

Preparation and Crystal Structure of Ordered and Disordered Lithium Nitride Dichloride, Li_5NCl_2

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Received August 23, 1996; in revised form January 14, 1997; accepted January 15, 1997

A previously unknown ordered low-temperature phase $\text{Li}_5\text{NCl}_2\text{-II}$ has been obtained from the disordered high-temperature phase $\text{Li}_5\text{NCl}_2\text{-I}$ by slow cooling ($100^\circ/\text{h}$), while prolonged annealing at 400°C resulted in a decomposition to Li_4NCl and LiCl . Neutron powder diffraction data were collected for both compounds and analyzed by the Rietveld method of profile refinement. $\text{Li}_5\text{NCl}_2\text{-II}$ crystallizes in the hexagonal rhombohedral space group $R\bar{3}m$, $a = 366.10$ (3), $c = 2851.6$ (3) pm with three formula units per unit cell. Its structure may be regarded as composed of lithium nitride-like $[\text{Li}_4\text{N}]^+$ layers and rock-salt-like $[\text{LiCl}_2]^-$ double-layers, stacked along the hexagonal c axis. A redetermination of the Li_2O -type structure of $\text{Li}_5\text{NCl}_2\text{-I}$ indicates the presence of N–Cl short-range order. © 1997 Academic Press

INTRODUCTION

Lithium nitride halogenides, $\text{Li}_{3-2x}\text{N}_{1-x}\text{Hal}_x$ ($\text{Hal} = \text{Cl}, \text{Br}, \text{I}$), provide the opportunity to study systematically the structure of complex lithium compounds of nitrogen. The lithium nitride halogenides were first reported in 1964 (1–3) and were investigated as possible Li-ion conductors in (4–7). However, only recently have they been characterized structurally by neutron powder diffraction (8–10). They all contain ordered N–Hal arrangements and N–Li sublattices, which generally are closely related to that of the Li_3N parent compound. The only exception is the title compound for which a (cation and anion disordered) Li_2O -type structure was originally reported (2). However, this anion disorder should be unfavourable at lower temperatures due to different formal charges and sizes of N^{3-} and Cl^- (radii of 150 and 180 pm, respectively, assuming ionic bonding). Therefore, an ordered low-temperature phase could be expected.

In the present work an attempt is made to determine the accurate stoichiometry of the title compound and to

determine the structure of an (up to now) unknown low-temperature phase $\text{Li}_5\text{NCl}_2\text{-II}$ by neutron powder diffraction. In addition, the structure of the disordered phase $\text{Li}_5\text{NCl}_2\text{-I}$ was redetermined looking for possible short-range order.

EXPERIMENTAL

Sample Preparation

$\text{Li}_5\text{NCl}_2\text{-I}$ was prepared from Li_3N and LiCl in a solid state reaction (2). Stoichiometric amounts of the educts were intimately ground using an agate mortar or, in one case, a ball mill, transferred into a cup of wrought iron, covered by a lid, and heated to a temperature of 450°C for 1 day under Ar. The reaction product was quenched by removing from the furnace, carefully reground, and heated again. Depending on the grain size of the starting materials, this procedure was repeated several times for complete reaction.¹

$\text{Li}_5\text{NCl}_2\text{-II}$ was prepared from $\text{Li}_5\text{NCl}_2\text{-I}$ by an annealing procedure involving the moderately fast ($100^\circ/\text{h}$) cooling of high-temperature material from 400°C down to room temperature. Alternatively, $\text{Li}_5\text{NCl}_2\text{-I}$ was kept at 400°C for short times (1/2 h) or kept at temperatures between 350 and 300°C for 12 up to 72 h. In any case the reaction product contained traces of Li_4NCl and LiCl .

LiCl (Merck, reinst) was further purified by melting, rinsing with HCl , and filtering *in vacuo* to remove any traces of LiOH and water. This procedure has been described earlier (11).

¹ In the original work on lithium nitride halogenides (2, 3) the stoichiometry of the title compound was assigned as $\text{Li}_5\text{N}_2\text{Cl}_3$. Our experiments however show that this composition does not lead to a single-phase reaction product.

Li_3N was prepared from Li (Aldrich 99.9%) and N_2 (Linde, 5.0) using Na as a solvent (12).

