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Anomalous heat capacity in LiAl near critical composition

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The heat capacity and electrical resistivity in the temperature range 77 – 300 K of the semimetallic compound LiAl are presented. A heat-capacity anomaly relating to an abrupt change in the resistivity at 95 K was observed near the critical composition corresponding to the Li-deficient region. Possible origins of anomalous behavior are discussed.

We have reported[1] that the electrical transport properties of LiAl correlate with the semimetallic band structure calculated by Zunger.[2] Furthermore, we found that an abrupt change in the electrical resistivity at 97 K is observed near the phase boundary of the Li-deficient region in β-LiAl.[3] β-LiAl (NaTl structure,[4] space group: $Fd3m$) is composed of two sublattices, each forming a diamond lattice and interpenetrating each other. The defect structure[5] in LiAl [β phase; about 48 – 56 at. % Li (Refs. 5, 6, and 7)] 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}. As a followup study, we investigated the heat capacity (C_p) of the Li-rich and Li-deficient LiAl in the temperature range 77 – 300 K.

The details of the sample preparation have already been published.[8] Heat-capacity measurements were made using a standard adiabatic calorimeter designed to give accurate absolute heat-capacity measurements over the temperature range 77 – 300 K. The calorimeter consists of an inner thin-walled and an outer thick-walled stainless can. The inner can contains a vacuum space isolated from the sample region and acts as the radiation shield. A copper-Constantan thermocouple, 0.06 mm in diameter, was used to detect the temperature of the sample and a Manganin wire, 0.05 mm in diameter of about 170 Ω was wound around the cylindrical side of the sample as the heater.

In order to achieve good thermal contact between the sample and the heater (or thermocouple), small amounts of GE 7031 varnish were used. Temperature control was carried out by a heat sink isolated from the inner can. The heat sink included a continuously operating auxiliary heater for balancing the heat leak. The sample was suspended by copper wire, 0.1 mm in diameter, which connects to the Manganin heater and all lead wires were led through the heat sink out of the inner can. When the present calorimeter was used to measure the heat capacity of 99.999% aluminum, results were 6% higher than the standard results[9] for aluminum at 300 K. Therefore, in order to obtain the absolute heat capacity the addenda (heater + thermocouple) heat capacities were subtracted from the total sample heat capacities. Typical samples used in this investigation were a 1.42 g Li-rich (53.5 ± 0.5 at. % Li) and a 1.63 g Li-deficient (47.5 ± 0.5 at. % Li) polycrystalline LiAl with a cylindrical shape. The standard x-ray diffraction analysis showed the crystals to be monophasic, exhibiting the NaTl structure. After the heat-capacity measurements, the electrical resistivities were measured for the same batches of crystals by the four-point method.

The results are summarized in Figs. 1 and 2, respectively. Figure 1 shows that an anomaly occurs near 95 K in the resistivity and C_p curve. A temperature difference between the resistivity ano-

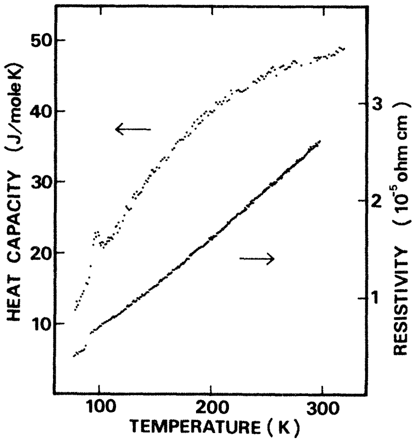

FIG. 1. The heat capacity and resistivity versus temperature for Li-deficient LiAl (47.5±0.5 at. % Li).

maly and the C_p peak is observed. This difference seems to occur by the different detection mechanism such as the thermal contact between the sample and the thermocouple. We suppose that the anomaly in the resistivity and the peak in C_p are due to the same mechanism at this stage.

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,[5] that is to say the abrupt increase of resistivity[3] 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. The similar behavior of electrical transport properties for variation of lithium content has been confirmed by the reflectance spectra analysis.[10] According to our previous results[3] in β-LiAl, the majority carriers that govern the transport properties are holes at 77 and 300 K and the Hall coefficient decreases with increasing C_{Li}. Therefore, the holes near the critical composition (Li-deficient phase boundary) are bound to the lithium vacancies more weakly than the bound holes in the Li-rich region, leading to a μ_h increasing strongly with decreasing C_{Li}. As μ_h is a decreasing function[1,3] such as

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

decreasing C_{Li} decreases ρ.

