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Nuclear-magnetic-resonance evidence for a new phase induced by pressure in the superionic conductor Li_3N

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By investigating the ^7Li quadrupolar NMR spectrum in a Li_3N single crystal at hydrostatic pressures up to 7 kbar we have detected a new phase which is pressure induced with a transition pressure of 4.2 kbar at 300 K. The new phase is stable at normal pressure at least for several months. Two inequivalent Li sites were found with quadrupole coupling constants 406 and 164 kHz, respectively. Spine-lattice relaxation and linewidth studies indicate that the Li mobility is higher in the pressure-induced new phase than in the normal *P*6/*mmm* phase.

I. INTRODUCTION

Because of its relatively simple structure, lithium nitride, Li_3N, serves as a model substance for studying fundamental questions in superionic conductors. Li_3N crystallizes in space group *P*6/*mmm*. The N atom is coordinated by six Li(2) atoms in a hexagonal Li_2N plane plus a Li(1) atom occupying a central site in the elementary cell on each side above and below the Li_2N plane.

In the past we have performed at normal pressure extensive NMR investigations[1-3] of Li_3N to study the Li diffusion processes. Using pressure as a variable in addition to temperature can help in trying to understand the mechanisms of ionic conduction[4] and may lead to the detection of new phases as we have shown[5] in the case of $RbAg_4I_5$. In this report we present results of a NMR study of Li_3N at hydrostatic pressures up to 7 kbar and, in particular, we would like to call attention to the detection of a pressure-induced phase transition at 4.2 kbar and 300 K. A brief account of our work has been given previously.[6]

II. EXPERIMENTAL PROCEDURE

As in our previous studies[1,2] a Czochralski-grown single crystal was used which we obtained from the Max-Planck-Institut für Festkörperforschung, Stuttgart. The ^7Li NMR spectra were observed with pulse spectrometers employing magnetic fields of 2.1 and 5.2 T. The spin-lattice relaxation time T_1 was measured by the conventional saturation method. The high-pressure investigations using He as the pressure transmitting medium were performed in a beryllium-copper NMR probe head described elsewhere.[7]

We have carried out the following types of experiments with the ^7Li nuclei: observation of the spectrum as a function of pressure and measurement of the quadrupole coupling constants, the spin-lattice relaxation time T_1, and the linewidth Δ in the pressure-induced phase after recovering this phase at normal pressure. We are going to discuss these static and dynamic properties separately.

III. PRESSURE DEPENDENCE OF Li SPECTRUM

Owing to electric quadrupole interaction the spin-3/2 ^7Li spectrum in normal Li_3N arising from Li(1) and Li(2) sites, respectively, consists of one central and two satellite lines. Since the quadrupole interaction is small with respect to the Zeeman interaction, the two central lines, being shifted only in second order, strongly overlap. At room temperature the ^7Li quadrupole coupling constants which have been determined previously[3,8] are $eQV_{zz}/h = 582 \pm 3$ kHz for Li(1) and 284 ± 1 kHz for Li(2), where V_{zz} is the principal component of the electric-field-gradient (EFG) tensor along the symmetry axis which is parallel to the hexagonal *c* axis.

The pressure dependence of the Li spectrum has been measured at room temperature for a crystal orientation where the *c* axis is parallel to the external magnetic field. Up to 4.2 kbar, the spectrum does not change with pressure. At higher pressure, however, new signals appear whose intensities increase with rising pressure while the intensity of the "old" spectrum (belonging to the *P*6/*mmm* structure) gradually decreases. As an example, the intensity loss of the satellite signals of the "old" spectrum is shown in Fig. 1. At 7 kbar only 2% of the intensi-

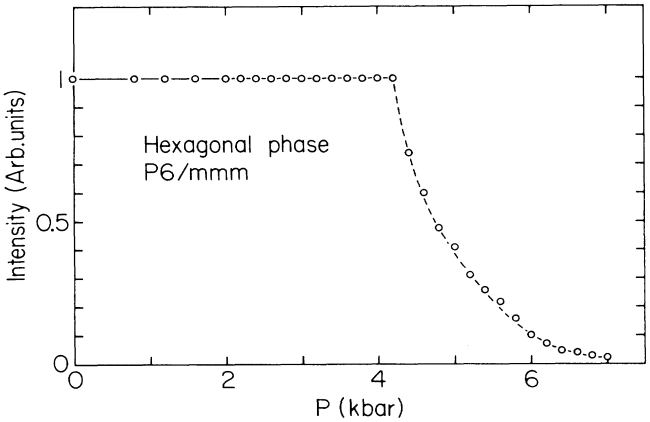

FIG. 1. Pressure dependence of the intensity (in arbitrary units) of the ^7Li satellite signals in Li_3N at 297 K.

ty of the total spectrum belongs to the *P*6/*mmm* structure. We thus conclude that normal Li_3N transforms into a new pressure-induced phase at 4.2 kbar and 300 K. The new phase can be recovered at normal pressure and is stable for at least several months. Annealing the crystal at elevated temperatures and normal pressure, for instance at 650 K for one day, restores the original *P*6/*mmm* phase at least partly.

