

## Hall mobility of positive carriers in the semimetallic compound LiAl

K. Kuriyama

College of Engineering and Research Center of Ion Beam Technology, Hosei University,  
3-7-2 Kajinocho, Koganei, Tokyo 184, Japan

T. Nozaki and T. Kamijoh\*

College of Engineering, Hosei University, 3-7-2 Kajinocho, Koganei, Tokyo 184, Japan

(Received 1 March 1982)

The temperature-dependent Hall coefficient and electrical resistivity above 77 K of the semimetallic compound LiAl are presented. A "positive" Hall-coefficient anomaly relating to an abrupt change in the resistivity at 95 K was observed near the Li-deficient phase boundary. It is proposed that an abrupt increase in hole concentration at the critical temperature is associated with the slight lowering effect of the Fermi energy (or the increasing effect of the Fermi level for holes) induced by the long-range ordering of Li vacancies at a lower temperature. In addition, the holes near the Li-deficient phase boundary are dominated by the lattice-phonon scattering.

We have reported<sup>1</sup> that the electrical transport properties of  $\beta$ -LiAl, possesses holes as the majority carriers, correlate with the semimetallic band structure calculated by Zunger.<sup>2</sup> Furthermore, we have found that an abrupt change at 95 K in the electrical resistivity<sup>3</sup> and the heat capacity<sup>4</sup> occurs near the phase boundary of the Li-deficient region in  $\beta$ -LiAl. As a result, we have proposed that these anomalies are associated with the lower-temperature ordering or clustering of Li vacancy rather than the charge-density-wave instability.<sup>2</sup>  $\beta$ -LiAl (NaTl structure,<sup>5</sup> space group:  $Fd\bar{3}m$ ) is composed of two sublattices, each forming a diamond lattice and interpenetrating each other. The defect structure<sup>6</sup> in LiAl [ $\beta$  phase; about 48–56 at. % Li (Refs. 6, 7, and 8)] exercises a considerable influence on the transport properties. The defect structure consists 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 the increasing Li content  $C_{Li}$ , while the Li concentrations in Al sites vary from 0 at. % to about 5.4 at. % with increasing  $C_{Li}$ . In a recent NMR study,<sup>9</sup> the lithium vacancy concentration on the Li sites near the Li-deficient phase boundary has been estimated to be 15.6%, which is larger than the value determined by the density method.

In this paper, we report that an abrupt change in Hall coefficient at 95 K is observed near the critical composition corresponding to the Li-deficient region, and discuss the origin of the anomalous Hall coefficient in consideration of the defect structure and the energy-band structure.

The details of the sample preparation have already been published.<sup>10</sup> Temperature-dependent Hall-effect

measurements were made using a modified ac Hall-effect measuring system<sup>11</sup> designed to diminish or eliminate the Ettingshausen effect with its accompanying unwanted thermal emf. This method makes use of constant magnetic fields and alternating driving currents. In order to minimize the generation of the unbalance voltage, the square shaped slabs were used as the samples; also, the voltage and current probes were located exactly on the corners of a sample. The alternating current of 200 mA, which is amplified by the audio amplifier, is provided into the sample through the isolation transformer. The low-level Hall voltage over the range 10 to 200 nV was amplified by a lock-in amplifier (Brookdeal 9503) through the preamplifier. Most measurements were carried out at frequency of 63 Hz, high enough to use a conventional audio-frequency transformer, and low enough to avoid skin effect in samples with metallic conductivity. Typical samples used in this investigation were a Li-rich ( $53.5 \pm 0.5$  at. % Li) and a Li-deficient ( $48.0 \pm 0.5$  at. % Li) LiAl. After the Hall-effect measurements, the electrical resistivities were measured for the same batches of crystals by four-point method.

