Eur. J. Solid State Inorg. Chem. t. 35, 1998, p. 197-209

Time-of-flight neutron diffraction study on lithium dinitride iodide, Li₇N₂I

R. MARX

Freie Universität Berlin, Institut für Anorganische und Analytische Chemie, Fabeckstr. 34/36, 14195 Berlin, Germany

(H. W. R., received February 5, 1998; accepted April 8, 1998.)

ABSTRACT. - The structure of Li₁N₂I has been redetermined from neutron diffraction data using the high resolution powder diffractometer (HRPD) at the spallation source ISIS, UK. The title compound crystallizes in the space group F4 3m (No.216), a=1038.797(1) pm, with eight formula units per unit cell. The Li₁N₂I-structure comprises a cationic Li_{.3}N₄⁺ framework which is built of monocapped octahedra. While all Li atoms at the vertices are shared between two neighbouring units, the capping metal atom is shared by four octahedra. The Li₁₃N₄⁺ network is closely related to the B₂X₆ octahedral framework observed in the pyrochlore structure. Large voids in the structure are occupied by iodide and a Li⁺T ion pair. There is evidence that the nonsphericity of the Li⁺T dipole induces a complicated Lidisorder in the Li-N framework.

INTRODUCTION

Lithium nitride halogenides, $Li_{3-2x}N_{1-x}Hal_x$: Hal=Cl, Br, I, were first reported in 1964 by Sattlegger and Hahn and were subsequently investigated as possible Li-ion-conducting compounds [1-6]. However, their structural characterization was hampered by the lack of single crystals, by the presence of a heavy atom beside the light atom Li, and by the complexity of the powder patterns. In the early work, crystal structures were proposed only for those compounds comprising a cubic unit cell, which includes the title compound. An N₂I anionic arrangement was suggested resembling the structure of the cubic Laves phase Cu,Mg (Figure 1). X-ray powder diffraction did not allow to determine the Li distribution over the 136 tetrahedral holes of the N,I packing. In the present work, the structure of Li,N,I was redeterminated by means of high resolution neutron powder diffraction. An attempt was made to elucidate the Li sublattice, which is essential not only for discussion of ion-conductivity mechanisms, but also to provide insight into the favourable geometries of complex Li-cations of nitrogen (here in the most easy case a pair of Li,N tetrahedra sharing one vertex, Li,N,⁺).



Fig. 1 The Li,N,I structural model based on early X-ray work. I and N occupy the sites of a cubic Laves phase. The two crosses in the lower left corner mark possible Li sites which correspond to the only conceivable ordered Li arrangement since assuming the space group $Fd\bar{3}m$ with the highest possible symmetry.

EXPERIMENTAL DETAILS

Sample preparation

 Li_7N_2I was obtained from Li_3N and dry and OH' free LiI in a solid state reaction. Stoichiometric amounts of the educts were ground, transferred into a cup of wrought iron covered by a lid and heated to 500°C under Ar. After one day the sample was quenched by removing the furnace, carefully reground and heated again. Dependent on the grain size of the powders used this procedure had to be repeated several times to obtain a single-phase reaction product⁴.

LiI, obtained from lithium iodide hydrate (Aldrich, 99%) by slowly heating to 270°C in vacuo was further purified by melting, rinsing with HI and filtering. This procedure has been described earlier [7].

Li₃N was prepared by the reaction of Li (Aldrich 99.9%) and N₂ (Linde 5.0) using Na as a solvent. The metals, mechanically cleaned from crusts, were heated to 400°C for one day under nitrogen. Na was then removed in vacuo at 360°C [8].

 $Li_{7}N_{2}I$, as well as $Li_{3}N$ and LiI is sensitive to moisture, and also to oxygen at higher temperatures. Thus, all manipulations were carried out under Ar (O₂ or H₂O impurities below 1 ppm). Glass and metal apparatus used were carefully heated in vacuo. Reaction products obtained were characterized optically (stereolupe) and by XRD using the Guinier Simon technique (samples ground, filled in glass capillaries and sealed).

Data collection

The neutron diffraction experiment was carried out using the high resolution powder diffractometer (HRPD) at the neutron spallation source ISIS, Rutherford Appleton Laboratory (UK) [9].