IV. Li ELECTRIC-FIELD-GRADIENT TENSORS

In order to determine the EFG tensors at the Li sites in the new phase we have measured the shift of the satellite lines with respect to the Larmor frequency ν_L as a function of orientation at room temperature and normal pressure. Two so-called rotations have been performed, one with the rotation axis being perpendicular to both the *c* axis (of the *P*6/*mmm* structure) and the magnetic field B_0, the other with the rotation axis being parallel to the *c* axis and perpendicular to B_0 (Fig. 2). According to standard theory of quadrupole splitting of NMR lines in high magnetic fields,[9] the shift of the Li satellite lines is given by

$$\nu-\nu_L=\pm\tfrac{1}{4}(eQV_{zz}/h)(3\cos^2\Phi-1)+\tfrac{3}{8}(eQV_{zz}/h)^2\nu_L^{-1}\cos^2\Phi\sin^2\Phi \qquad (1)$$

provided the EFG tensor is axially symmetric; Φ is the angle between B_0 and the symmetry axis of the tensor.

The horizontal dashed lines in Fig. 2 denote the positions of the satellites of the "old" spectrum which do not shift with rotation because $\Phi=90°$ for this rotation pattern. A few points at these positions arising from remnants of the *P*6/*mmm* structure can be found. With the exception of only a few unidentified points, all the remaining points of Fig. 2 which correspond to the new structure can be comprised in six pairs of satellites (denoted by solid curves) with V_{zz} directions perpendicular to the *c* axis. Since the curves of Fig. 2 are arranged in groups of two pairs, each having the same phase but different "amplitude," the V_{zz} directions must be pairwise parallel. Since the rotation pattern shows a 120° periodicity the V_{zz} axes are arranged with threefold rotational symmetry in the plane perpendicular to the *c* axis with two axes each pointing into the same direction. The solid lines in Fig. 2 are fits of Eq. (1) to the data points using the quadrupolar coupling constants $eQV_{zz}/h=164$ and 406 kHz, respectively. Since the absolute sign of the EFG tensor components cannot be determined by our NMR experiment, the true symmetry of the V_{zz} axes rotation pattern could be 6 rather than 3. The signals associated with the smaller coupling constant are twice as intense as those of the larger constant.

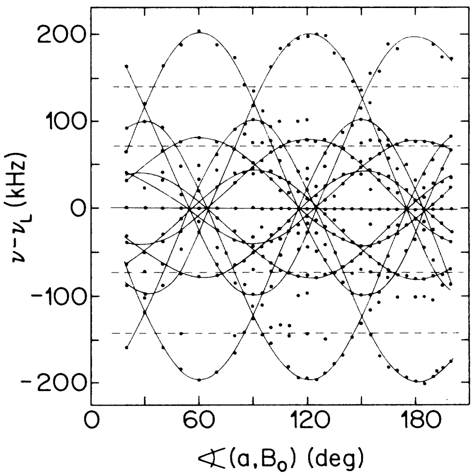

FIG. 2. Shift of the ^{7}Li satellite signals with respect to the Larmor frequency in the pressure-induced phase of Li_3N as a function of the angle between the *a* axis of the *P*6/*mmm* structure and the external field B_0. The *c* axis is always perpendicular to B_0. Dashed lines denote the corresponding rotation pattern in the normal phase. The solid curves are fits of Eq. (1) to the data.

Since the EFG tensors are axially symmetric, an *n*-fold rotation axis with $n>2$ must pass through the corresponding Li sites.[9] Thus our spectra require the existence of a hexagonal arrangement of *n*-fold rotation axes ($n>2$) in the plane perpendicular to the "old" *c* axis. Since such an ensemble of symmetry elements does not form a space group, we conclude that at the pressure-induced phase transition domains rather than a single phase are formed, these domains being arranged in a hexagonal symmetry pattern around the *c* axis. Within each domain there are two inequivalent Li sites having V_{zz} axes parallel to each other and perpendicular to the *c* axis.

