

Transport properties of LiAl

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In "real" LiAl (NaTl structure: $Fd\bar{3}m$), the majority carriers govern the transport properties are holes at 77 and 300 K. The decrease in Hall coefficients and the increase in electrical resistivity with the increase of Li composition are understood in terms of the "defect" structure of LiAl. The relationship between the transport properties and band structure is discussed using the semimetallic band structure proposed by Zunger.

In a recent paper Zunger reports¹ a fully self-consistent band structure on the "ideal" LiAl (NaTl structure²: $Fd\bar{3}m$) within the local-density formalism. The band structure and density of states have characteristics similar to that of the tetrahedrally bonded IV-IV semiconductors, however the indirect $\Gamma_{25'} - X$, band gap becomes negative in LiAl. At the same time, Kishio and Brittain suggest³ the "defect" structure of LiAl (β phase; 48–56 at. % Li) which consists of the coexistence of two types of defects, namely, vacancies in the lithium sublattice and lithium anti-structure atoms in the aluminum sublattice. As a result, they find that the average number of valence electrons per site (e/a) varies from about 1.96 in the low Li content C_{Li} to about 1.93 in the high C_{Li} . The value of e/a in stoichiometric "ideal" LiAl is 2. And also, as the NaTl structure possesses equal numbers of like and unlike atoms in the nearest-neighbor lattice, this type of crystal (LiAl, LiGa, LiIn, NaIn, NaTl, LiZn, and LiCd) exhibits the complex bonding characters^{4,5} in contrast to the diamond lattice.

We report that the majority carriers on the transport are holes, and discuss the relationship between the transport properties and band structure.

Samples prepared are three; one (51.0 at. % Li) exhibits single crystallinity and another (51.5 and 53.0 at. % Li) polycrystallinity with large grain boundaries. C_{Li} was estimated with an accuracy of ± 0.5 at. % Li from the relation of the lattice parameters versus composition.^{3,6} The lattice parameters vary linearly with C_{Li} in the β phase from 6.36 to 6.39 Å. The electrical resistivity ρ and Hall coefficient R_H were

measured by the four-point or Van der Pauw technique⁷ with the tungsten point contacts. The potential and current were measured using a Keithley 180 digital nanovoltmeter and a Keithley 174 digital multimeter, respectively. The expected absolute accuracy of ρ is about 5% due to contact pressure and nonuniform sample thickness. The calibration of R_H was carried out using a Sb-doped germanium single crystal.

The resistivities are shown in Fig. 1. ρ increase with C_{Li} from $6.7 \times 10^{-5} \Omega \text{ cm}$ (51.0 at. % Li) to $10.2 \times 10^{-5} \Omega \text{ cm}$ (53.0 at. % Li) at 300 K. And also, the linear characteristics of ρ are observed at the temperature range from 100 to 300 K. The values of Hall coefficient at 77 and 300 K are listed in Table I. Hall coefficients at these temperatures decrease with C_{Li} and all the coefficients show the "positive" value at 77 and 300 K. The values (except the sample of 53.0 at. % Li) increase to about 15% at 77 and 300 K. The value of R_H reported by Yahagi *et al.*⁸ show qualitatively similar features but there are important variations in magnitudes. For example, in Li-rich region at 300 K we find $R_H = 0.36 \times 10^{-3} \text{ cm}^3/\text{C}$ while they obtain $1.1 \times 10^{-3} \text{ cm}^3/\text{C}$.

The schematic band structure proposed¹ by Zunger is shown in Fig. 2. He points out that LiAl is not only a semimetal with a hole pocket around Γ and electron pocket along $\Gamma - X$ (close X), but also the X_1 conduction state and the minima along the Δ direction, is lower than the $\Gamma_{25'}$ in the entire lattice parameter range, yielding a semimetallic character. The energy separation is -0.18 eV for $\Gamma_{25'} - X$ and -0.53 eV

TABLE I. Hall coefficients and electrical resistivities at 77 and 300 K.

Li (at. %)	$R_{H(77 \text{ K})} (10^{-3} \text{ cm}^3/\text{C})$	$R_{H(300 \text{ K})} (10^{-3} \text{ cm}^3/\text{C})$	$\rho_{(77 \text{ K})} (10^{-5} \Omega \text{ cm})$	$\rho_{(300 \text{ K})} (10^{-5} \Omega \text{ cm})$
51.0	1.74	1.49	4.9	6.7
51.5	0.72	0.64	7.0	8.1
53.0	0.40	0.38	9.4	10.2

