxation is, however, in good agreement, $\Delta_6 = 0.47$ eV.

## III. Interpretation

The difference between $\Delta_6$ and $\Delta_7$ can be understood by noting that for relaxation by paramagnetic impurities *any* hop produces a change in the local dipolar field, but only a hop to an inequivalent site changes the efg. Thus paths $A \rightarrow C \rightarrow A'$ and $B \rightarrow D \rightarrow B'$ of Fig. 1 contribute to $\sigma_\parallel$ but not to $^7$Li relaxation by a fluctuating efg. We consider the $^6$Li relaxation further by assuming that in the high-temperature, rapid-hopping regime many impurities must be encountered during the relaxation time $T_1$. One can then show that

$$T_1^{-1} = \frac{2}{3}\rho_A \frac{\langle \Delta\omega_A^2 \rangle \tau_A}{1+\omega^2\tau_A^2} + \frac{1}{3}\rho_B \frac{\langle \Delta\omega_B^2 \rangle \tau_B}{1+\omega^2\tau_B^2}. \tag{1}$$

The quantities multiplying $\frac{2}{3}\rho_A$ and $\frac{1}{3}\rho_B$ are the respective relaxation rates an ion experiences at A and B sites in the neighborhood of an impurity, and $\frac{2}{3}\rho_A$ and $\frac{1}{3}\rho_B$ represent the probabilities (proportional to impurity concentration) of an ion being at an A or B site which has an impurity neighbor. (The factors $\frac{2}{3}$ and $\frac{1}{3}$ express the fact that there are twice as many A sites as B sites.) Equation (1) thus states that $T_1^{-1}$ is given by an average rate for the medium in the rapid-hopping limit. The relaxation rate at a type $i$ site ($i = $ A or B) is shown in Eq. (1) as a function of the second moment of the electronic–nuclear interaction $\langle \Delta\omega_i^2 \rangle$, the effective correlation time $\tau_i$, and the NMR frequency $\omega$. If the electronic spin-lattice relaxation rate is much less than the hopping rate, $\tau_i$ is just the mean time for an ion to hop away from a particular type $i$ site. We assume this is the case at high temperature and further, in the region of the $T_1$ minimum for $^6$Li at about 500 K, that $\omega\tau_A \ll 1$ and $\tau_A \ll \tau_B$. Thence the first term in Eq. (1) is negligible if $\rho_A\langle \Delta\omega_A^2 \rangle$ and $\rho_B\langle \Delta\omega_B^2 \rangle$ are comparable and we deduce that the hopping rate inferred from the high-temperature $^6$Li relaxation is

$$\tau_B^{-1} = \tilde{W}_{BA} + \tilde{W}_{BB'}. \tag{2}$$

Here $\tilde{W}_{ij}$ is an effective rate for the two step process through an interstitial as illustrated in Fig. 1 and we have assumed that the Li(1) intraplane rate $\tilde{W}_{BB}$ is negligible. [Equation (1) also predicts a $T_1$ minimum at a lower temperature where $\omega\tau_A \sim 1$. Complete data do not exist in this region.] The experimental fact (ii) is that $\tau_B \propto \tau_\parallel$, i.e., the activation energy for conductivity parallel to $c$ is observed in the $^6$Li NMR. But fact (i) tells us that $\tilde{W}_{BA} \ll \tau_B^{-1}$, since the activation energy for efg fluctuation in $^7$Li NMR is close to a factor of 2 greater than that for $\tau_B$ and, from Eq. (2) and Fig. 1, the net $\tau_B$ is determined by the faster of the parallel $B \rightarrow D \rightarrow A'$ and $B \rightarrow D \rightarrow B'$ rates, only the former of which produces a changing efg for $^7$Li relaxation. The inescapable conclusion seems to be that

$\tau_{\parallel}^{-1} \propto \tilde{W}_{\mathrm{BB'}}$. This means that $\tilde{W}_{\mathrm{BB'}} \gtrsim \tilde{W}_{\mathrm{AA'}}$ since otherwise the A → C → A′ process would dominate $\tau_{\parallel}$. Note that these arguments do not directly involve the prefactors for the various rates.

