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## NMR-Study of Structure and Diffusion Processes in $\text{Li}_3\text{N}$

R. Messer, H. Birli and K. Differt

Max-Planck-Institut für Metallforschung, Institut für Physik, Stuttgart, Germany

**Résumé.** — Nous avons analysé les spectres quadrupolaires de  $^7\text{Li}$  et  $^{14}\text{N}$  dans des monocristaux de  $\text{Li}_3\text{N}$  en fonction de l'orientation dans le champ magnétique. Les résultats sont en bon accord avec le modèle de liaison ionique. L'évolution des spectres quadrupolaires et des relaxations spin-réseau  $T_1$  en fonction de la température conduit au moins à deux processus de diffusion, en accord avec la forte anisotropie de la conductivité ionique. Au-dessous de 300 K la diffusion est réalisée dans les couches de  $\text{Li}_2\text{N}$  avec une enthalpie d'activation d'environ 0,25 eV. La mobilité des noyaux s'accélère, si la concentration d'hydrogène dans les échantillons est augmentée. Aux températures plus élevées on note une diffusion interplans importante, mettant en jeu les deux sites du lithium.

**Abstract.** — Quadrupole split NMR-spectra of  $^7\text{Li}$  and  $^{14}\text{N}$  in single crystals of  $\text{Li}_3\text{N}$  were measured as a function of orientation to the magnetic field. The results confirm the model of ionic bonding. From the temperature dependence of both the  $^7\text{Li}$  spectra and the relaxation rate  $T_1$  of  $^7\text{Li}$  at least two diffusion processes could be determined which are in agreement with the strong anisotropy of the ionic conductivity. Below 300 K nearly all diffusion takes place in the  $\text{Li}_2\text{N}$  layer with an activation enthalpy of about 0.25 eV. The jump rate of the ions can be increased by doping the crystals with hydrogen. At higher temperatures there is a considerable amount of interplanar diffusion involving both Li positions.

**1. Introduction.** — The crystal structure of  $\text{Li}_3\text{N}$  is hexagonal consisting of alternately  $\text{Li}_2\text{N}$  and Li planes as shown in figure 1 [1]. Zintl and Brauer [2] in 1935 suggested ionic bonding between  $\text{N}^{3-}$  and  $\text{Li}^+$  ions while lateron Hückel [3] and Krebs [4] supposed covalent bonding which was supported by NMR studies of polycrystalline  $\text{Li}_3\text{N}$  [5, 6]. By recent measurements [7] a relatively high ionic conductivity was found comparable with that of Li- $\beta$ -alumina which hardly can be understood within a covalent bonding model. Now the existence of single crystals of  $\text{Li}_3\text{N}$  of high quality and sufficient size [8] makes it possible to take up again the question if the NMR-data contradict the ionic bonding model.

The ionic conductivity in single crystals shows a strong anisotropy with  $\sigma^{\parallel} < 10^{-5} (\Omega\text{cm})^{-1}$  parallel and  $\sigma^{\perp} = 10^{-3} (\Omega\text{cm})^{-1}$  perpendicular to the hexa-

gonal  $c$ -axis at RT. The mechanisms of the diffusion processes involved are not yet completely understood. Schulz *et al.* [9] concluded from X-ray investigations that the ionic conductivity perpendicular to the  $c$ -axis is a vacancy induced diffusion process in the  $\text{Li}_2\text{N}$  plane. Wahl [10] had shown that this process depends on the hydrogen concentration in the sample. We examined three samples with different hydrogen concentration and measured the temperature dependence of (i) the quadrupolar splitting of the  $^7\text{Li}$ -NMR-spectra, (ii) the linewidth of the resonance lines (motional narrowing, lifetime broadening), and (iii) the relaxation rate  $T_1$  in the temperature range from 80 K to 700 K to get a detailed picture of the microscopic diffusion processes in  $\text{Li}_3\text{N}$ . Details of our investigations are given in [11]. In this paper we will restrict ourselves to some special aspects.