HRPD is a time-of-flight (TOF) instrument. It operates with a pulsed polychromatic neutron beam which is generated by the spallation process and is moderated by liquid methane at 100 K. The neutron flux on the instrument ranges from 50 to 1000 pm with a maximum around 200 pm. Neutrons scattered by the sample are recorded by fixed angle ZnS scintillation detectors. Particles of different wavelengths are discriminated by their time of arrival since t~ $1/v_n \sim \lambda_n \sim d$, where t is the neutron time of flight, v_n is the neutron velocity, λ_n is the neutron wavelength and d is the spacing

^a In the original work on lithium nitride halogenides a range of composition Li_{3.2x}N_{1.3}I_x, x: 0.33 \ge x \ge 0.25 was assigned for the title compound. Characterization of samples prepared at 500° and 650°C using X-ray and neutron powder diffraction shows that a single-phase reaction product is obtained only for the stoichiometry Li_{2.33}N_{0.67}I_{0.33}, that is Li₇N₂I.

of the lattice planes. As the instrumental resolution $\Delta d/d\approx 8x10^{-4}$ is not only high but effectively constant over the whole spectrum the powder patterns comprise less overlap at the short d-spacings compared to those obtained by ordinary constant wavelength maschines. HRPD has been shown to be a competitive alternative to conventional single crystal studies [10,11].

Diffraction data collected at ambient temperature for some 16 hours were corrected for neutron flux and detector efficiency which are wavelength dependent. This normalisation procedure is standard and described elsewhere [12]. Sample attenuation effects and remaining background were accounted for as part of the profile refinement procedure.

Data analysis

The normalized data were analysed by the Rietveld method of profile refinement using the local program package for TOF data [13]. Initially an intensity-only or Pawley refinement [14] was performed confirming the face-centered cubic cell suggested by the early x-ray work. Intensities extracted from the long d-spacing section of the powder pattern (49 not completely overlapping reflections in the TOF range from 40 to 150 ms) did not show any further systematic absences. Possible space groups were thus restricted to $Fm\bar{3}m$, $F\bar{4}3m$, F4,32 and subgroups with the same translational symmetry. Of these $F\overline{4}$ 3m was chosen as the most reasonable^{*}. The N-I atomic arrangement given in Figure 1 served as a starting model for the Rietveld refinement. After refining the N atomic coordinate together with an overall temperature factor the Li sublattice was determined. Refinement proceeded via a number of iterative steps: a suitable Li site (for instance a trigonal planar N,I site) was chosen and appropriate atomic coordinates calculated from an estimated Li-N bond length of about 205 pm and (if helpful) a Li-I distance of about 290 pm. This intermediate structural model was then refined. In the case of an increase of the χ^2 value obtained the Li site chosen was rejected, a decrease in χ^2 , on the other hand, was taken as a hint that it was approximately correct^b. Proceeding in this way, three Li sites, constituting 52 out of the 56 atoms, were located, χ^2 decreasing from 20 to 6. At this stage individual isotropic temperature factors were introduced for N and I. The final Li site (Li4) was then located leading to a

^a The space group $Fm\overline{3}m$ and subgroups have to be rejected because the 4-fold axis present does not allow for an atomic arrangement given in Figure 1. F4₁32 however must be regarded as a possible space group which cannot be ruled out from the point of systematic absences. Thus a Rietveld refinement was also carried out in this space group. A convincing structural model, however, was not obtained.

^b $\chi^2 = 1/(N-P+C) \sum_i w_i |Y_i(obs) - Y_i(calc)|^2$; characterizing the quality of the refinement

very slight decrease in χ^2 from 4.0 to 3.9. This part of refinement was concluded by introducing individual temperature factors for all Li atoms. A χ^2 of 3.5 and a R_t of 7.1% was obtained. Inspection of the structural model obtained showed large thermal displacement parameters for Li2 and Li4. Such Li clouds were assumed to hide disordered Li atoms shifted slightly away from their positions on the twofold and threefold axes, respectively. Accordingly in a second part of the refinement procedure, a number of Li split site models were investigated in order to resolve this disorder.

The final structural model involves a twofold split site for Li2 and a twelve fold split site for Li4. A χ^2 of 2.7 and an R₁ value of 4.1% were obtained (Figure 2, Table I, Table II).



Fig. 2 The observed, calculated and difference profiles of Li_1N_1I using HRPD ((a): calculated peak positions for Li_2N_1I ; (b): peak positions for the containment material Ti).

