Radiation effects on Li-vacancy ordering in β-LiAl

K. Kuriyama, Takashi Kato, and Tomoharu Kato*
College of Engineering and Research Center of Ion Beam Technology, Hosei University, Koganei, Tokyo 184, Japan

H. Sugai and H. Maeta
Department of Radioisotopes and Materials Science and Engineering, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1, Japan

M. Yahagi
Faculty of Engineering, Aomori University, Aomori 030, Japan
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Radiation effects on the Li-vacancy ordering in β-LiAl [NaTl structure (space group $Fd3m$)] have been studied by Li-ion irradiation. The Li-vacancy ordering in β-$Li_{0.50}Al_{0.50}$ was destroyed by the irradiation, indicating a relatively weak interaction between the Li vacancies that originate from the long-range ordering. On the other hand, the Li-vacancy ordering in β-$Li_{0.48}Al_{0.52}$ was not collapsed by the irradiation, suggesting a relatively strong interaction between Li vacancies. This is responsible for the body-centered-tetragonal arrangement of Li vacancies observed in neutron-diffraction studies. The increase in the residual resistivity after the irradiation suggests the existence of two Frenkel-type defects: a lithium interstitial and Li vacancy pair, and an aluminum interstitial and Al vacancy pair. The latter defect is important for an annealing stage above the Li-vacancy ordering temperature. These defects disappeared completely by annealing at room temperature.

I. INTRODUCTION

The LiAl alloy is one of the useful materials for solid blankets in nuclear fusion[1,2] as well as a suitable anode material.[3] The good mixed conductor β-LiAl has been characterized as a semimetallic intermetallic compound,[4–6] yet there is very fast motion of the Li atoms.[3,7] The β-LiAl compound [NaTl structure;[8] space group $Fd3m$ (O_h^7)] is composed of two interpenetrating sublattices, each forming a diamond lattice.

Electrical conductivity of β-LiAl below room temperature has been reported.[9–11] The important features of the conduction mechanism for β-LiAl are governed by positive carriers (holes)[12,13] in the $\Gamma_{25'}$ valence band, which overlaps the X_1 conduction band. The electrical conductivity based on these holes is considerably affected by the defect structure[14] in β-LiAl (about 48–56 at. % Li). The resistivity at room temperature increases from ~17 to ~100 μΩ cm with increasing Li content, C_{Li}. The defect structure at room temperature consists of two types of defects: vacancies in the lithium sublattice (V_{Li}), and lithium antistructure atoms in the aluminum sublattice (Li_{Al}). The Li-vacancy concentration decreases from about 3.5 to about 0.2 % with increasing C_{Li}, while the Li concentration in Al sites varies from 0 to about 5.4 at. % with increasing C_{Li}. Furthermore, a recent study[15] showed the dependence of the lithium diffusion constant on the defect concentration as a result of a V_{Li}-Li_{Al} attractive interaction at the nearest-neighbor distance. We have also determined the concentrations of the free V_{Li}, free Li_{Li} defects, and V_{Li}-Li_{Al} complex defects in β-LiAl.[16] On the other hand, heat-capacity[17] and "positive" Hall-coefficient[12] anomalies relating to an abrupt change in the resistivity at 95 K have been observed near the Li-deficient phase boundary. The anomalous behavior is closely correlated with the lower-temperature ordering[18] or clustering of Li vacancies.[12,17]

In this paper, we report the relation between the lithium-vacancy ordering and lithium-ion irradiation in β-LiAl with three different Li contents.

II. RESULTS AND DISCUSSION

Samples were prepared by resistance-furnace melting of 99.9% pure lithium and 99.999% pure aluminum. The details of sample preparation have been described previously.[19] Li-ion irradiation was performed using a tandem accelerator at the Japan Atomic Energy Research Institute (JAERI). 60 MeV $^7Li^{3+}$ ions were used in this study. The projected range of $^7Li^{3+}$, evaluated using TRIM simulation, was 0.56 mm. The dimensions of the samples are about $5\times5\times1.5$ mm^3. The electrical resistivity before and after Li-ion irradiation was measured in a helium cryostat using the van der Pauw method. The specimen during ion irradiation was kept below about 40 K, which is below the Li-vacancy ordering temperature.