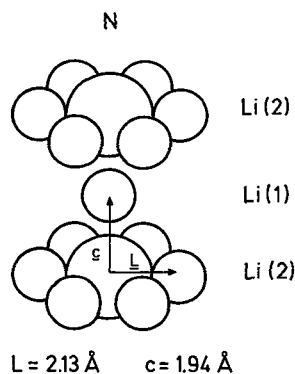


Fig. 1. — Crystal structure of lithium nitride.

**2. Experimental.** — Single crystals of  $\text{Li}_3\text{N}$  were grown by the Czochralski technique [8]. One of the samples was doped with hydrogen but also the other samples investigated contain a considerable concentration of hydrogen which was determined by infrared transmission and reflexion [10].

**3. Discussion of structure and ionic bonding.** — The orientation dependence of the quadrupole split spectra of  $^7\text{Li}$  and  $^{14}\text{N}$  was measured by rotations relative to the magnetic field about axis parallel and perpendicular to the  $c$ -axis. According to the spin

quantum numbers the <sup>7</sup>Li spectra shows two triplets due to the Li(1) and Li(2) positions, whereas the <sup>14</sup>N spectra consist of a doublet. Within the experimental error the orientation dependence follows the theoretical expressions (see e.g. Volkoff [13]) for first and second order quadrupole splitting. We found that the electric field gradient at all three sites is axially symmetric around the *c*-axis and therefore can be described by only one constant, the coupling constant  $A = e^2 q \cdot Q/h$ , where  $eQ$  is the nuclear electric quadrupole moment and  $eq$  the diagonal component of the electric field gradient along the *c*-axis.

Table I. — Experimental (exp) and theoretical (th) values describing the quadrupole interaction at the sites of the nuclei Li(1), Li(2), and N ( $T = 293$  K). The opposite signs of the experimental values of Li(1) and Li(2) follow from high temperature measurements.

	$(q_\alpha \cdot Q_\alpha)_{\text{exp}} [\text{cm}^{-1}]$	$(q_\alpha \cdot Q_\alpha)_{\text{th}} [\text{cm}^{-1}]$	$A_{\text{exp}} [\text{kHz}]$
Li(1)	0.016 8	0.044 9	$582 \pm 2$
Li(2)	- 0.008 2	- 0.019 0	$- 284 \pm 2$
N	0.014 5		$505 \pm 2$

In table I values of the determined quadrupolar coupling constants  $A$  together with experimental and theoretical values of  $q \cdot Q$  are summarized. The theoretical values of  $q \cdot Q$  for <sup>7</sup>Li(1) and <sup>7</sup>Li(2) were calculated [11] with  $Q = -4.1 \times 10^{-26} \text{ cm}^2$  and the antishielding factor  $\gamma_{\text{Li}^+} = -0.213$  [14] from the electric field gradient determined with the assumption of point charges  $\text{Li}^+$  and  $\text{N}^{3-}$  situated at the lattice sites (see e.g., Cohen, Reif [15]). The theoretical values of  $q \cdot Q$  are by a factor 2... 3 too high which may arise from the uncertainty of the value of the antishielding factor  $\gamma_{\text{Li}^+}$  but they are in correct order which contradicts the statements of earlier investigations [5, 6]. Furtheron the theoretical results reflect the experimental fact that the greater quadrupolar splitting comes from the nuclei of Li(1). Also the theoretical ratio of  $(q \cdot Q)_{\text{Li(1)}} / (q \cdot Q)_{\text{Li(2)}} = -2.36$  is in acceptable agreement with the corresponding experimental one of  $-2.04$ . The negative sign of the experimental ratio can be derived from the high temperature quadrupole splitting (see the following section).

The slight discrepancy of the experimental to the theoretical ratio can be removed when we take into account the experimental result that the chemical shift tensor of <sup>14</sup>N is not spherical symmetric. The electron cloud of the  $\text{N}^{3-}$  ion has a deformation in *c*-direction which leads to a quadrupole moment of the electron cloud of  $\text{N}^{3-}$  itself and thus gives a contribution to the field gradients at the different sites. Finally we obtained an antishielding factor for the  $\text{N}^{3-}$  ion of about 20 which is of reasonable order [11].