V. RELAXATION TIMES AND LINEWIDTH

We have measured the spin-lattice relaxation rate $1/T_1$ of the ^{7}Li central signal in the pressure-induced new phase after recovering this phase at normal pressure. The relaxation shows a slight deviation from exponential behavior which could be caused by a distribution of T_1 values due to the presence of differently oriented domains. The T_1 values quoted are the times at which the magnetization has decayed to $1/e$ of its initial value.

At 300 K the relaxation depends only slightly on the angle between the old *c* axis and B_0, the maximum variation

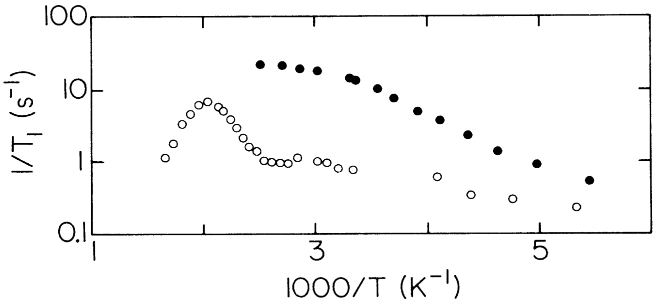

FIG. 3. Spin-lattice relaxation rate of ^{7}Li vs reciprocal temperature in the normal ○ and in the pressure-induced phase (●) at 35.0 MHz and $c \parallel \mathbf{B}_0$.

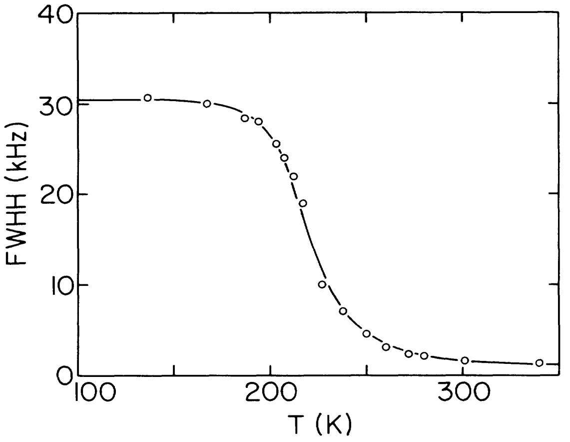

FIG. 4. Temperature dependence of the full width at half height (FWHH) of the ^{7}Li central signal in the pressure-induced phase at 35 MHz and $c \parallel \mathbf{B}_0$.

being about ±10%. All further measurements of the temperature dependence of the relaxation rate were performed with the magnetic field (2.1 T) being parallel to the c axis (Fig. 3). Measurements in the new phase were done only up to about 400 K in order to avoid a transformation of the crystal back into the normal structure.

For comparison Fig. 3 also shows the ^{7}Li relaxation rates in the *P*6/*mmm* phase for the same orientation. The relaxation below about 400 K exhibiting no strong dependence on orientation has been attributed[1] to vacancy-induced Li diffusion within Li_2N layers. The enhancement of this rate in the new structure by more than one order of magnitude is taken as evidence for an increased ionic conductivity. This conclusion is further supported by the motional narrowing of the central signal linewidth (Fig. 4). Standard expressions were fitted to the data,[10] yielding an activation energy of 0.22 eV for the Li movements. Since this value is smaller than the 0.25 eV obtained in the *P*6/*mmm* structure[11] we conclude that the Li mobility increases at the pressure-induced phase transition.

VI. SUMMARY

By applying a hydrostatic pressure of 4.2 kbar at 300 K the normal *P*6/*mmm* structure of Li_3N can be transformed into a new phase which can be recovered at normal pressure. Although the crystal structure of the new phase is not yet known,[12] NMR relaxation and linewidth measurements indicate an increased Li mobility in the new phase. This could be important for technological applications.

As in the *P*6/*mmm* structure the pressure-induced new structure contains two inequivalent Li sites we may call Li(1) and Li(2) having a multiplicity ratio of $\frac{1}{2}$. The point group symmetries are at least 3 as in the normal phase. Surprisingly, the Li point group rotation axes in the new structure are at right angles to those of the *P*6/*mmm* structure and their quadrupolar coupling constants eQV_{zz}/h are drastically reduced from 582 and 285 kHz to 406 and 164 kHz. Thus considerable structural changes must be associated with the phase transition. Whether this transition involves the formation of a large number of crystalline defects as in PbF_2 which can also be recovered at normal pressure[4] remains to be shown.

ACKNOWLEDGMENT

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