Figure 1 shows the temperature dependences of resistivity of β-LiAl before and after Li-ion irradiation. The Li doses are 1.2×10^{15} cm^{-2} for a specimen with $C_{Li}=50.0$ at. % [specimen no. 1; Fig. 1(a)], 8.0×10^{15} cm^{-2} for $C_{Li}=49.5$ at. % [no. 2; Fig. 1(b)], and 3.1×10^{15} cm^{-2} for $C_{Li}=48.0$ at. % [no. 3; Fig. 1(c)]. Before the irradiation, an abrupt change in the resistivity was observed at around 80 K for specimen, around 75 K for specimen 2, and around 95 K for specimen 3. This anomalous behavior has been associated with the low-temperature ordering[12,17,18] of Li vacancies. In specimen

1 after irradiation, the resistivity shows a tendency to increase in the temperature range below the ordering temperature [see closed circles in Fig. 1(a)]. This behavior is interpreted as the destruction of the ordered arrangement of Li vacancies due to the Li-ion irradiation. This suggests a weak V_{Li}-V_{Li} interaction in the long-range ordering of V_{Li} due to a relatively lower V_{Li} concentration in the specimen with $C_{Li}=50.0$ at. %. Since the free V_{Li} concentration[16] in this specimen is about $\frac{1}{3}$ of that with $C_{Li}=48.0$ at. %, the mean space between the Li vacancies is larger. On the other hand, in specimen 2 with $C_{Li}=49.5$ at. %, the ordered structure of V_{Li} is not completely destroyed by the Li-ion irradiation. In particular, the destruction of Li-vacancy ordering does not occur at all in specimen 3 with $C_{Li}=48.0$ at. % corresponding to the deficient β-phase boundary. There is a slight increase in the resistivity. The phase boundary[14] contains a large number of V_{Li}, suggesting this ordered structure of V_{Li} has a relatively strong V_{Li}-V_{Li} interaction. Indeed, a neutron-diffraction study[18] showed a body-centered-tetragonal unit cell of the ordered vacancy structure embedded in six face-centered-cubic unit cells for the NaTl structure of β-LiAl below 97 K in a specimen with $C_{Li}=48.6$ at. %.

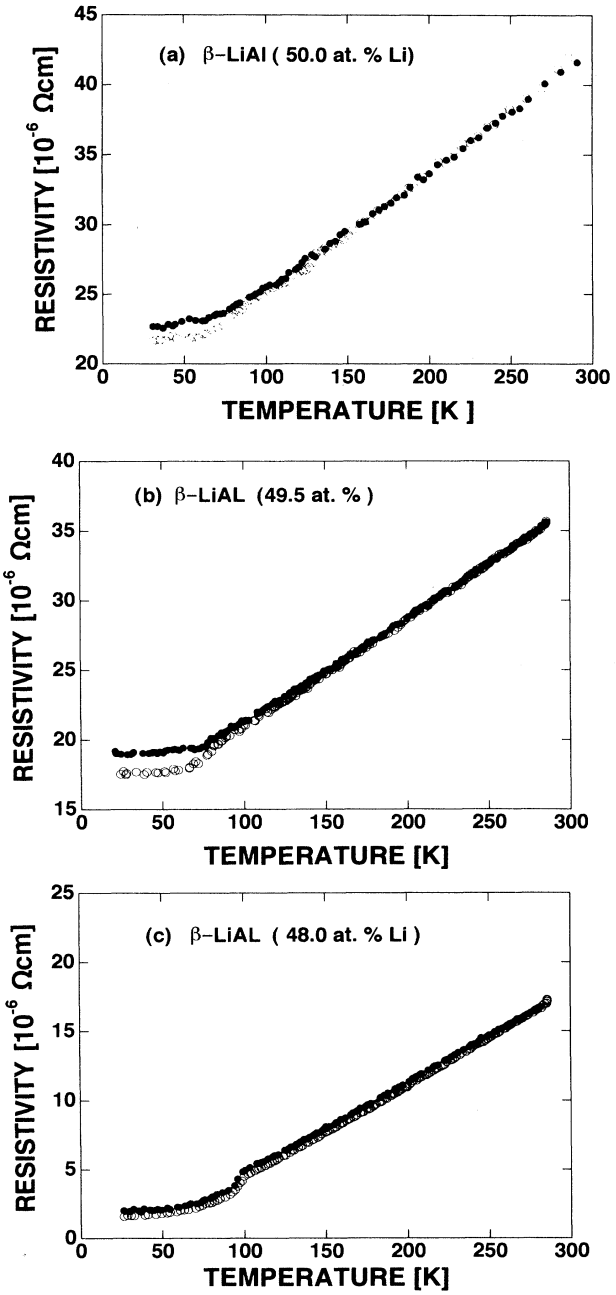

FIG. 1. Temperature-dependent electrical resistivities for various composition of β-LiAl. (a), (b), and (c) show results for specimens with 50.0, 49.5, and 48.0 at. % Li, respectively. The open circles and closed circles represent the data before and after Li-ion irradiation, respectively.

