Anomalous electrical resistivity in LiAl near critical composition

K. Kuriyama, T. Kamijoh, and T. Nozaki College of Engineering, Hosei University, 3-7-2, Kajinocho, Koganei, Tokyo 184, Japan (Received 4 February 1980)

An abrupt change in the electrical resistivity at 97 K is observed near the critical composition corresponding to the Li-deficient region in the semimetallic compound LiAl. Possible origins of anomalous differential resistivity are discussed.

We have reported¹ that the electrical transport properties of Li-rich LiAl have correlated with the semimetallic band structure calculated by Zunger.² Our experimental data support the results of the band-structure calculation which indicates that the hole pocket at Γ_{25} , is slightly sharper in comparison with the broader electron pocket extending to the Brillouin-zone boundary. LiAl (NaTl structure,^{3,4} space group; Fd3m) is composed of two sublattices, each forming a diamond lattice and interpenetrating each other. The defect structure in LiAl (Refs. 5 and 6) (β phase; 48–56 at. % Li) exercises a considerable influence on the transport properties. The defect structure⁵ consists of the coexistence of two types of defects, namely, vacancies in the lithium sublattice and lithium antistructure atoms in the aluminum sublattice. The Li vacancy concentrations decrease from about 3.5 at. % to about 0.2 at. % with increasing the Li content C_{Li} , while the Li concentrations in Al sites vary from 0 at. % to about 5.4 at. % with increasing C_{Li} .



FIG. 1. The electrical resistivities vs temperature for LiAl. Specimen No.1 (53.5 at. % Li), No.2 (52.4 at. % Li), No.3 (50.0 at. % Li), No.4 (49.8 at. % Li), No.5 (49.4 at. % Li), No.6 (48.2 at. % Li), and No.7 (48.8 at. % Li).

We report that the abrupt change in the electrical resistivity at 97 K is observed near the critical composition corresponding to the Li-deficient region.

The details of the sample preparation have already been published.⁷ The Li content C_{Li} was estimated with an accuracy of ± 0.5 at. % from the relation of the lattice parameters versus composition.⁵ The lattice parameters vary linearly with C_{Li} in the β phase from 6.36 to 6.39 Å. The electrical resistivity and Hall coefficient were measured by the four point and Van der Pauw technique,⁸ respectively. The potential and current were measured using a Keithley 180 digital nanovoltmeter and a Keithley 174 digital multimeter.

The electrical resistivities and Hall coefficients are shown in Figs. 1 and 2, respectively. In β -LiAl, the electrical resistivity increases with increasing C_{Li} , while Hall coefficient decreases with increasing C_{Li} . The tendency of electrical transport properties for variation of lithium content does not contradict with previous reports.^{1,6} All the Hall coefficients in β phase show the "positive" value and these coefficients of Li-deficient region increase comparing with the Li-rich region. Therefore Hall coefficient of LiAl is



FIG. 2. Hall-coefficient variation of β -LiAl with Li content at 300 K.

<u>22</u>

470

©1980 The American Physical Society

positive indicating that the holes have a higher mobility than the electrons in the β phase LiAl. The holes near the critical composition (Li-deficient phase boundary) are bound to the lithium vacancies weaker than the bounded holes in Li-rich region, leading to a μ_h increasing strongly with decreasing C_{Li} . As $\mu_h(C_{\text{Li}})$ is a decreasing function and as

$$\rho \sim (N_h \mu_h + N_e \mu_e)^{-1}$$

decreasing $C_{\rm Li}$ decrease ρ .

On samples near the β -phase boundary, resistivity measurements show an abrupt increase of the resistivity at about 95 K [Fig. 3(a)]. The differential resistivities of LiAI [Fig. 3(b)] in the 77–120 K indicate, a sharp peak of the temperature derivation of the resistivity occurs around 97 K. Anomalous behavior is able to reproduce from the same batches of crystals which are observed in the sharp rise in resistivity measurements. And also, the differential resistivity of the different sample near the phase boundary indicates the similar profile (Fig. 3). The similar behavior,⁹ which occurs in Li-deficient LiA1 around 105 K, has been reported by Cristea et al. According to the interesting speculation for anomalous resistivity proposed by Zunger,² a very similar behavior of the differential resistivity with temperature occurs in TiSe₂,¹⁰ where it was associated with charge-density-wave (CDW) instabilities, presumably induced by coupling of electrons and holes that exist in the semimetallic pockets around Land Γ , respectively. In the same way, as the band structure of LiAl consists of the coexistence of a hole pocket at Γ_{25} , and an electron pocket along Γ -X, it seems possible that an anomalous resistivity based on the CDW state relating to the electron-hole coupling. The other possible speculation is a lattice instability such as order-disorder transition induced to high Li vacancy concentration near the β -phase boundary. However, according to the thermodynamical calculation¹¹ of the superstructure in LiAl, it has indicated that the transition from NaTl (B32) structure to the CsCl (B2) structure occurs at a high temperature than a melting point of LiAl. At the present time, in order to establish whether a structural change accompanies the discontinuity in resistivity, we are considering of a detailed crystal analysis such as tempera-

- ¹K. Kuriyama, T. Kamijoh, and T. Nozaki, Phys. Rev. B (in press).
- ²A. Zunger, Phys. Rev. B <u>17</u>, 2582 (1978).
- ³E. Zintl and G. Brauer, Z. Phys. Chem. Abt. B <u>20</u>, 245 (1933).
- ⁴K. Kuriyama and N. Masaki, Acta Crystallogr. Sect. B <u>31</u>, 1793 (1975).
- ⁵K. Kishio and J. O. Brittain, J. Phys. Chem. Solids <u>40</u>, 933 (1979).



FIG. 3. (a) The detailed profiles of resistivity vs temperature in the 77–120 K range for specimens No. 6 and No. 7. (b) Derivative of resistivity vs temperature (intervals of approximately 1 K were used in calculating $\Delta \rho / \Delta T$).

ture-dependent neutron diffraction.

The authors wish to thank Professor J. O. Brittain of Northwestern University for the offer of their paper concerning the defect structure and Professor K. Iwamura and Professor M. Nogami of Hosei University for their encouragement throughout this work. This work was partially supported by the Matsunaga Science Foundation.

- ⁶M. Yahagi, Bull. Graduate Studies <u>3</u>, 161–171 (1979).
- ⁷K. Kuriyama, S. Saito, and K. Iwamura, J. Phys. Chem. Solids <u>40</u>, 457 (1979).
- ⁸L. J. Van der Pauw, Philips Tech. Rev. <u>20</u>, 220 (1958). ⁹Reference 10 in Ref. 2.
- ¹⁰F. J. DiSalvo, D. E. Moncton, and J. V. Waszczak, Phys. Rev. B 14, 4321 (1977).
- ¹¹A. B. Makhnovetskii and G. L. Krasko, Phys. Status Solidi B <u>80</u>, 341 (1977).