Instrument	HRPD
moderator	liquid methane
total flight path [m]	95.896
2 [°]	168.33
range of time of flight [µs]	25000 - 110000
collection time [h]	16
space group	F 4 3 m
Z	8
a [pm]	1038.797(1)
V [10 ⁶ pm ³]	1120.964(3)
number of reflections	457
number of refined structural parameters	15
number of refined profile parameters	13
RI	4.1
R _{wp}	5.9
Re	3.6

Table I Experimental details and crystallographic data for the neutron powder diffraction experiment on Li_1N_2I at ambient temperature.

Table II Atomic coordinates, site occupation factors and isotropic temperature factors for the Li_1N_2I structure involving a twofold and a twelvefold split site for Li2 and Li4, respectively.

Atom	in	x/a	y/b	z/c	U [pm²]	site
I 1	4a	1/2	1/2	1/2	210(10)	1
I2	4c	3/4	3/4	3/4	280(10)	1
N	16e	0.11882(3)	0.11882(3)	0.11882(3)	108(2)	1
Lil	4b	0	0	0	450(20)	1
Li2	48h	0.0216(2)	0.0216(2)	-0.2123(3)	210(10)	1/2
Li3	24f	1/4 .	1/4	0.0746(3)	230(10)	1
Li4	48h	0.919(1)	0.919(1)	0.857(2)	230(50)	1/12

RESULTS AND DISCUSSION

In the structure of $\text{Li}_{7}N_{2}I$, nitrogen and lithium form a 3d network with the composition $\text{Li}_{13}N_{4}^{*}$. Within this open cationic framework iodide and a Li^{*}T ion pair occupy the voids. The nonsphericity of the Li-I unit induces a complicated Li disorder in the Li-N network.

The Li₁₃N₄⁺ network

The Li-N framework is most easily described by its relationship to the structure of Li_2O . The oxygen arrangement (1) of a Li_2O facecentered cubic cell doubled in each direction may be divided into the subsets (2) and (3). Each of these equivalent subsets contains atoms grouped together into tetrahedra which themselves share all their vertices with neighbouring units. While one of these subsets is not occupied, the other, say (2), provides the sites for the N atoms.



52 of 56 Li atoms per unit cell may be attributed to the Li-N network. All occupy sites which correspond to the tetrahedral voids of the original cubic close packing (1). Four Li atoms (Li1) occupy each next-but-one of the 8 N_4 tetrahedra. 48 Li atoms (Li2, Li3) are situated above the edges of the N_4 tetrahedra. In the case of Li3, the NLiN triangles formed exactly point along the cubic cell edges. Li2 occupying a twofold split site is found to be shifted some 30 pm away from this ideal site.

A Li₇N monocapped octahedral unit is the characteristic building block of the Li-N framework. This unit shares its capping metal atom with four and the atoms at the vertices with one neighbouring entity (Figure 3, for selected



Fig. 3 A schematic view of the Li₂N₃I structure. Monocapped octahedral Li₂N units comprise a pyrochlore type threedimensional network of the composition $\text{Li}_{12}\text{N}_4^*$. Its large cavities are occupied by Γ and Li^T. For simplicity, Li atoms attached to the Li-N framework are given only for the lower left octant of the cubic cell. Li4 atoms attached to the iodine atoms are omitted. The disorder of the Li2 atoms is shown at the lower left corner of the figure by dotted circles. All other Li2 atoms are given at the midpoints between the two split positions.

bondlengths and angles see Table III). Apart from the capping this octahedral framework is essentially that of B and X in the structure of pyrochlore [15], $[A_2X^{\circ}][B_1X_6]$.

L171 21.						
N-Lil	*1*	213.8(0)	N-Li1-N	*6	109.47°	
N-Li2	*3	202.2(2)	N-Li2-N	*1	119.4(2)°	
N-Li3	*3	198.1(1)	N-Li2-11	*2	117.4(1)°	
N-Li4		212.9(12)	N-Li3-N	*1	153.2(2)°	
I1-Li2	*6	300.6(3)	N-Li4-N	*1	110.1(6)°	
I2-Li2	*12	337.9(2)	N-Li4-I2	*2	124.1(6)°	
I2-Li3	*6	337.3(3)	Li1 Li2	*6	222.8(2)	
I2-Li4	*1	271.6(14)	Lil Li4	*1	191(1)	
Li1-N-Li2	*3	64.7(1)°	Li2 Li2	*2	280.1(3)	
Li1-N-Li3	*3	131.3(1)°	Li2 Li4	*1	167(2)	
			Li3 Li3	*2	257.7(3)	

Table III Selected bond lengths (pm), angles and nonbonding Li--Li distances for $Li_{,}N_{,}I_{.}$

* *n denotes how often a distance or angle is found for one given N, I or Li atom.