All reaction products, as well as LiCl and Li_3N , are sensitive to moisture and also to oxygen at higher temperatures. All manipulations were thus carried out under Ar gas (O_2 and H_2O impurities below 1 ppm). Each glass and metal apparatus was carefully heated *in vacuo* before use. The reaction products obtained were characterized optically (stereoloupe) and by X-ray diffraction using the Guinier–Simon technique (samples were ground, filled in glass capillaries, and sealed).

Annealing Experiments

In order to characterize the $\text{Li}_5\text{NCl}_2\text{-I} \rightleftharpoons \text{Li}_5\text{NCl}_2\text{-II}$ transition in a first set of annealing experiments, $\text{Li}_5\text{NCl}_2\text{-I}$ was heated to 400°C and quenched to room temperature after 8, 30, 120, and 480 min, respectively, to remove a small amount of the reaction product for XRD characterization. In a second set a sample of $\text{Li}_5\text{NCl}_2\text{-I}$ was heated for typically 8 h. After quenching, the reaction product was characterized by X rays. The sample was then reheated to 450°C for 15 h to obtain the high-temperature phase. In this way annealing was performed at 200, 300, 325, 350, 375, and 395°C , respectively.

STRUCTURE DETERMINATION

Data Collection

The neutron powder diffraction experiments were carried out using the flat-cone and powder diffractometer E2 at the rebuilt research reactor BERII, Hahn-Meitner-Institut Berlin. Data were collected in the 2θ range 20° – 100° ($\lambda = 121.6$ pm). Experimental details are summarized in Tables 1 and 2. Additional X-ray powder diffraction data were recorded for $\text{Li}_5\text{NCl}_2\text{-II}$ using a Stoe powder diffractometer STADI/P; data were collected in the 2θ range 27° – 100° ($\text{CuK}\alpha_1$ radiation).

Data Analysis

Li₅NCl₂-II. The structure determination proved to be straightforward in the case of $\text{Li}_5\text{NCl}_2\text{-II}$. The unknown lattice parameters were first determined and refined (automatic indexing (13), intensity-only refinement (14, 15)) using the X-ray data. $\text{Li}_5\text{NCl}_2\text{-II}$ crystallizes hexagonal rhombohedrally, $a = 366.10(3)$, $c = 2851.6(3)$ pm, $V = 331.0(6)$ pm³, and contains three formula units per unit cell (compare the Li_5NCl_2 molecular volume of 110 pm³ calculated from the ion increments). Analysis of observed reflections does not reveal any further systematic absences. Thus possible space groups are restricted to $R\bar{3}m$ and (rhombohedral) subgroups. An inspection of the fitted profile shows that the

TABLE 1
Experimental Details and Crystallographic Data for the Neutron Powder Diffraction Experiment on $\text{Li}_5\text{NCl}_2\text{-LT}$

Instrument	Flat-cone and powder diffractometer
Monochromator	Ge
Plane of reflection	(311)
Wavelength [pm]	121.57 ^a
Collimator in front of monochromator	10'
Collection time [h]	19
2θ range [$^\circ$]	20–97
Step size [$^\circ$]	0.1
Phase I	$\text{Li}_5\text{NCl}_2\text{-LT}$
Space group	$R\bar{3}m$
Z	3
a [pm]	366.10(3)
c [pm]	2851.6(3)
V [10 ⁶ pm ³]	331.0(6)
Number of reflections	110
Number of refined structural parameters	8
Number of refined profile parameters	15
R ₁	3.8
R _{wp}	4.2
R _e	2.0
Phase II	Li_4NCl
Space group	$R\bar{3}m$
Z	3
a [pm]	366.7(3)
c [pm]	1972(3)
V [10 ⁶ pm ³]	229.7(7)
Number of reflections	79
Number of refined structural parameters	4
Number of refined profile parameters	3
R ₁	7.2
Phase III	LiCl
Space group	$Fm\bar{3}m$
Z	4
a [pm]	514(1)
V [10 ⁶ pm ³]	135.9(8)
Number of reflections	16
Number of refined structural parameters	2
Number of refined profile parameters	2
R ₁	8.4

^aThis accurate neutron wavelength was determined during the Rietveld refinement by assuming a rough value and refining the already properly known cell parameters (X-ray data).

