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## Tetragonal low-temperature structure of LiAl

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### Abstract

The cubic face-centered structure of LiAl ( $Fd\bar{3}m$ ,  $a = 6.35971(3)$  Å at 290 K) transforms into a tetragonal body-centered structure ( $I4_1/amd$ ,  $a = 4.47831(1)$  Å,  $c = 6.34435(2)$  Å at 12 K). This first-order phase transition at about 93(2) K during heating is probably the reason for the so-called “100 K anomalies” in some physical properties like specific heat, electrical resistivity and nuclear-spin lattice relaxation. This transition seems to be correlated with the composition Li:Al of the alloy and the amount of Li vacancies.

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### 1. Introduction

The interest in low-weight and high-capacity anode materials for secondary lithium batteries has initiated a detailed investigation of the binary Li–Al system.  $\beta$ -LiAl is one of the seven binary Zintl phases with NaTl-type structure, see Fig. 1, and exists in a composition range from 48% to 55% Li [1]. The phase diagram has been determined from room temperature to melt, including a detailed investigation about increasing delocalization effects and vacancies in the Li sublattice [2], but only one structural study at low-temperature is described in literature [3]. Accordingly, additional satellite reflections at 78 K are observed in neutron diffraction from a single crystal and explained by an ordering of vacancies in a tetragonal superstructure. The anomalies in specific heat [4] and nuclear-spin lattice relaxation [5] at or below 100 K support the assumption of a structural phase transition in this temperature region. However, details of a potential low-temperature structure and the corresponding phase transition are still lacking. Therefore, high-resolution synchrotron diffraction has been performed down to 10 K to elucidate the low-temperature structure of LiAl. The results will be discussed in

the light of the recently reported tetragonal distortion in LiIn at 170(10) K [6].

### 2. Experimental details

Appropriate amounts of metallic lithium (99.9%, Chemetall, Frankfurt) and aluminum (99.999%, Alfa, Karlsruhe) were filled into small tantal crucibles under dry argon atmosphere and mechanically closed with tantal lids. Outside the glove box the crucibles were sealed by argon arc welding. The alloy formation was initiated by heating the crucibles to 800°C within a preheated sand bath, well above the melting point of LiAl at about 700°C. After a few minutes the crucibles were heavily shaken using a pair of tweezers. Annealing at 800°C and successive shaking were repeated several times to guarantee the complete reaction of the educts. The crucibles were cooled down to room temperature rapidly by removing the crucible from the sandbath into ambient conditions. The reaction product is very sensitive to moisture and had to be ground in an agate mortar within a dry glove box for further analyses by X-ray powder diffraction. Several iterations were needed to optimize the overall reaction time for a complete transformation into LiAl without an onset of a reaction between the aggressive molten Al and Ta from the

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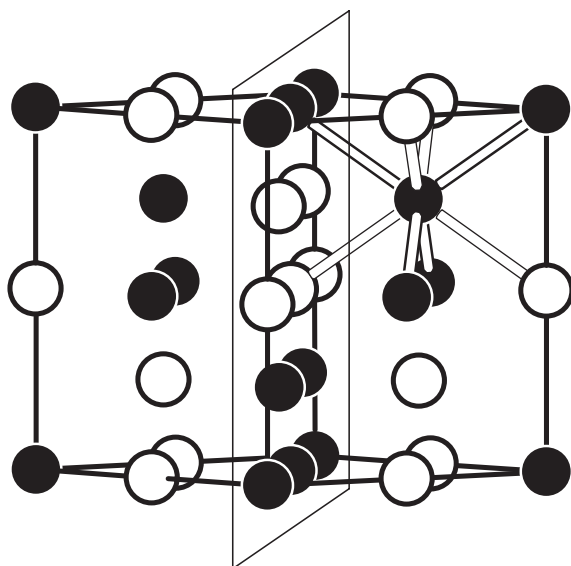


Fig. 1. NaTl-type structure. The first coordination sphere is shown for a representative atom by bonds to the next nearest neighbors. The (110) plane is marked and shows the characteristic sequence along the [001] direction with two successive rows of identical atoms.