204



Fig. 4 Part of the Li₁N₂I structure showing the interstitials I and Li^{*}T within the Li₁N₄^{*} framework. For simplicity the disorder of the Li2 atoms is shown only for one atom (upper right corner). The twelvefold orientationally disordered Li^{*}T dipole (d(Li-N): 272(1) pm) is given in only one possible orientation, other orientations are marked by broken circles. Sizes of the Li₆ cavity around (1/2,1/2,1/2) and for the Li₁₈ cavity around (3/4,3/4,3/4) are some 450pm and 530pm, respectively.

The anionic sublattice

Occupation of the tetrahedra midths of sublattice (3) leads to the diamond type lattice (4). (4) gives the centers of the large cavities within the Li-N framework and serves as sites for iodine. Due to the symmetry of the Li-N net, sites at (1/2, 1/2, 1/2) (I1) and at (3/4, 3/4, 3/4) (I2) are not equivalent.

Four of 56 metal atoms (Li4) may be assumed to be attached to the iodine sublattice. I2 and Li4 form an ion pair for which a Li-I distance of 272(1) pm is obtained. This unit is twelvefold orientationally disordered (Table III, Figure 4).

The postulate of a Li⁺I unit and the corresponding distinction between metal atoms attached to nitrogen and others attached to iodine is based mainly on distance considerations summarized in Table IV^a. It is supported by the results from a large number of refinements on slightly different structural models including one with I2 in symmetric two-coordination by Li.

^a A possible systematic error of the I2-Li4 distance estimated to about 10 pm should be noted. It is a paradox, but the accurate positions of the twelvefold disordered Li4 atoms are probably known more accurately than that of the I2 atom. This is because the disorder of the Li4 atom might induce disorder of the I2 atom which is masked by a relatively large isotropic displacement parameter. Attempts to model this possible disorder by applying a fourfold, sixfold or twelvefold split model failed as they did not lead to improved R, values. The same argument applies for I2-Li2 and I2-Li3 distances.

compound	structural unit	bond length [pm]
Li ₇ N ₂ I	I2(Li4)	272(1)
	$I2(Li2)_{12}$	338(0)
	12(Li3) ₆	337(0)
	$(Li4)N_2$	213(1)
LiI (vapour state) [16]	ILi	239(0)
LiI (liquid state) [17]	ILi₄	280
LiI (solid state) [18]	ILi,	300
Li ₁₀ N ₃ Br [19]	LiN ₂	193.6(0), 196.7(7), 208.5(6)

Table IV Evidence for a Li⁺I structural unit from distance considerations.

Li disorder within the Li-N framework

The $Li_{13}N_4$ framework may be formally divided into Li_7N_4 units involving metal atoms Li1 and Li2 and further metal atoms (Li3) interconnecting these units. The $Li_{r}N_{4}$ fragments represent those parts of the Li-N net in the vicinity of the positive ends of the Li⁺¹ dipoles. For simplicity the Li₂N₄ blocks have been described thus far in an ideal form (Figure 5a) ignoring the disorder of the Li2 atoms obtained by refinement (Figure 5b). This disorder over two split positions, some 30 pm away from their ideal sites on the twofold axes, may be explained as due to the nonspherical shape of the Li⁺T unit. Consider a Li⁺T dipole attached to the Li₂N₄ fragment of the Li-N sublattice (Figure 5c). In an ionic picture the six Li2 atoms will experience repulsive forces of different strengths depending on their distance to the Li4 atom. Accordingly, they may be assumed to be redistributed around the N-N edge at a constant Li-N distance. Due to the local C_s symmetry four sites, labelled Li21-Li24, with weights of 1, 2, 2 and 1, respectively, may be expected^a. Averaging over a larger part of the structure and thus allowing for all possible orientations of the Li⁺T unit then would lead to T, molecular symmetry and superposition of all sites Li21 to Li24 across each N-N connection line (Figure 5d). The best and most simple way of modelling such a configuration is the twofold split model given in Figure 5b as it provides averaging over the split positions Li22 and Li23 with the larger weights and neglects the positions Li21 and Li24 with the smaller weights. Despite the excellent quality of the diffraction data all attempts to model a more elaborate scheme of disorder by introducing the Li2 arrangement of Figure 5d, followed by split models for I2 and Li1, were less satisfying as they lead to an improved R, value only for the first step (Table V).