sample is impure and contains small amounts of LiCl and Li_4NCl . A starting model for the unknown structure was derived by exploiting the close structural relationship between $\text{Li}_5\text{NCl}_2\text{-II}$ and the parent compounds Li_3N and LiCl (hexagonal setting) as indicated by the almost identical *a*-lattice parameters a (Li_3N) = 364.8 (16), $a(\text{LiCl})$ = 363.4 (17), $a(\text{Li}_5\text{NCl}_2)$ = 366.1 pm. For this purpose Li_3N was assumed to be composed of layers of Li_4N^+ and Li_2N^- (Fig. 1). Let Li_4N^+ units and Cl–Li–Cl double layers be stacked along the hexagonal *c* axis. Out of several possible stacking sequences $\text{N}_0^A\text{Cl}_{0.11}^C\text{Cl}_{0.22}^A\text{N}_{1/3}^C\text{Cl}_{0.44}^B\text{Cl}_{0.55}^C\text{N}_{2/3}^B$

TABLE 2
Experimental Details and Crystallographic Data for the
Neutron Powder Diffraction Experiment on $\text{Li}_5\text{NCl}_2\text{-HT}$

Instrument	Flat-cone and powder diffractometer
Monochromator	Ge
Plane of reflection	(311)
Wavelength [pm]	121.57
Collimator in front of monochromator	10'
Collection time [h]	16
2θ range [°]	20.5–100.5
Step size [°]	0.1
Phase I	$\text{Li}_5\text{NCl}_2\text{-HT}$
Space group	$Fm\bar{3}m$
Z	4
a [pm]	541.60(3)
V [10^6 pm ³]	158.86(2)
Number of reflections	18
Number of refined structural parameters	3
Number of refined profile parameters	15
R_1	3.0
R_{wp}	4.1
R_c	2.4
Phase II	LiCl
Space group	$Fm\bar{3}m$
Z	4
a [pm]	515.7(4)
V [10^6 pm ³]	137.1(3)
Number of reflections	16
Number of refined structural parameters	2
Number of refined profile parameters	2
R_1	33

$\text{Cl}_{0.77}^{\text{A}}\text{Cl}_{0.88}^{\text{B}}\text{N}_0^{\text{A}}$ is chosen which allows a rock-salt-type octahedral coordination of Cl and Li situated between the chlorine layers. Using this model, a three-phase Rietveld refinement (18, 19) was carried out using the neutron data (Fig. 2, Table 1) leading to an R_1 value of 3.8% in the space group $R\bar{3}m$ (Table 1). No attempt was made to refine the structure in a lower symmetry space group. The final structural model involves isotropic displacement parameters for each atom (Table 3). The strong absorption caused by ^6Li

TABLE 3
Atomic Coordinates and Isotropic Temperature Factors for
 $\text{Li}_5\text{NCl}_2\text{-LT}$ (Neutron Powder Data)

Atoms	In	x/a	y/b	z/c	U [pm ²]
N	3a	0	0	0	71(18)
Cl	6c	0	0	0.2182(2)	60(16)
Li1	6c	0	0	0.6789(11)	241(39)
Li2	6c	0	0	0.0683(11)	252(35)
Li3	3b	0	0	1/2	165(65)

was accounted for by a cylindrical sample absorption correction.

$\text{Li}_5\text{NCl}_2\text{-I}$. The HT structure was refined using the model obtained by Sattlegger and Hahn from X-ray data. A two-phase Rietveld refinement (the sample turns out to contain a trace of LiCl) led to an R_1 value of 3.0% (Fig. 3, Table 2). The final structural model has N and Cl atoms in the ratio 1:2 distributed randomly over the sites of a cubic close packed structure, Li atoms randomly occupying 5/6 of all the tetrahedral voids and isotropic displacement parameters for cations and anions (Table 4). An absorption correction was again required.

An attempt was made to analyze the Li distribution within the tetrahedral voids formed by disordered N and Cl atoms. Accordingly, a number of split models were investigated including Li atoms shifted along [001], [111], or $[\bar{1}\bar{1}\bar{1}]$, away from their ideal position at (1/4, 1/4, 1/4) and compared with respect to the R_1 values and Li temperature factors obtained during refinement. The shift was either calculated assuming a Li–N distance of 197 pm or, for the more simple models, refined. For the more sophisticated models comprising several Li sites individual site occupation factors were introduced and refined. In fact the ideal (1/4, 1/4, 1/4) site is not occupied nor is the octahedral (1/2, 1/2, 1/2) site. Instead Li atoms are found shifted along [001], [111], and $[\bar{1}\bar{1}\bar{1}]$. This final structural model is based on 18 reflections observed, includes six