**4. Temperature dependence of the <sup>7</sup>Li-NMR-spectra.** — The temperature dependence of the linewidth

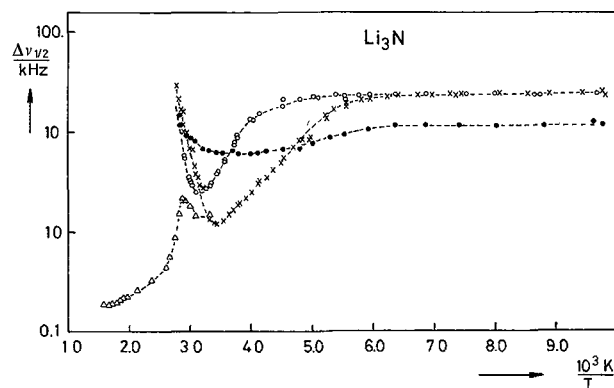


Fig. 2. — Temperature dependence of the linewidth  $\Delta\nu_{1/2}$  of satellites and central line. Satellites : Li(2), sample 180,  $H_0 \perp c$  (×); Li(2), sample 113,  $H_0 \perp c$  (○); Li(1), sample 180,  $H_0 \perp c$  (●), central line : Li(2), sample 131,  $H_0 \parallel c$  (Δ).

$\Delta\nu_{1/2}$  (linewidth at half intensity of the power spectra) of the satellites and central lines are shown in figure 2. The rigid lattice value of the dipolar linewidth is reached below 130 K to 250 K, depending on the sample. It can be calculated from the Van Vleck-expression and yield within the experimental accuracy the experimental values. The motional narrowing of the two Li positions is quite different. Whereas the Li(2) position reduces its linewidth with increasing temperature down to about 1 kHz the Li(1) position reduces only to about half the value of the rigid lattice linewidth. If we calculate the contribution of the two different Li sites to the total linewidth at each site it can be shown that only the Li(1) ions contribute to the motional narrowing process. The nuclei on the Li(1) position are up to 300 K relative immobile and don't affect the low temperature diffusion process in Li<sub>3</sub>N. The temperature dependence of the motional narrowing is strongly sample dependent. In the hydrogen doped sample 180 the diffusion process is more than a factor of 10 faster than in the other samples investigated. The conductivity perpendicular to the *c*-axis and the diffusion process in the Li<sub>3</sub>N layers determined by the motional narrowing data have nearly the same activation enthalpies. We found also that the jump frequencies determined from NMR and conductivity are closely correlated. From the hydrogen concentration dependence we suppose that the intra-layer diffusion process is vacancy induced.

Above 300 K the satellite lines of both sites broaden simultaneously and decrease, the two central lines merge into a single, narrow line. To explain this broadening behaviour we used the fundamental models (see e.g., Abragam [16], p. 445) for the exchange of magnetization between two environments which are in our case the Li(1) and Li(2) sites. The jump rates determined from the broadening data agree well with the jump rates derived from the conductivity data parallel to the *c*-axis. Therefore we conclude that the essential process for the inter-layer diffusion is given by jumps between the Li(1) and Li(2) positions.

At temperatures above 500 K the coupling constant  $A$  is drastically reduced as already shown by Brinkmann *et al.* [12]. We conclude that in this temperature range the exchange between the Li sites becomes so fast, that the Li ions measure a mean value of the field gradients which yield a coupling constant according to  $A_{\text{eff}} = 1/3 A_{\text{Li}(1)} + 2/3 A_{\text{Li}(2)}$ . If we follow the theory that  $A_{\text{Li}(1)}$  and  $A_{\text{Li}(2)}$  have opposite signs,  $A_{\text{eff}}$  takes the value of  $4.7 \pm 2$  kHz which is in excellent agreement with the experimental value of

$$3.5 \pm 0.3 \text{ kHz}$$

at 500 K.