^a In principle similar considerations should apply for Li1 and Li3. Due to larger distances to the Li⁺I dipole shifts of Li3 can be expected to be smaller compared to that of Li2. Li1 shifts, on the other hand, hide behind a large isotropic thermal displacement parameter.

Table V Atomic coordinates and site occupation factors for an elaborate Li sublattice involving a four-site split model (labelling Li21 to Li24) for Li2. Refinement of this sophisticated structural model was performed by applying geometrical constraints compelling uniform Li2i-N bond lengths and an overall temperature factor for Li21 to Li24. An R_1 value of 2.9% was obtained.

Atom	in	x/a	y/b	z/c	site	
Li1	4b	0	0	0	1	
Li21	24f	0	0	-0.2180(4)	1/6	
Li22	48h	0.0133(9)	0.0133(9)	-0.2162(4)	1/6	
Li23	48h	0.0305(7)	0.0305(7)	-0.2084(6)	1/6	
Li24	48h	0.0489(11)	0.0489(11)	-0.1901(15)	1/12	
Li3	24f	1/4	1/4	0.0749(3)	1	
Li4	16e	0.9102(15)	0.9102(15)	0.8797(39)	1/12	



Fig. 5 Interpretation of the Li disorder within the $\text{Li}_{13}\text{N}_4^*$ framework as a result of Li^{*}-Li^{*} repulsion between metal atoms of the Li_,N₄ fragment and the Li^{*}T dipole: **a**) Idealized Li_,N₄ unit. Li2 atoms are given at the midpoints of two split positions; **b**) disordered Li_,N₄ unit with T_a molecular symmetry as obtained by refinement; **c**) Postulated distortion of the Li_,N₄ unit in the vicinity of a Li^{*}T dipole (C_s molecular symmetry; ideal Li2 positions given by broken lines and circles; the Li^{*}T unit given in only one of 12 possible orientations); **d**) Postulated Li distribution across a N-N corner of the Li_,N₄ unit after allowing for all possible Li^{*}T orientations.

EUR. J. SOLID STATE INORG. CHEM.

Ion-conductivity models

As suggested by one of the referees a note is added in how the presented structure fits to possible models for ion transport within Li₂N₂I.

First, there is mentioned the close structural relationship between the Agion-conductors $RbAg_4I_5$ and Ag_7GeS_5I and the Li-ion-conductor Li_7N_2I . The rigid part of these structures formed by rubidium and iodine ($(Rb_4I_{12})I_8$), sulfur and iodine ($S_{16}(S_4I_4)$) and nitrogen and iodine ($N_{16}I_8$), respectively, is a Cu_2Mg type arrangement of atoms. This array consists of 136 tetrahedra which share all their faces with neighbouring units. Ag-ion-conductivity was suggested to take place by a migration of Ag⁺ through a common face from one tetrahedron into a vacant neighbouring tetrahedron [20-22].

Now, it seems possible to elaborate this early conductivity model to be applied to $\text{Li}_7\text{N}_2\text{I}$, taking into account the structural results given in the preceeding. Li-ion transport involving only the Li atoms Li2 and Li4 may be achieved by two distinct processes. The first process could be the motion of a Li4 atom onto a neighbouring Li2 position and simultaneously, motion of the affected Li2 atom onto a second (unoccupied) Li4 position. The other process necessary, would be a reorientational motion of the Li⁺T dipoles. So, after creating the activated centres I and Li₂I⁺ from two Li⁺T units via process one, these centres could travel through the lattice via process one and two. Relevant distances for the Li motions are about 110 pm (Li4--Li2) and about 90 and 410 pm (Li4--Li4; Li⁺T reorientation).