crucible. After only 9 min undissolved Al could easily be detected in the slightly ductile reaction product by X-ray diffraction. However, after a total of 15 min reaction time at 800°C, the reaction product came out very brittle and contained only tiny traces of undissolved Al-metal. This sample was then used for further evaluations. High-resolution synchrotron powder diffraction data from such a sample have been recorded at the beamline B2 of the Hamburger Synchrotronstrahlungslabor HASYLAB at DESY, Germany, in Debye–Scherrer mode. Capillaries of 0.3 mm were filled with ground samples and loaded into a closed-cycle cryostat with controlled atmosphere in the sample chamber [7]. The sample was exposed with monochromatic synchrotron radiation of 1.11954 Å wavelength, and diffracted intensities from a rotating capillary have been measured for temperatures between 10 and 290 K using a scintillation counter with an analyzing Ge(111) crystal in front of it. The software package Fullprof [8] was used for the Rietveld refinement of the proposed structure model.

### 3. Results and discussion

A first-order phase transition from the cubic face-centered NaTl-type structure into a tetragonal distorted structure is observed for LiAl. A range of coexistence of both phases is found between 85 and 93 K during heating, see Fig. 2, while the transition from cubic to tetragonal phase during cooling is shifted to slightly

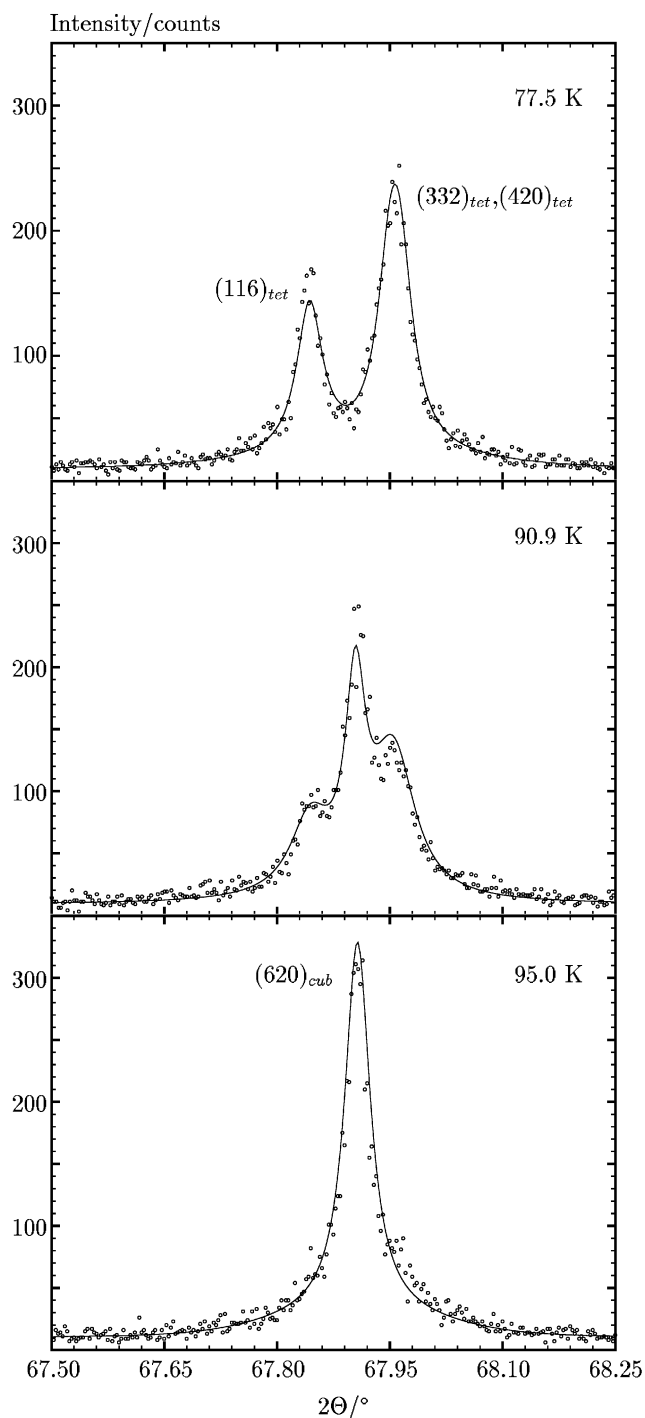


Fig. 2. Coexistence of the tetragonal and cubic phase at 90.9 K (b). The corresponding sections of the patterns are shown for the tetragonal phase at 77.5 K (a) and for the cubic phase at 95 K (c) for comparison. Drawn lines represent profiles as calculated by the Rietveld method.