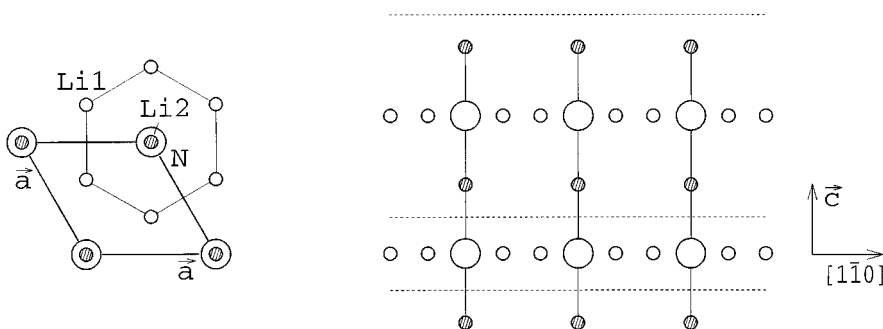


FIG. 1. A schematic view of the Li_3N structure along [001] and [110]. A formal separation in Li_4N^+ and Li_2N^- layers is indicated by broken lines.

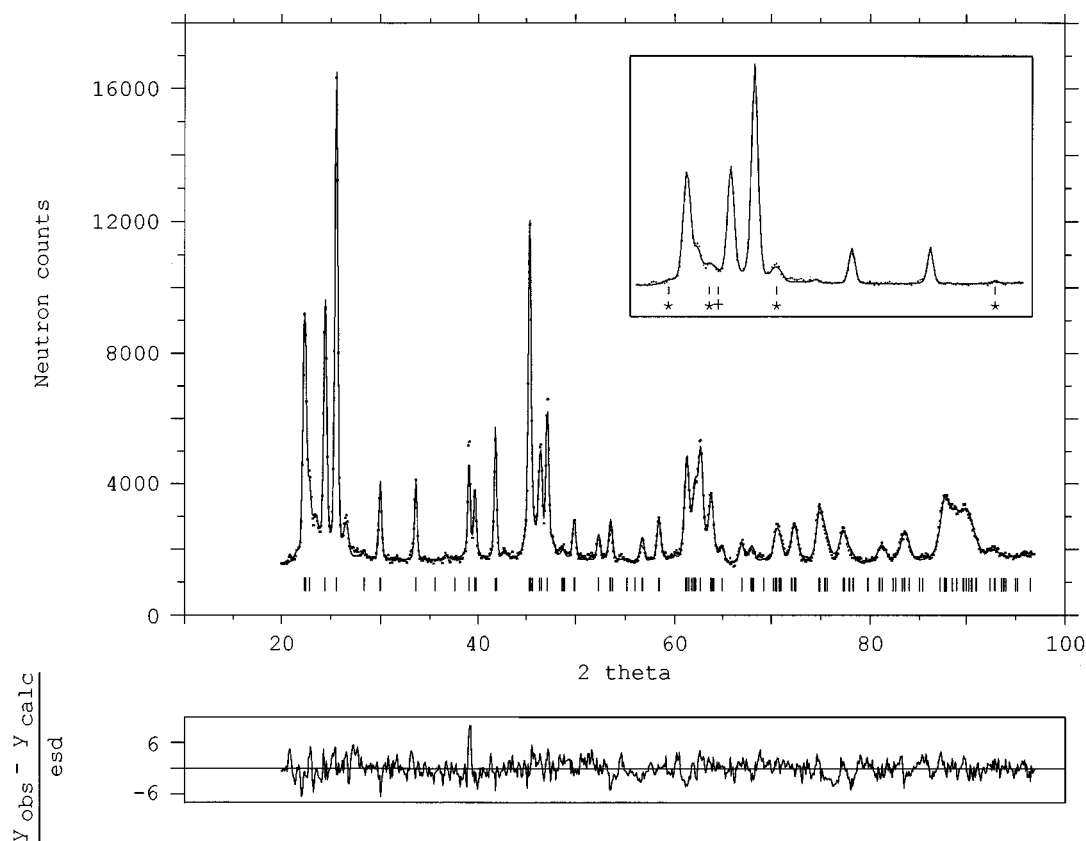


FIG. 2. The observed, calculated, and difference profiles of Li_5NCl_2 -LT. As shown in an enlargement in the upper right corner the sample contains small amounts of Li_4NCl and LiCl (strongest reflections marked by * and +, respectively).

refinable structural parameters, and gave an R_1 value of 2.9% (Table 5).