Temperature-dependent electrical resistivities and positive Hall coefficients for Li-deficient and Li-rich specimen are shown in Figs. 1 and 2, respectively. Figure 1 shows that an anomaly occurs near 95 K in the resistivity and  $R_H$  curve. The resistivity curve is characteristic of a monotonious increase with increasing temperature except for the anomalous part.  $R_H$  curve, on the other hand, increases slightly to the critical temperature ( $T_c = 95$  K) as the temperature is decreased, and makes an abrupt decrease from  $T_c$ . For Li-rich sample as shown in Fig. 2, an anomalous feature is not observed over the measured tempera-

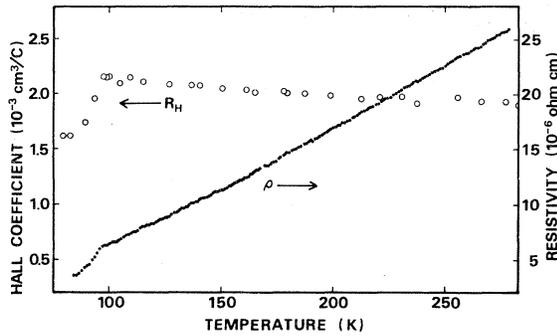


FIG. 1. Hall coefficient and electrical resistivity of Li-deficient LiAl ( $48.0 \pm 0.5$  at. % Li) as a function of temperature.

ture range as well as the heat capacity<sup>4</sup> for Li-rich LiAl. The electrical resistivity for the Li-rich sample exhibits a higher value than the Li-deficient sample (Figs. 1 and 2). This result greatly depends on the coexistence of two types of defects,<sup>6</sup> that is to say, the tendency of the increase<sup>3,12</sup> in resistivity with Li concentration over 48–54 at. % may be closely correlated with the increase of Li-atom defects on the Al sites, since the Li atom (valency 1) on the Al site (valency 3) must be much more effective as a scatterer than a vacancy on the Li site. On the other hand, the Hall coefficient for Li-rich sample exhibits a smaller value than the Li-deficient one. Moreover, the tendency of decreasing<sup>3</sup> in the *positive* Hall coefficients with increasing  $C_{Li}$  has already been confirmed by the Van der Pauw technique at room temperature.

The "ideal" energy-band structure proposed by Zunger<sup>2</sup> points out that LiAl is not only a semimetal with a hole pocket around  $\Gamma$  and electron pocket along  $\Gamma$ - $X$  (close  $X$ ), but also the  $X_1$  conduction state and the minima along the  $\Delta$  direction is lower than the  $\Gamma_{25'}$  in the entire lattice parameter range, yielding a semimetallic character. Hence the difference of  $R_H$  observed here is expected to base on the behavior of holes and electrons as the carriers. As the Hall coef-

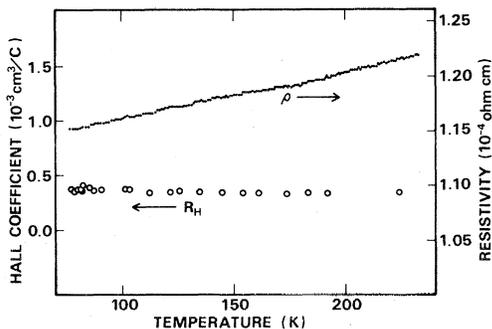


FIG. 2. Hall coefficient and electrical resistivity of Li-rich LiAl ( $53.5 \pm 0.5$  at. % Li) as a function of temperature.

cient<sup>1</sup> except for the Li-deficient critical composition behaves,

$$R_H \approx \frac{N_h \mu_h^2 - N_e \mu_e^2}{(N_h \mu_h + N_e \mu_e)^2} \quad (1)$$

and  $\mu_h > \mu_e$ ,  $N_h \mu_h^2$  decreases with  $C_{Li}$ , while  $N_h$  alone increases because of the increase effect of the conduction-band overlap with the valence band, since the lattice parameters vary linearly with  $C_{Li}$  in the  $\beta$  phase from 6.36 to 6.39 Å.<sup>6</sup> On the other hand, a recent theoretical calculation<sup>13</sup> of the band structure for the "real" defect phase LiAl constructed from the stoichiometric composition has indicated a lowering of the Fermi energy by 17 mRy. As the result of the shift, the large hole pocket surrounding  $\Gamma$  overwhelms the small electronic pockets at the  $X$  points. Therefore the increasing effect of vacancies near the Li-deficient phase boundary, which has 15.6% vacancies<sup>9</sup> on the Li sites and 0% Li atoms on the Al sites, is a remarkably lowered Fermi energy. Hence it is expected to hold approximately  $N_h \gg N_e$  (Ref. 14) in Eq. (1) according to the reduction of overlap in the  $\Gamma_{25'}$ - $X_1$  "negative" band gap and lowering the Fermi level. The Hall coefficient near the Li-deficient phase boundary is as follows:

$$R_H = \frac{1}{eN_h} \quad (2)$$

Substituting the  $R_H$  and resistivity values in Fig. 1 in Eq. (2), the temperature-dependent hole concentration  $N_h$  and Hall mobility ( $\mu_h = R_H/\rho$ ) are estimated, as shown in Fig. 3. The Hall mobility decreases almost exponentially with increasing temperature except for the anomalous part, whereas the hole concentration decreases almost linearly to the critical temperature ( $T_c$ ) as the temperature is decreased, and makes an abrupt increase at  $T_c$ .

The more possible speculation<sup>4</sup> for anomalous behavior is a lattice instability such as the order-disorder transition. In order to interpret the anomalous feature, we should pay attention to the

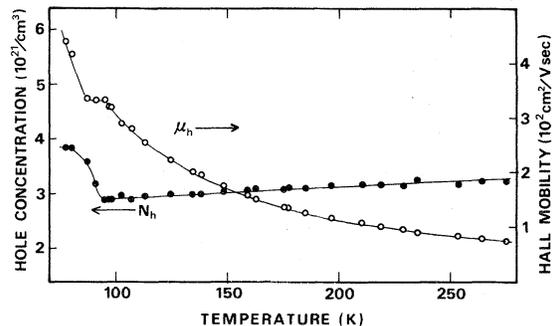


FIG. 3. Hall mobility and hole concentration for Li-deficient LiAl as a function of temperature.

behavior of the Li vacancies. Since in the Li-deficient phase boundary, the *real* LiAl has 15.6% vacancies on the Li sites, whereas the Li-rich sample has about 0.3% vacancies on the Li sites and 7% Li atoms on the Al sites, the Li-vacancy effect is expected to have a great influence on the Li-deficient region. Furthermore, since the resistivity change observed here is more characteristic of a freezing out of some scattering channel, and also a speculation for anomalous heat capacity proposed by us<sup>4</sup> has been associated with the freezing effect induced by order-disorder transition of the Li vacancies in LiAl, an abrupt increase in the hole concentration might be explained in the slight lowering effect of the Fermi energy (or the increasing effect of the Fermi level for holes in LiAl) induced by the long-range ordering of Li vacancies at lower temperature as the deformation of the density of states at the Fermi surface based on the long-period superlattice observed in CuAu alloy.<sup>15</sup> Thus the phase transition from random configuration of Li vacancies to an orderly one might appear in the Li-deficient LiAl containing a large number of vacancies at the critical temperature. On the other hand, in the Li-rich region containing a small number of vacancies, this effect is expected to disappear. The other interpretation for the anomalous behavior is the deformation of the Fermi surface induced by the lattice distortions near a vacancy. Such distortions are as high as 20% (Ref. 16) of the atomic spacing in LiAl.

In order to survey the origin of the scattering center for holes near the Li-deficient phase boundary, the  $\ln\mu_h$  vs  $\ln T$  curve is plotted in Fig. 4. The Hall mobility can be fairly well represented by a power-law dependence on the temperature, with the power of  $-1.4$ . This value is smaller than the exponent of  $T$  for scattering between carriers in different valley observed in bismuth.<sup>17</sup> In either the electron-hole or the anisotropic-carrier case, the temperature dependence is at  $T^{-2}$ . On the other hand, the temperature dependence of the mobility associated with lattice scattering follows approximately the  $T^{-3/2}$  law predicted by the simple theory.<sup>18</sup> Therefore over the range 77 to 300 K, the holes near the Li-deficient phase boundary essentially might be dominated by the lattice-phonon scattering rather than the ionized impurity scattering based on the field of a Li