below 80 K. The same kind of tetragonal distortion as for LiIn is observed, but with a significant lower elongation of the *c*-axis,  $\eta = c/(\sqrt{2}a) = 1.0017$  as compared to 1.0045 for LiIn [6]. The Li and Al atoms occupy the (4*a*) and (4*b*) sites, respectively, in space

group  $I4_1/amd$ . This phase transition is *translationen-gleich*, and only three more structural parameters appear in the low-temperature structure as compared to the cubic NaTl-type structure. The additional structural degrees of freedom are the tetragonal distortion  $\eta$  and anisotropic thermal displacement parameters  $u_{11} \neq u_{33}$  for both the Li- and the Al-site. The structural distortion is shown in Fig. 3 for the (110) plane in the cubic face-centered cell, which becomes the (100) plane in the tetragonal body-centered cell. The slightly compressed Li–Al–Li bond angle is shown, while the simultaneously stretched angle lies in a perpendicular plane. For analytical expressions of changes in bond lengths and angles with the distortion parameter  $\eta$  see [6].

The temperature dependence of lattice parameters is summarized in Table 1 as obtained from Rietveld refinements, based on the synchrotron diffraction data. The discontinuity of the order parameter  $\eta$  clearly reveals the first-order nature of this phase transition, further supported by the observed hysteresis effect and the coexistence range. The tetragonal distortion is merely constant in the stability region of the tetragonal phase, see Fig. 4.

In the earlier neutron diffraction study on a single crystal of LiAl at 78 K [3] the temperature was probably not low enough to transform the cubic phase into the tetragonal one completely, and the minor contributions from a tetragonal phase have been interpreted as satellites related to the ordering of vacancies.

The LiAl-phase with NaTl-type structure is labeled  $\beta$ -LiAl in the phase diagram of the Li–Al system, and

the dependence of the lattice parameter on actual lithium content has been reported for the stability range of  $\beta$ -LiAl from 48 at% Li to 55 at% [9]. Accordingly, our sample has significant Li deficiency and represents a composition very close to the phase boundary, i.e.  $\text{Li}_{0.48}\text{Al}_{0.52}$ . Such a composition shows a significant

Table 1  
Lattice parameters and phase fractions at different temperatures for LiAl

$T$ (K)	$a$ (Å)	$c$ (Å)	$c(a\sqrt{2})$	wt%
11.9(3)	4.47831(1)	6.34484(2)	1.001746(6)	100
25.0(1)	4.47838(2)	6.34436(4)	1.001733(11)	100
39.0(2)	4.47832(2)	6.34430(4)	1.001737(11)	100
49.4(1)	4.47821(3)	6.34420(5)	1.001745(15)	100
57.4(1)	4.47840(3)	6.34435(5)	1.001727(15)	100
62.4(1)	4.47849(3)	6.34452(5)	1.001733(15)	100
67.5(1)	4.47861(2)	6.34467(4)	1.001730(11)	100
71.3(1)	4.47874(2)	6.34480(4)	1.001722(11)	100
74.3(1)	4.47875(2)	6.34487(4)	1.001731(11)	100
77.5(2)	4.47886(2)	6.34505(3)	1.001734(9)	100
84.6(1)	4.47905(2)	6.34511(4)	1.001701(11)	94(1)
90.9(1)	4.47900(6)	6.34496(9)	1.00169(3)	70(3)
84.6(1)		6.33949(6)	1	6(1)
90.9(1)		6.33894(4)	1	30(3)
95.0(1)		6.33871(4)	1	100
104.0(1)		6.33896(3)	1	100
150.0(1)		6.34236(3)	1	100
220.0(1)		6.34950(3)	1	100
290.0(1)		6.35971(3)	1	100