RESULTS AND DISCUSSION

In the LT structure of Li_5NCl_2 nitrogen and chlorine atoms form a 1:2-ordered variant of a close sphere packing (Fig. 4). Layers of N are separated by two layers of Cl and vice versa. The stacking along the hexagonal c axis, *ABABCBCACA*, is such that each N layer is surrounded by two Cl layers as in cubic close packing, while each Cl layer is surrounded by an N and a Cl layer as in hexagonal close packing. It is thus similar to the stacking in the structure of elemental Sm. Compared to ideal close packing, the N-Cl arrangement is distorted. The Cl-Cl interlayer distance is about 2% shorter and the N-Cl interlayer distance is about 10% larger than the ideal value calculated from the closest intralayer distance. Li is found in three types of coordination. Of the metal atoms, 2/5 (Li1) occupy the roughly triangular voids of the N layers, only slightly shifted toward a neighboring Cl atom along the c axis. Another 2/5 of the Li atoms (Li2) are situated in the tetrahedral holes formed by one N and three Cl, while the rest (Li3) are not attached

to an N atom but are located in the octahedral holes formed by subsequent Cl layers. As a result, nitrogen is in hexagonal bipyramidal coordination by Li. The coordination polyhedron of chlorine is a distorted octahedron with C_{3v} point symmetry. Li_5NCl_2 -II distances and angles are summarized in Table 6. They compare, within three standard deviations, to the corresponding values recently obtained for Li_4NCl (Ref. 20) which shows the same type of structure except that $[\text{LiCl}_2]^-$ is replaced by Cl^- . The geometry within the $[\text{LiCl}_2]^-$ fragment is identical to that of LiCl . Focusing on the Li-N sublattice the cationic $[\text{Li}_4\text{N}]^+$ layer is the characteristic structural unit of the Li_5NCl_2 -II structure. It comprises a (slightly puckered) graphite-like 6^3 net of Li. Further Li atoms are situated exactly above and below the centers of the hexagons which themselves are occupied by N atoms. In this picture the complete Li_5NCl_2 structure may simply be obtained from the LiCl parent compound by replacing every other Li^+ layer along the (111) plane by a Li_4N^+ layer.

Li_5NCl_2 -I has a lithium-oxide-type lattice. N and Cl are disordered over the sites of a cubic close packed structure, while Li is distributed over the tetrahedral voids in such a way that, on average, each site is 5/6 occupied. This Li