**5. Measurement of the spin-lattice relaxation rate  $\Gamma_1$ .** — The spin-lattice relaxation rates  $\Gamma_1$  are dependent from temperature, external magnetic field and its orientation to the crystal axes. Furtheron especially at lower temperatures the rates increase strongly with defect concentration in the samples investigated. Restricting ourselves here to the results from one sample and the orientation  $\mathbf{H}_0 \perp \mathbf{c}$  figure 3 shows  $\Gamma_1$  against the reciprocal temperature.

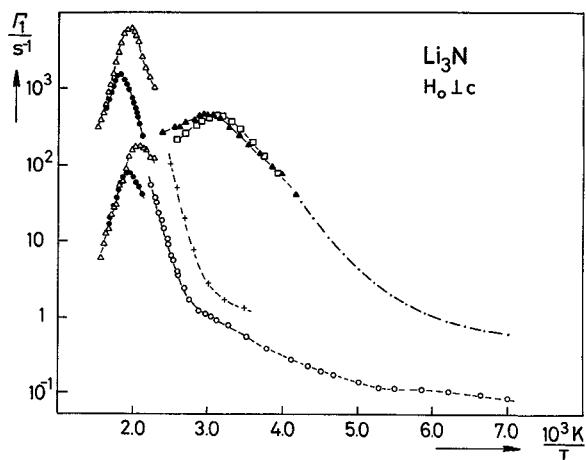


Fig. 3. — Spin-lattice relaxation rate  $\Gamma_1$  of  ${}^7\text{Li}$  as a function of reciprocal temperature, orientation  $H_0 \perp c$ , sample 113. Broadband excitation 34.5 MHz (●, ○), 8 MHz (Δ, +); narrow-band excitation on the central lines 34.5 MHz (□) and 8 MHz (▲). The dotted-dashed line are results from other samples.

As stated in the last section above 490 K the exchange between all Li ions is so fast, that one effective spin system has to be considered. The dipolar

interaction can be neglected. The spin-lattice relaxation is determined only by quadrupolar interaction of the quadrupole moment of the  ${}^7\text{Li}$  nuclei with the fluctuating electric field gradient and can be described by two relaxation rates  $\Gamma_{11}, \Gamma_{12}$ . The magnitude of the relaxation maxima nearby 500 K and the orientation dependence of both relaxation rates on the high temperature side of these maxima can be calculated and yield a satisfying agreement with experimental data previously published [12]. In a first attempt we used exponential correlation functions to analyse the temperature dependence of the relaxation rates. We obtained jump frequencies of the  ${}^7\text{Li}$  nuclei which agree well with the inter-layer diffusion process. Activation enthalpies range from 0.63 to 0.82 eV and are probably temperature dependent.

The highly complex relaxation behaviour below 450 K strongly depends on the initial conditions.

If all resonance lines are saturated together by a pulse-sequence they recover their equilibrium magnetization very slowly but with almost the same time constant for central line and satellites. This relaxation process (low relaxation rate in figure 3) comes up from (i) quadrupolar interaction showing an almost regular frequency dependence and (i) interactions with paramagnetic impurities.

If a narrow band RF-pulse is applied to the two central lines or to one of the satellite lines tipping the associated magnetization through an angle  $\pi/2$  or  $\pi$  we observe at least two relaxation rates at each resonance line, a faster one, which yield relaxation maxima nearby 300 K and a lower one practically identical to the relaxation rate of the saturation experiments. The fast relaxation rate shows an unfamiliar behaviour because it does not depend on frequency. We found that it is caused by dipolar interactions between the  ${}^7\text{Li}$  spins and that the relaxation maxima is nearby  $\omega_Q \cdot \tau = 1$  where  $\omega_Q$  is the frequency difference of the resonance lines involved and  $\tau$  the reciprocal jump frequency of the Li nuclei. The activation enthalpy and the jump frequencies determined from this relaxation process are in good agreement with the motional narrowing data and confirm the intra-layer diffusion process.

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