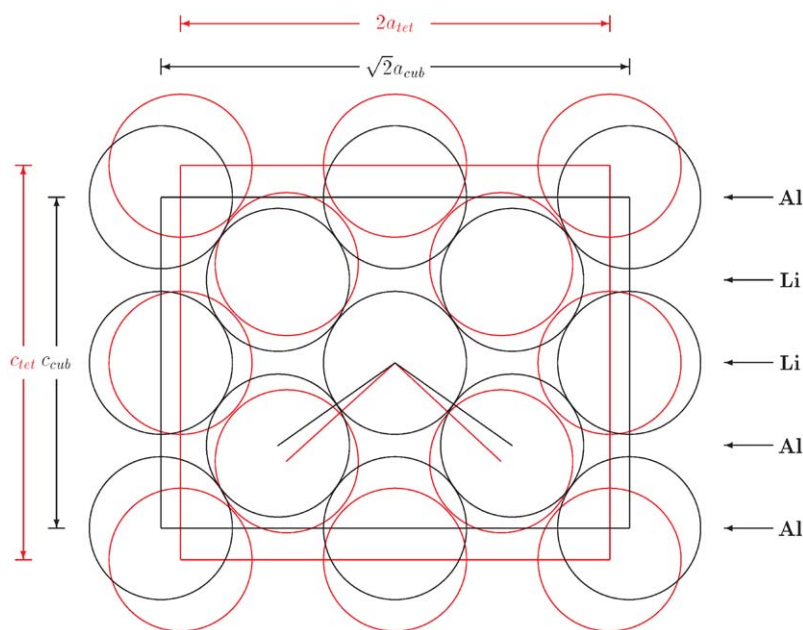


Fig. 3. Transition from the ideal cubic NaTl-type structure into the tetragonal structure of LiAl at low temperature, based on the marked cubic (110) plane in Fig. 1. Note that a tetragonal distortion of  $\eta = 1.3$  at constant cell volume was used for the plot in comparison to the observed value of 1.00172(2), i.e. the effect is overemphasized by a factor of nearly 175.

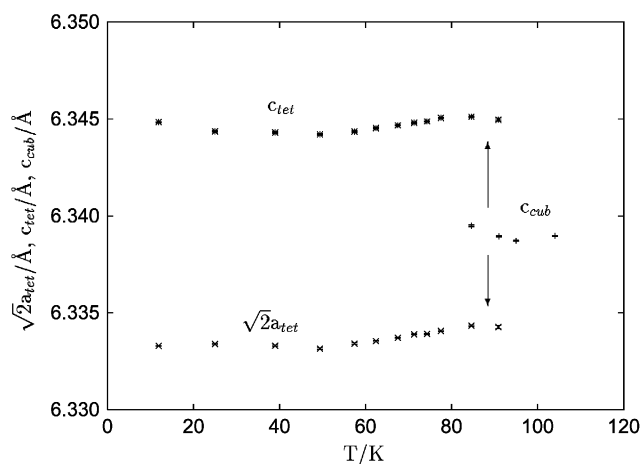


Fig. 4. Temperature dependence of the lattice parameters of LiAl. The tetragonal  $a$ -axis length has been multiplied by  $\sqrt{2}$  for better comparison with the cubic cell.

anomaly in the temperature dependence of the electrical resistivity just below 100 K [10], very well in agreement with the observed structural transition temperature. For compositions closer to 50% Li this anomaly is shifted to lower temperatures, indicating that the structural transition is correlated with Li vacancies.

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## References

- [1] K.M. Myles, F.C. Mrazek, J.A. Smaga, J.L. Settle, Proceedings of the Symposium and Workshop on Advanced Battery Research and Design, U.S.ERDA Report, ANL-76-8, 1976, p. B-50.
- [2] M. Tadin, J. Schneider, H. Boysen, F. Frey, Mater. Sci. Forum 79–82 (1991) 635–641.
- [3] T.O. Brun, S. Susman, Solid State Commun. 45 (1983) 721–724.
- [4] K. Kuriyama, S. Yamada, T. Nozaki, T. Kamijoh, Phys. Rev. B 24 (1981) 6158–6160.
- [5] T. Tokuhito, S. Susman, Solid State Ion. 5 (1981) 421–424.
- [6] H. Ehrenberg, H. Pauly, T. Hansen, J.-C. Jaud, H. Fuess, J. Solid State Chem. 167 (2002) 1–6.
- [7] J. Ihringer, A. Küster, J. Appl. Crystallogr. 26 (1993) 135–137.
- [8] J. Rodriguez-Carvajal, Abstracts of the Satellite Meeting on Powder Diffraction on the XV Congress of the IUCr, Toulouse, France, 1990, p. 127.
- [9] K. Kishio, J.O. Brittain, J. Phys. Chem. Solids 40 (1979) 933–940.
- [10] K. Kuriyama, T. Kato, T. Kato, H. Sugai, H. Maeta, M. Yahagi, Phys. Rev. B 52 (1995) 3020–3022.