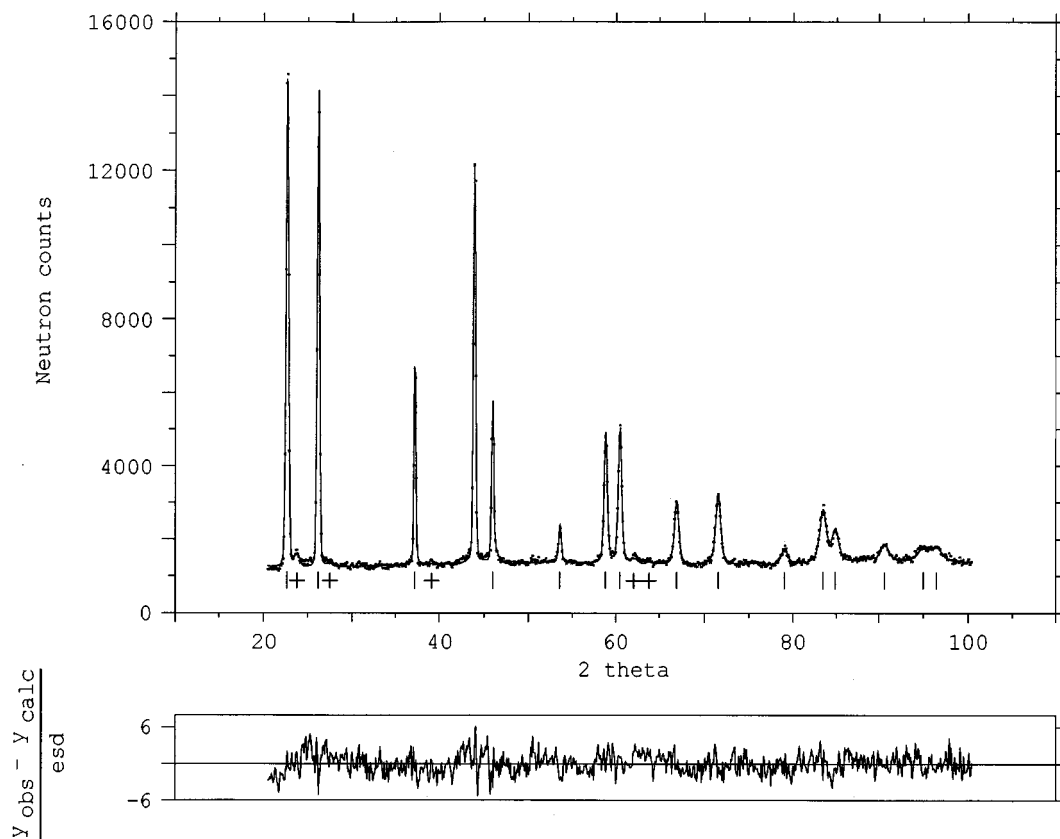


FIG. 3. The observed, calculated, and difference profiles of $\text{Li}_5\text{NCl}_2\text{-HT}$. The sample contains a trace of LiCl (strongest reflections marked by +).

cloud must mask Li atoms with slightly different equilibrium positions, due to the composition and the orientation of their $\text{N}_{4-n}\text{Cl}_n$ coordination polyhedra. Namely, Li atoms unshifted and shifted toward a vertex, an edge, and a face of the tetrahedra could be expected for a Cl_4 , a NCl_3 , a N_2Cl_2 , and a N_3Cl unit, respectively. For a fully randomly distributed N-Cl arrangement these tetrahedra should have the weights 0.2, 0.4, 0.3, and 0.1, respectively. The powder diffraction experiment does not allow the determination of these weights directly. They may, however, be deduced from the accurate Li distribution within a tetrahedral void which is worked out by Li-split models. Table 5 shows that the Li-split sites which correspond to a NCl_3 and a N_3Cl

tetrahedron are favored compared to those which belong to a N_2Cl_2 and a Cl_4 tetrahedron. Therefore one must conclude that Li_5NCl_2 has a N-Cl arrangement which is not

TABLE 4
Atomic Coordinates and Isotropic Temperature Factors for $\text{Li}_5\text{NCl}_2\text{-HT}$ (Neutron Powder Data)

Atoms	In	x/a	y/b	z/c	U [pm^2]	Site
N	4a	0	0	0	174(6)	$1\bar{3}$
Cl	4a	0	0	0	U_{N}	$2\bar{6}$
Li1	8c	1/4	1/4	1/4	1197(35)	6.6

TABLE 5
Atomic Coordinates and Isotropic Temperature Factors for $\text{Li}_5\text{NCl}_2\text{-HT}$ in an Alternative Description by a Three-Site Li-Split Model

Atoms	In	x/a	y/b	z/c	U [pm^2]	Site
N	4a	0	0	0	175(7)	$1\bar{3}$
Cl	4a	0	0	0	U_{N}	$2\bar{6}$
Li1	32f	0.21	0.21	0.21	330(8)	3.2(6)
Li2	32f	0.29	0.29	0.29	U_{Li1}	1.3(3)
Li3	48g	1/4	1/4	0.085	U_{Li1}	2.1(5)

Note. Compared to Table 4 the $(1/4, 1/4, 1/4)$ Li site characterized by its large temperature factor is replaced by the 4-fold split sites Li1 and Li2 and the 6-fold split site Li3, which correspond to a NCl_3 , a N_3Cl , and a N_2Cl_2 coordination polyhedron, respectively. The site occupation factors obtained in course of the Rietveld refinement add up satisfactorily to the theoretical value and are found almost unaffected by the accurate Li atomic coordinates which were chosen by will and kept constant. The (ideal) Li site $(1/4, 1/4, 1/4)$ which corresponds to a Cl_4 coordination polyhedron is found not to be occupied.

