*Acta Cryst.* (1975). B31, 1793

# The crystal structure of LiAl.

By K. Kuriyama, *College of Engineering, Hosei University*, 3-7-2, *Koganei, Tokyo* 184, *Japan* and N. Masaki, *JAERI*,* *Tokai* 319-11, *Japan*

(*Received* 14 *January* 1975; *accepted* 1 *February* 1975)

The crystal structure of LiAl ($a=6\cdot37\pm0\cdot01$ Å, $d=1\cdot76$ g cm$^{-3}$ and $Z=8$) has been determined by the neutron diffraction method. It was confirmed that LiAl has a NaTl-type structure.

Two different crystal structures for LiAl have been reported on the basis of X-ray powder diffraction determinations. Pastorello (1931) proposed the CsCl (*B*2) type, while Zintl & Woltersdorf (1935) and Komovsky & Maximov (1935) proposed the NaTl (*B*32) type. The *B*32 structure is composed of two sub-lattices, each forming a diamond lattice and interpenetrating each other. If the Na atom gives up its single valency electron to the more electronegative Tl atom, the Tl has four electrons to form a diamond substructure using $sp^3$ orbitals (Hückel, 1951). It will be either a narrow-gap semiconductor or a semimetal with low carrier concentration (Bennett, 1966). We have obtained data definitely confirming the NaTl-type structure for LiAl by neutron diffraction.

Polycrystalline samples of LiAl were prepared by direct reaction between equimolar amounts of $^7$Li (99·99% pure) and Al (99·99% pure) in the same manner as for LiIn single crystals (Kuriyama, 1974). Since $^6$Li has a large absorption coefficient for neutrons, $^7$Li was used in this study. The crystals synthesized above 700°C have a metallic lustre and are bluish-grey. Samples were powdered under helium atmosphere and packed in a cylindrical aluminum holder for neutron work.

The experiment was carried out at room temperature with a diffractometer installed at the JRR-3 reactor. Neutrons were obtained from the (111) planes of a copper transmission-type monochromator, which reflects at about 1·53 Å. A Soller slit of 15′ angular divergence was placed between the reactor and the monochromator, 30′ in front of the BF$_3$ detector. The conventional $\theta$–$2\theta$ observation was made on the specimen in the range $0\cdot11<(\sin\theta/\lambda)<0\cdot42$ Å$^{-1}$. To obtain the X-ray powder diffraction pattern of LiAl, an X-ray experiment was performed using Cu $K\alpha$ radiation.

The X-ray result indicated that LiAl had the diamond lattice with a cell edge of $a=6\cdot37\pm0\cdot01$ Å. The density of LiAl is 1·76 g cm$^{-3}$. Therefore the cell unit contains 8(LiAl). A summary of the relative neutron intensities together with calculated values for the NaTl and CsCl type structures is given in Table 1. The value of $2B$ in the Debye–Waller temperature factor was determined from the slope of the plot of the logarithm of $I_o/I_c$ *versus* $(\sin^2\theta/\lambda^2)$. In the neutron experiment, the scattering lengths of $^7$Li and $^{27}$Al have favorable values [$b(^{27}\text{Al})=0\cdot35\times10^{-12}$, $b(^7\text{Li})=-0\cdot21\times10^{-12}$ cm; Bacon, 1962] for locating the lithium atoms in the lattice. As listed in Table 1, the comparison of observed and calculated relative neutron intensities of reflexions shows unambiguously that the structure is of the NaTl type, *i.e.* *Fd*3*m*, Al 8(*a*) and Li 8(*b*).

Table 1. *Observed and calculated relative neutron diffraction intensities for* LiAl *with* $\lambda=1\cdot53$ Å

| | | $I_{calc}$ | |
|---|---|---|---|
| *h k l* | $I_{obs}$ | NaTl type | CsCl type† |
| 1 1 1 | 100 | 100 | 0 |
| 2 2 0 | 10 | 7 | 7 |
| 3 1 1 | 80 | 85 | 0 |
| 4 0 0 | 0 | 2 | 2 |
| 3 3 1 | 50 | 51 | 0 |
| 4 2 2 | 4 | 5 | 5 |
| 3 3 3, 5 1 1 | 55 | 50 | 0 |

* $I_{calc}\propto|F|^2 . p . [1/(\sin\theta\sin2\theta)]\exp(-2B\sin^2\theta/\lambda^2)$.

† The lattice parameter of the CsCl-type is half that of the NaTl-type.

The *B* value of 0·37 Å$^2$ as obtained above was also used to calculate $\bar{u}$, the root-mean-square displacement of an average lattice point in a direction perpendicular to the reflecting plane according to the relation:

$$B=M/(\sin\theta/\lambda)^2=8\pi^2\bar{u}^2.$$

A $\bar{u}$ of 0·07 Å was obtained for LiAl from this expression.

The authors are grateful to Professor K. Iwamura for many useful discussions. We also thank Dr Y. Hamaguchi of Japan Atomic Energy Research Institute and Dr R. Nakajima of Hosei University for their interest in the work, and Mr M. Yahagi, a graduate student of Hosei University, for the preparation of LiAl compounds.

## References

Bacon, G. E. (1962). *Neutron Diffraction*, 2nd ed., pp. 30–33. Oxford Univ. Press.

Bennett, L. H. (1966). *Phys. Rev.* **150**, 418–420.

Hückel, W. (1951). *Structural Chemistry of Inorganic Compounds*, p. 829. Amsterdam: Elsevier.

Komovsky, G. & Maximov, A. (1935). *Z. Kristallogr.* **92**, 274–283.

Kuriyama, K. (1974). *J. Cryst. Growth*, **23**, 160–162.

Pastorello, S. (1931). *Gazz. Chim. Ital.* **61**, 47–51.

Zintl, E. & Woltersdorf, G. (1935). *Z. Elektrochem.* **41**, 876–879.

---

* Japan Atomic Energy Research Institute.