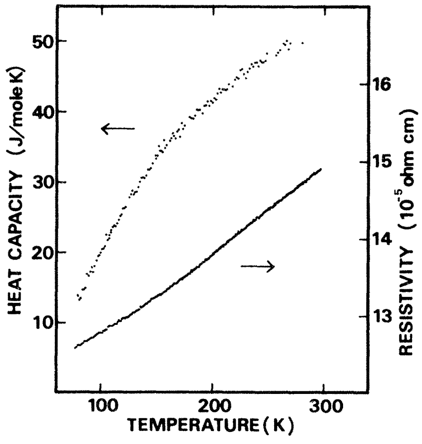

FIG. 2. The heat capacity and resistivity versus temperature for Li-rich LiAl (53.5±0.5 at. % Li).

A recent theoretical calculation[11] 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 Γ overwhelms the small electronic pockets at the X points. Therefore the increasing effect of vacancies near the Li-deficient phase boundary, which has 7% vacancies on the Li sites and 0% Li atoms on the Al sites,[5] is a remarkably lowered Fermi energy. Hence the density of states in this region might be characteristic of metallic conduction rather than a semimetallic one.

We can see in Fig. 1 (C_p curve) that a second-order transition occurs at 97 K and indicates the presence and importance of fluctuations. We have calculated the excess enthalpy (ΔH) under this heat-capacity curve by fitting a smooth background. Uncertainty in establishing the background heat capacity limits the accuracy of ΔH to ± 10%. Our estimate obtains the values of the enthalpy of 36 J/mole and excess entropy (ΔS) of 0.37 J/mole K. ΔS is approximately equal to $\Delta H/T_0$. T_0 is the peak temperature of the phase transition; $T_0 = 97$ K. Although lower temperature resistivity and heat-capacity measurements below 77 K are needed to verify whether an anomalous features appears in the Li-rich LiAl, no significant change in heat capacity and electrical resistivity was observed in the Li-rich region above 77 K (Fig. 2). However, a small difference in heat capacity was found in the Li-rich region which corresponds to the Li antistructure atoms on the Al sublattices. The heat capacity in a dominant region of Li vacancies exhibits a slightly smaller value (about 3% at 140–300 K) than a dominant region of the Li antistructure atoms on the Al sublattices. Although the interesting speculation for anomalous resistivity proposed by Zunger[2] has been associated with charge-density-wave (CDW) instability induced by electron-hole interaction effects, the excess entropy observed at the critical temperature seems too large for electronic specific-heat effects except for the excess entropy ($\Delta S = 0.460$ J/mole K) of the second-order transition of $2H$-TaSe$_2$.[12] Therefore, we suggest that these anomalies are not associated with CDW. If this were, indeed, electrically driven, the resistivity anomaly should show an increase in resistivity as the gap opens up, as it does in other CDW transitions.[12,13]

The more possible speculation for anomalous behavior is a lattice instability such as the order-disorder transiton. However, according to the thermodynamical calculation[14] of the superstructure in LiAl, the transition from NaTl ($B32$) structure to the CsCl ($B2$) structure occurs at a higher temperature than the melting point (966 K) of LiAl. Indeed, preliminary x-ray-diffraction experiments in the temperature range 77–300 K did not show the characteristic diffraction lines of a superlattice except for a change in the diffraction intensities. Although it is difficult to discuss quantitatively why the Li-deficient sample should have a phase transition and the Li-rich sample should not at this stage, we should pay attention to the behavior of the Li vacancies. Since in the Li-deficient phase boundary, the "real" LiAl has 7% vacancies on the Li sites,[5] whereas the Li-rich sample (53.5 ± 0.5 at. % Li) has about 0.6% vacancies on the Li sites and 7% Li atoms on the Al sites,[5] the Li-vacancy effect is expected to have a great influence on the Li-deficient region. Indeed, on the Li-deficit side of the ideal stoichiometry, the chemical diffusion coefficient[6] increases with decreasing Li concentration, becoming about 10^{-4} cm^2/s near the phase boundary. On the other hand, it is composition independent with an average value of 2.4×10^{-6} cm^2/s at 415 °C for the Li-rich side. Hence, even if the LiAl crystal is kept at low temperatures, the self-migration of vacancies near the Li-deficient phase boundary might be expected to have an extremely high value. Furthermore, since the resistivity change observed here is more characteristic of a freezing out of some scattering channel, an anomalous heat capacity might be explained in the freezing effect induced by order-disorder transition (or cluster formation) of the Li vacancies in LiAl. Therefore, the freezing effect is expected to have a great influence on the configuration entropy of Li vacancies. Thus, the phase transition from random configuration of Li vacancies (or clusters) to 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.

In conclusion, we have observed an anomalous resistivity and heat capacity for the Li-deficient sample. We proposed that the anomalous behavior is closely correlated with the lower temperature ordering or clustering of Li vacancies. And also this effect disappears from the Li-rich region with a small Li-vacancy concentration.

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