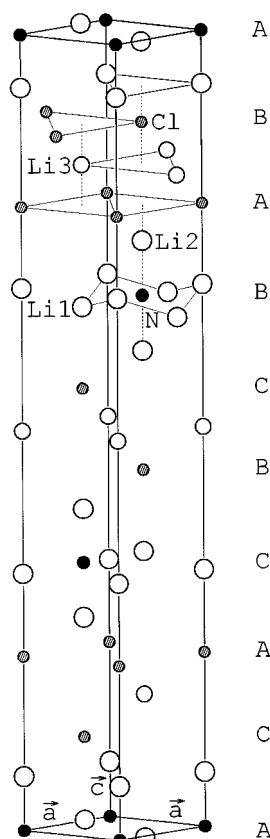


FIG. 4. The Li_5NCl_2 -LT structure. Ellipsoids of 80% probability; A, B, and C note the N-Cl stacking along c ; atoms belong to the coordination spheres of the N, Cl, and Li2, Li3 central atoms grouped together by thin lines.

TABLE 6
Interatomic Distances (μm) and Angles in Li_5NCl_2 -LT

Ni-Li1	*6	214.2(6)	Li2-Cl-Li2	*3	94.1(7) $^\circ$
N-Li2	*2	194.7(34)	Li2-Cl-Li3	*6	87.6(5) $^\circ$
Cl-Li1	*1	293.7(35)	Li3-Cl-Li3	*3	90.7(2) $^\circ$
Cl-Li2	*3	250.1(18)	N-Li1-N	*3	117.4(5)
Cl-Li3	*3	257.4(4)	N-Li1-Cl	*3	96.4(4)
Li1-N-Li1	*6	62.6(4) $^\circ$	N-Li2-Cl	*3	122.3(7)
Li1-N-Li2	*6	117.4(4) $^\circ$	Cl-Li2-Cl	*3	94.1(9)
Li1-N-Li2	*6	80.7(9) $^\circ$	Cl-Li3-Cl	*6	90.7(1)
Li1-N-Li2	*6	99.3(9) $^\circ$	Cl-Li3-Cl	*6	89.3(1)
Li2-N-Li2	*1	180 $^\circ$			

completely random but is dominated by NCl_3 and N_3Cl units. Cl_4 units, if present at all, should not be occupied by Li.

The Temperature Dependence of Li_5NCl_2

The disordered high-temperature phase Li_5NCl_2 -I is obtained from the binary compounds Li_4NCl and LiCl or Li_5NCl_2 -II at 450 $^\circ\text{C}$. It is not stable at temperatures lower than 400 $^\circ\text{C}$. The reaction products depend on temperature, reaction time, and/or rate of cooling in a complicated manner. Despite a number of experiments a fully consistent account of the reaction behavior cannot yet be made although the following conclusions may be drawn: (i) Li_5NCl_2 -I can be obtained metastably at room temperature by quenching (100 $^\circ/\text{min}$). (ii) An order/disorder phase transition to Li_5NCl_2 -II is observed for short annealing times at 400 $^\circ\text{C}$ (30 min). (iii) Li_5NCl_2 -I completely decom-