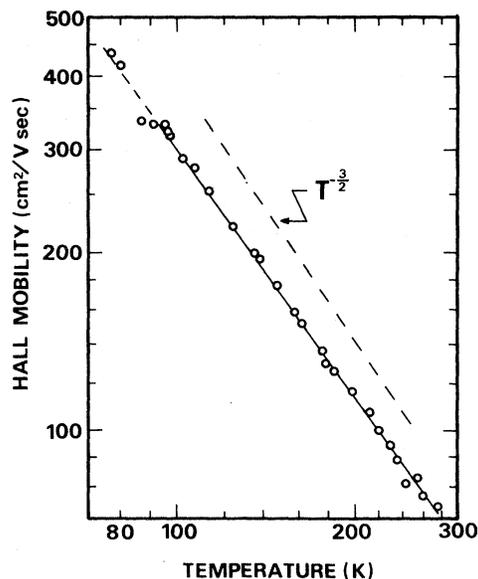


FIG. 4.  $\ln\mu_h$  vs  $\ln T$  plot for Li-deficient LiAl. The exponent of  $T$  was determined to be  $-1.4$  by a least-squares method, which is compared with the value ( $-1.5$ ) of the lattice-phonon scattering.

vacancy.

In conclusion, we have observed an anomalous Hall coefficient near 95 K for the Li-deficient sample. We proposed that an abrupt increase in hole concentration at the critical temperature is associated with the slight lowering effect of the Fermi energy (or the increasing effect of the Fermi level for holes in LiAl) induced by the long-range ordering of Li vacancies at lower temperature. Also, the holes near the Li-deficient phase boundary are dominated by the lattice-phonon scattering.

#### ACKNOWLEDGMENTS

The authors wish to thank Professor K. Iwamura and Dr. M. Yahagi for helpful discussions of the results. The present work was supported in part by the Grant-in-aid (No. 56740132) for scientific research from the Ministry of Education.

\*Present address: Research Laboratory, Oki Electric Industry Co., Ltd. 550-5, Higashi-Asakawa, Hachioji, Tokyo 193, Japan.

<sup>1</sup>K. Kuriyama, T. Kamijoh, and T. Nozaki, *Phys. Rev. B* **21**, 4887 (1980).

<sup>2</sup>A. Zunger, *Phys. Rev. B* **17**, 2582 (1978).

<sup>3</sup>K. Kuriyama, T. Kamijoh, and T. Nozaki, *Phys. Rev. B* **22**,

470 (1980).

<sup>4</sup>K. Kuriyama, S. Yanada, T. Nozaki, and T. Kamijoh, *Phys. Rev. B* **24**, 6158 (1981).

<sup>5</sup>E. Zintl and G. Brauer, *Z. Phys. Chem. Abt. B* **20**, 245 (1933).

<sup>6</sup>K. Kishio and J. O. Brittain, *J. Phys. Chem. Solids* **40**, 933 (1979).

- <sup>7</sup>C. John Wen, B. A. Boukamp, R. A. Huggins, and W. Weppner, *J. Electrochem. Soc.* **126**, 2258 (1979).
- <sup>8</sup>E. Veleckis, *J. Less-Common Met.* **73**, 49 (1980).
- <sup>9</sup>K. Kishio, J. R. Owers-Bradley, W. P. Halperin, and J. O. Brittain, *J. Phys. Chem. Solids* **42**, 1031 (1981).
- <sup>10</sup>K. Kuriyama, S. Saito, and K. Iwamura, *J. Phys. Chem. Solids* **40**, 457 (1979).
- <sup>11</sup>G. L. Guthrie, *Rev. Sci. Instrum.* **36**, 1177 (1965).
- <sup>12</sup>M. T. Ratajack, K. Kishio, J. O. Brittain, and C. R. Kannewurf, *Phys. Rev. B* **21**, 2144 (1980).
- <sup>13</sup>T. Asada, T. Jarlborg, and A. J. Freeman, *Phys. Rev. B* **24**, 510 (1981).
- <sup>14</sup>M. Yahagi, *Phys. Rev. B* **24**, 7401 (1981).
- <sup>15</sup>K. Teramoto and M. Tachiki, *Phys. Rev.* **166**, 656 (1968).
- <sup>16</sup>Reference 18 in Ref. 9.
- <sup>17</sup>R. Hartman, *Phys. Rev.* **181**, 1070 (1969).
- <sup>18</sup>For example, J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University, Cambridge, 1972), p. 211.