CONCLUSIONS

In the early work on $\text{Li}_7\text{N}_2\text{I}$ using x-ray powder diffraction [1], an ordered and highly symmetric Li-distribution was proposed (Figure 1), corresponding to a $\text{Li}_{14}\text{N}_4^{2+}$ net built of Li_8N rhombohedra. The present neutron diffraction study leaves no doubt that such an arrangement is not realized. Instead, careful data analysis leads to a $\text{Li}_{13}\text{N}_4^+$ net composed of monocapped Li_7N octahedra, beside a Li^+T unit. It must be concluded that, for reasons which at present are not known, such a $\text{Li}_{14}\text{N}_4^{2+}$ net is a less favourable arrangement for a complex Li-cation of nitrogen, then is the $\text{Li}_{13}\text{N}_4^+$ net. For the latter an idealized geometry may be assumed as given in Figure 3. Disorder of Li2 as obtained by refinement should arise from the nonspherical shape of the Li⁺T unit which carries the extra Li atom. The $\text{Li}_{13}\text{N}_4^+$ net may be regarded as a threedimensional analogue to the $\text{Li}_{10}\text{N}_3^+$ Kagomé net realized in $\text{Li}_{10}\text{N}_3\text{Br}$ [19].

The structure of $\text{Li}_7 N_2 I$ is a complicated disordered system. To confirm existence and accurate geometry of the structural features proposed structure determination on an ordered phase would seem most promising. Therefore experiments are planned at low temperature to look for an

томе 35 — 1998 — N° 3

209

order/disorder transition. In addition experiments are planned to investigate ordering by means of chemical substitution.

Acknowledgements. - The author acknowledges Dr. R.M. Ibberson, ISIS science division, Rutherford Appleton Laboratory (UK), and Dr. H.-M. Mayer, Institut für Kristallographie der Universitat Tübingen, c/o Hahn-Meitner-Institut Berlin (Germany) for help with the neutron scattering experiments at HRPD and at the flat-cone and powder diffractometer E2. He would like to thank Prof. Dr. K. Seppelt for kindly supporting this work.

REFERENCES

- [1] H.Sattlegger, H.Hahn, Naturwissenschaften 1964, 51, 534.
- [2] H.Sattlegger, Dissertation 1964, Univ. Würzburg.
- [3] P.Hartwig, W.Weppner, W.Wichelhaus, Mater. Res. Bul. 1979, 14, 493.
- [4] P.Hartwig, W.Weppner, W.Wichelhaus, A.Rabenau, Solid State Commun. 1979, 30, 601.
- [5] P.Hartwig, W.Weppner, W.Wichelhaus, A.Rabenau, Angew. Chem. 1980, 92, 72.
- [6] P.Hartwig, A.Rabenau, W.Weppner, J.Less-Common Metals 1981, 80, 81.
- [7] C.R.Boston, G.P.Smith, J.Phys.Chem. 1958, 62, 409.
- [8] M.G.Down, M.J.Haley, P.Hubberstey, R.J.Pulham, A.E.Thunder, J.Chem.Soc.(Dalton), 1978, 1407.
- [9] W.I.F. David, D.E. Akporiaye, R.M. Ibberson, and C.C. Wilson, Rutherford Appleton Laboratory Report, 1988, RAL-88-103.
- [10] W.I.F. David and J.D. Jorgensen, in R.A. Young (ed.), The Rietveld Method in IUCr Monographs on Crystallography 1993, Oxford Univ., Oxford.
- [11] R. Marx, J. Alloys Compd. 1997, 256, 196.
- [12] R.M. Ibberson, W.I.F. David, and K.S. Knight, Rutherford Appleton Laboratory Report, 1992, RAL-92-031.
- [13] W.I.F. David, R.M. Ibberson, and J.S Mathewman, Rutherford Appleton Laboratory Report, 1992, RAL-92-032.
- [14] G.S. Pawley, J.Appl.Cryst. 1981, 14, 357
- [15] M.A. Subramanian, G. Aravamudan, G.V. Subba Rao, Prog. Solid St. Chem. 1983, 15, 55.
- [16] A. Honig, M. Mandel, M.L. Stitch, C.H. Townes, Phys. Rev. 1954, 96, 629.
- [17] J. Li, J.M. Titman, G.E. Carr, N. Cowlam, J.-B. Suck, *Physica B* 1989, 156&157, 168. [18] Li-I distance in ordinary LiI.
- [19] R. Marx, Z.Naturforsch. 1995, 50b, 1061.
- [20] S. Geller, Science, 1967, 57, 310.
- [21] S. Geller, in W. van Gool (ed.), Fast lon Transport in Solids, 1973, 607, North Holland Publ., Amsterdam.
- [22] B. Cros, M. Laqibi, S. Peytavin, M. Ribes, Rev. Chim. Miner. 1986, 23, 796.