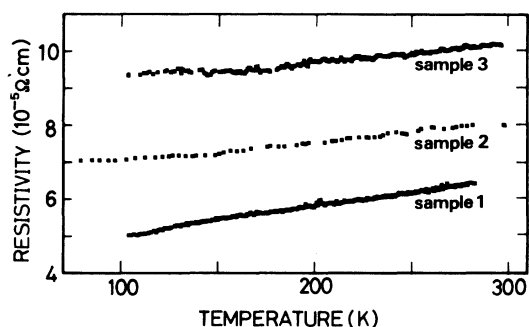


FIG. 1. Electrical resistivities vs temperature for LiAl. Sample 1 (51.0 at. % Li), sample 2 (51.5 at. % Li), and sample 3 (53.0 at. % Li).

for $\Gamma_{25'}-\Delta_m$ (minimum point in the lowest $\Gamma-\Delta-X$ conduction band). The band structure reproduced schematically in Fig. 2 indicates that in ideal LiAl, there is a coexistence of holes and electrons. We may expect the existence of holes according to the suggestion³ that the number of electrons in the Brillouin zone on "defect" lattice is less than one of the "ideal" lattice. As the number of valence electrons per site varies from about 1.96 to about 1.93 as a function of C_{Li} , therefore, electrons in a unit cell decrease from 31.36 to 30.88. The decrease of 1.7% for electrons per cell brings the increase in the relative number of holes. Although the increase in C_{Li} increases the hole concentration N_h , it also decreases the mobility $\mu_h(C_{Li})$. As the Hall coefficient behaves

$$R_H \sim \frac{N_h \mu_h^2 - N_e \mu_e^2}{(N_h \mu_h + N_e \mu_e)^2}$$

and $\mu_h > \mu_e$, $N_h \mu_h^2$ decreases with C_{Li} while N_h alone increases. As increasing C_{Li} causes an increase in the lattice constant, this in turn increases the conduction-band overlap with the valence band¹ and results in a higher hole concentration. In "real" LiAl a stoichiometric (ideal) semimetal is not formed even if the increase of C_{Li} compensates the vacancies in "defect" LiAl, which show a decrease in Li vacancy concentration from about 3.5% to about 0.2% with C_{Li} . Because as increasing C_{Li} , the excess Li atoms occupy³ Al sites without the formation of the aluminum vacancies. And also, the Li concentrations in

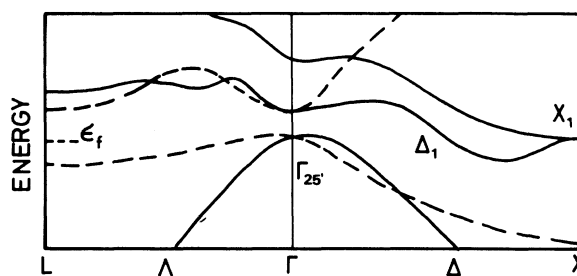


FIG. 2. Energy-band structure of LiAl along symmetry direction as calculated by Zunger (Ref. 1). Dashed line indicate doubly degenerate representations.

Al sites vary from 0% to about 5.4% with C_{Li} . The holes are bound to these species stronger than the binding of "free" holes, leading to a μ_h decreasing strongly with C_{Li} . As $\mu_h(C_{Li})$ is a decreasing function and

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

increasing C_{Li} increases ρ . Therefore Hall coefficient of LiAl is positive at 77 and 300 K indicating that the holes have a higher mobility than the electrons at these temperatures. This supports the results of the band-structure calculation which indicates that the hole pocket at $\Gamma_{25'}$ is slightly sharper in comparison with the broader electron pocket extending to the zone boundary.

In conclusion, we find that that majority carriers govern the transport properties are holes at 77 and 300 K. The increase in the resistivity with C_{Li} bases on the defect structure. And also we propose that the hole pocket at $\Gamma_{25'}$ is slightly sharper in comparison with the broader electron pocket along $\Gamma-X$.

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¹A. Zunger, Phys. Rev. B **17**, 2587 (1978).

²E. Zintl and G. Brauer, Z. Phys. Chem. B **20**, 245 (1933).

³K. Kishio and J. O. Brittain, J. Phys. Chem. Solids **40**, 933 (1979).

⁴K. Kuriyama and S. Saito, Phys. Rev. B **13**, 1528 (1976).

⁵K. Kuriyama, S. Saito, and K. Iwamura, J. Phys. Chem. Solids **40**, 457 (1979).

⁶E. D. Levine and E. J. Rapperport, Trans. Metall. Soc. AIME **227**, 1204 (1963).

⁷L. J. Van der Pauw, Phillips Tech. Rev. **20**, 220 (1958).

⁸M. Yahagi, H. Ishizaka, M. Osaka, and K. Iwamura, Presented at the meeting of Japan Society of Applied Physics, Kinki University, Osaka, Oct. 1978. (unpublished).