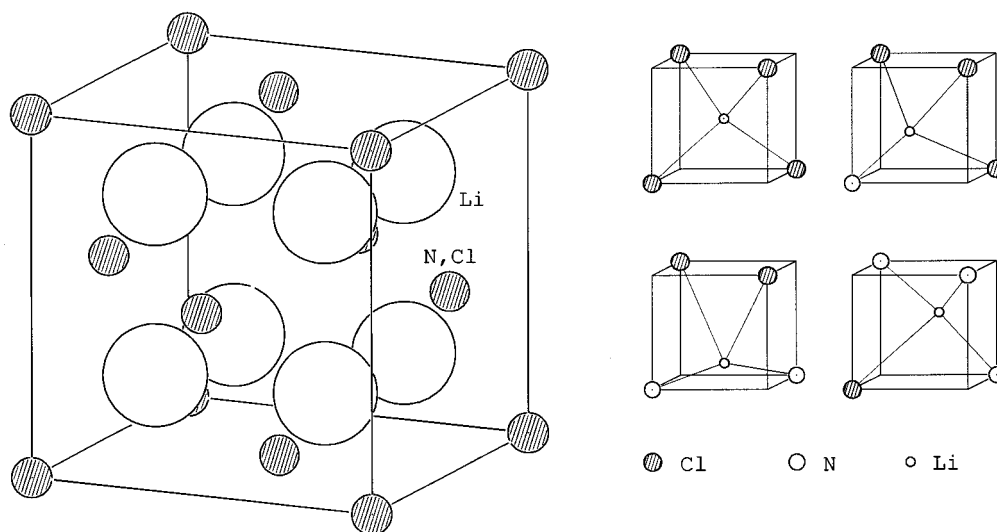


FIG. 5. The Li_2O -type structure of Li_5NCl_2 -HT (ellipsoids of 80% probability). The thermal displacement parameter of Li indicates different equilibrium positions for the metal atom due to the composition of the $\text{N}_{4-n}\text{Cl}_n$ coordination polyhedron (small cubes, only one possible orientation given). As the refinement of various split models shows, a Cl_4 coordination polyhedron is not realized.

poses to Li_4NCl and LiCl for long annealing times at 400°C (8 h). (iv) $\text{Li}_5\text{NCl}_2\text{-II}$ is metastable with respect to a decomposition reaction below 300°C .²

This unusual behavior may be rationalized as follows. It has to be assumed that (at a temperature of 400°C) the free energy of the ordered phase lies between that of the disordered phase and that of the decomposition products. However, while the $\text{Li}_5\text{NCl}_2\text{-II}$ structure is readily adopted by the atoms, the separation into two phases requires long diffusion paths and thus long reaction times. Similar behavior is known from certain metallic alloys, which, splat cooled, form metastable phases (21).

ACKNOWLEDGMENTS

The neutron diffraction experiments were performed at the Berlin Neutron Scattering Center BENSCH using the flat-cone and powder diffractometer E2. E2 is financially supported by the BMFT. The authors thank Prof. Dr. K. Seppelt for kindly supporting this work.

REFERENCES

1. H. Sattlegger and H. Hahn, *Naturwissenschaften* **51**, 534 (1964).
2. H. Sattlegger and H. Hahn, *Z. Anorg. Allg. Chem.* **379**, 293 (1970).
3. H. Sattlegger, Dissertation, Univ. Würzburg, 1964.
4. P. Hartwig, W. Weppner, and W. Wichelhaus, *Mater. Res. Bull.* **14**, 493 (1979).
5. P. Hartwig, W. Weppner, W. Wichelhaus, and A. Rabenau, *Solid State Commun.* **30**, 601 (1979).
6. P. Hartwig, W. Weppner, W. Wichelhaus, and A. Rabenau, *Angew. Chem.* **92**, 72 (1980).
7. P. Hartwig, A. Rabenau, and W. Weppner, *J. Less-Common Met.* **80**, 81 (1981).
8. R. Marx, *Z. Naturforsch. B* **50**, 1061 (1995).
9. R. Marx and H. M. Mayer, *Z. Naturforsch. B* **50**, 1353 (1995).
10. R. Marx and H. M. Mayer, *Z. Naturforsch. B* **51**, in press.
11. C. R. Boston and G. P. Smith, *J. Phys. Chem.* **62**, 409 (1958).
12. M. G. Down, M. J. Haley, P. Hubberstey, R. J. Pulham, and A. E. Thunder, *J. Chem. Soc. (Dalton)*, 1407 (1978).
13. J. W. Visser, *J. Appl. Crystallogr.* **2**, 89 (1969).
14. G. S. Pawley, *J. Appl. Crystallogr.* **14**, 357 (1981).
15. W. I. F. David, "Program CN13LS," ISIS Science Division, Rutherford Appleton Laboratory, Chilton, Didcot, England.
16. A. Rabenau and H. Schultz, *J. Less-Common Met.* **50**, 155 (1976).
17. Swanson and Tatge, *Natl. Bur. Std. Circ.* **539**, 1, 62 (1953).
18. H. M. Rietveld, *J. Appl. Crystallogr.* **2**, 65 (1969).
19. J. Rodriguez-Carvajal, "Program Fullprof," Institut Laue-Langevin, Grenoble, France.
20. R. Marx, *J. Solid State Chem.*, in press.
21. W. B. Pearson, "The Crystal Chemistry and Physics of Metals and Alloys." Wiley-Interscience, New York, 1972.

² An attempt to prepare $\text{Li}_5\text{NCl}_2\text{-II}$ from extremely fine powders of Li_3N and LiCl (ball mill) at 300°C leads to Li_4NCl and LiCl . This shows that Li_5NCl_2 is, although kinetically stable, not thermodynamically stable at 300°C .