## IV. Discussion

Consideration of *both* the $^6$Li and $^7$Li $T_1$ data has led us to propose that the B → D → B′ process, whereby an ion passes from one Li(1) plane to another Li(1) plane by going through the intermediate Li(2) plane without being trapped there, is at least as strong as the analogous A → C → A′ process. One must ask whether this is compatible with the known structure and whether the above interpretation is unique.

In regard to the structure, the A → C → A′ mode seems to be very reasonable because of the openness of the Li(1) plane and has been mentioned as the mechanism for $\sigma_{\parallel}$. On the other hand, there does not appear to be room for an ion to pass through the crowded Li(2) plane except for the possibility of a small number of Li(2) vacancies (*1*, *8*). We suggest two alternatives which might allow such passage. First there may be a strong correlation between A → C → A′ and B → D → B′ events as sketched in Fig. 2. When an ion leaves the A site and pauses at an interstitial C site it both creates room for the B site ion to jump into an intermediate D site and produces a repulsion to force the ion out of its B site. Thus we might expect a B → D hop to be coincident with the A → C hop. If, contrary to published data (*1*, *7*), the number of B-site and A-site vacancies are comparable at high temperature, the successive D → B′ and C → A′ transitions might also occur at about the same rate, hence making $\tilde{W}_{\mathrm{BB'}} \approx \tilde{W}_{\mathrm{AA'}}$. Note that we cannot allow the ion originally at a B site to fall into the hole left by that coming from an A site, since if it resides there for an appreciable time, we would have $\tilde{W}_{\mathrm{BA}} > \tilde{W}_{\mathrm{BB'}}$ and thus a more rapid rate for efg fluctuation than for parallel conductivity.

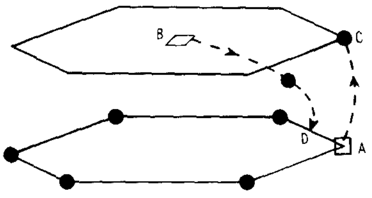

FIG. 2. Possible correlated hop in which A → C triggers B → D.

A second possibility is that the electron density maps of Ref. (*8*) show considerable delocalization in the Li(2) plane which indicates large departures from equilibrium A sites. Thus one might visualize a coincidence event as in Fig. 3 in which an ion can move through the D interstitial in the Li(2) plane during the time neighboring ions are in positions to provide an opening.

We must acknowledge that there is no X-ray evidence to support *any* motion of the B-site ions. However, if the time spent away from equilibrium B sites is very short, such movement would not show up in time-average crystallography studies, and, quite apart from the $T_1$ considerations of this paper, the previously discussed (*3*, *5*) averaging of the quadrupole spectrum can only be explained by A–B interchange.

There seems to be no alternative explanation of the data within the framework of simple hopping pictures. The question can always be raised as to whether peculiar

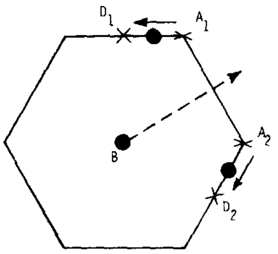

FIG. 3. Situation in which intraplane displacement of ions from equilibrium sites $A_1$ and $A_2$ toward $D_1$ and $D_2$ allows ion from B site above or below to move through plane.

effects are involved which would make the apparent activation energy observed by NMR be different from that observed by conductivity even though the same hopping process is monitored. There is a wealth of data (*9*), however, which shows that NMR and conductivity activation energies generally agree for $Li^+$ and other conductors. Further, discrepancies (*10*) are such as to make the NMR activation energy *less* than that for conductivity. To explain the present results on this basis would require the opposite and the agreement for $^6Li$ to be purely coincidental.

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PETER M. RICHARDS

*Sandia Laboratories**
*Albuquerque, New Mexico 87185*
*and*
*Physik Institut*
*Universität Zürich*
*Zürich, Switzerland*

*Received December 26, 1979*

* Permanent and present address.