In addition to the modification of the ordered arrangement of V_{Li} due to the Li-ion irradiation, radiation defects were introduced by the irradiation. The residual resistivity increases after the irradiation. The increase in the resistivity is observed at temperatures up to around 200 K for the specimen with $C_{Li}=49.5$ at. %, and to around 300 K for the specimen with $C_{Li}=48.0$ at. %, while the specimen with $C_{Li}=50.0$ at. %, which undergoes the destruction of Li-vacancy ordering, shows a slight increase in the resistivity up to around 150 K. The increase in the resistivity does not arise from the creation of Li_{Al} and the destruction of the V_{Li}-Li_{Al} complex defects. The former antisite defect would cause an increase in the resistivity, since the Li atoms (valency 1) on the Al site (valency 3) must be much more effective as scatterers than a vacancy on the Li site. However, the Li_{Al} defect[14] is stable at room temperature in β-LiAl and the resistivity recovers completely on annealing at room temperature, as discussed later (see Fig. 2). Therefore the Li_{Al} antisite defect is eliminated as a cause of the resistivity increase. On the other hand, the destruction of the V_{Li}-Li_{Al} complex defect would cause a decrease in the resistivity as observed in neutron-irradiated β-^{6}LiAl.[16]

We suggest that the increase in resistivity after the Li-ion irradiation arises from two types of Frenkel defects: a lithium interstitial (Li_i) and lithium vacancy (V_{Li}) pair, and an aluminum interstitial (Al_i) and aluminum vacancy (V_{Al}) pair. Nuclear magnetic resonance linewidth studies gave values of 0.15+0.02 eV (Ref. 20) and 0.12+0.04 eV (Ref. 21) for the activation energy of Li diffusion in near-stoichiometric β-LiAl. Therefore it is expected that the Li atoms in β-LiAl will move easily via the motion of Li vacancies at lower temperatures, leading to the annihilation of the Li_i-V_{Li} pair defect. Although the displacement energy of Al and the activation energy of Al_i migration in β-LiAl have not been reported, the V_{Al}-Al_i pair defect would also be introduced in Li-ion-irradiated β-LiAl. The displacement energies of Al and Si atoms in electron-irradiated Al (Ref. 22) and Si (Ref. 23) are 32 and 15.8 eV, respectively. Since a study[4] of charge redistribution effects in β-LiAl indicates that, while the Li-Al bond is ionically polarized covalent bond, the Al-Al bonds are metalliclike and the Li-Li bonds are essentially nonbonding, the displacement energy of Al in

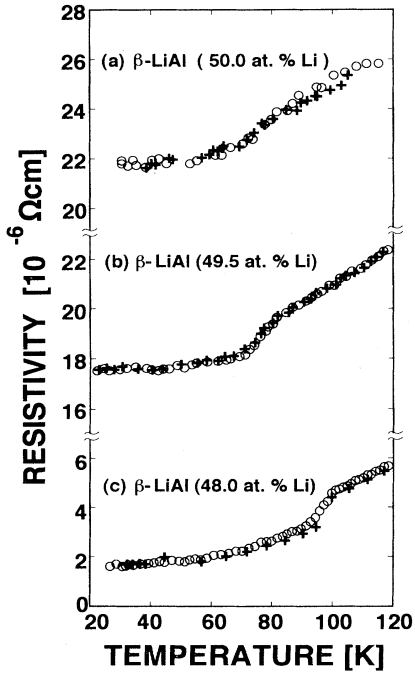

FIG. 2. Temperature-dependent electrical resistivities for various composition of β-LiAl. The open circles and crosses represent the data before Li-ion irradiation and after annealing at room temperature, respectively.

β-LiAl would be a few tens of eV. By analogy with the annealing stages[22] of Al irradiated with 1.5 MeV electrons, which show recovery of the resistivity at a temperature range above about 50 K, the annihilation of V_{Al}-Al_i pairs should occur at high temperatures, above the Li-vacancy ordering temperature.

Figure 2 shows the temperature dependences of resistivity of β-LiAl before the Li-ion irradiation and after the room-temperature annealing of as-irradiated specimens. The resistivities after the annealing were coincident with those before the irradiation. Therefore the Li-ion-irradiation-induced defects are annihilated completely by room-temperature annealing, together with recovery of the Li-vacancy ordering.

III. CONCLUSION

In conclusion, the Li-vacancy ordering in β-$Li_{0.50}Al_{0.50}$ was destroyed by Li-ion irradiation, indicating a relatively weak interaction between the Li vacancies in long-range ordering. On the other hand, the Li-vacancy ordering in β-$Li_{0.48}Al_{0.52}$ did not collapse on irradiation, suggesting a short-range ordering of Li vacancies with a strong interaction between Li vacancies. This situation is closely correlated with the results of neutron diffraction,[18] which shows the body-centered-tetragonal unit cell of the ordered vacancy structure embedded in six face-centered unit cells of the NaTl structure of β-LiAl. The increase in the residual resistivity after irradiation suggests the existence of Frenkel-type defects consisting of a lithium interstitial and Li vacancy pair, and an aluminum interstitial and Al vacancy pair. These defects were annihilated completely by annealing at room temperature.

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*Present address: Mitsubishi Materials Corporation, Central Research Institute, 1-297, Kitabukuro-cho, Omiya, Saitama 330, Japan.

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