# Defect structure in neutron-irradiated $\beta$ -<sup>6</sup>LiAl and $\beta$ -<sup>7</sup>LiAl: Electrical resistivity and Li diffusion

Hiroyuki Sugai and M. Tanase

Department of Radioisotopes, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-11, Japan

M. Yahagi,\* T. Ashida,<sup>†</sup> H. Hamanaka, K. Kuriyama, and K. Iwamura

College of Engineering and Research Center of Ion Beam Technology, Hosei University, Koganei, Tokyo 184, Japan (Received 27 January 1995; revised manuscript received 10 April 1995)

The neutron-irradiation effects on the electrical resistivities of  $\beta$ -<sup>6</sup>LiAl and  $\beta$ -<sup>7</sup>LiAl with 48–54 at. % Li at room temperature are presented. A remarkable decrease of the electrical resistivity is observed in the neutron-irradiated  $\beta$ -<sup>6</sup>LiAl with around 50 at. % Li, but not in the neutron-irradiated  $\beta$ -<sup>7</sup>LiAl. It is suggested that the defect complex ( $V_{Li}$ -Li<sub>Al</sub>) composed of  $V_{Li}$  (a vacancy at the Li site) and Li<sub>Al</sub> (a Li antisite atom at the Al site) is an effective scatterer for carriers in  $\beta$ -<sup>6</sup>LiAl, and the breakup of the  $V_{Li}$ -Li<sub>Al</sub> complex due to the knock on of neutron transmuted <sup>3</sup>H and <sup>4</sup>He induces the abrupt decrease of the electrical resistivity. A carrier-scattering model based on the defect structure of  $\beta$ -LiAl explains consistently the electrical resistivity of  $\beta$ -LiAl before and after neutron irradiation. The Li self-diffusion constant shows a linear relationship for [ ${}^{f}V_{Li}$ ] (Li content  $\leq 51.9$  at. %) or [ $V_{Li}$ -Li<sub>Al</sub>] (Li content  $\geq 51.9$  at. %) using a conventional diffusion model. This strongly suggests that defect concentrations estimated in the present work are reasonable. We also find that the Li out diffusion is obstructed by the breakup of the  $V_{Li}$ -Li<sub>Al</sub> complex due to neutron irradiation.

# I. INTRODUCTION

The intermetallic compound  $\beta$ -LiAl (48-56 at. % Li) crystallizes in the NaTI-type structure<sup>1</sup> [space group  $Fd3m(O_h^7)$ ] composed of two interpenetrating diamond sublattices such that each atom has eight nearest neighbors: four like and four unlike atoms, as shown in Fig. 1. This compound has been studied as an electrode material for secondary batteries<sup>2,3</sup> and a blanket material for nuclear fusion reactors, <sup>4-6</sup> because of the high electronic conductivity and the high diffusivity of Li. We have measured the electrical resistivity of  $\beta$ -LiAl below room temperature<sup>7-9</sup> and at higher temperatures.<sup>10</sup> The electrical conduction of  $\beta$ -LiAl with a semimetallic band<sup>11,12</sup> is governed by positive carriers (holes), <sup>7-9</sup> and considerably affected by the defect structure.<sup>13,14</sup> The Li diffusion in



FIG. 1. Crystal structure of NaTl type (Ref. 1).

0163-1829/95/52(6)/4050(10)/\$06.00

 $\beta$ -LiAl is governed by Li vacancies.<sup>13-22</sup> Thus both electrical and diffusion properties of  $\beta$ -LiAl have a close relation with the defect structure.

The defect structure at room temperature consists of two types of defects, i.e., vacancies in the lithium sublattice  $(V_{\text{Li}})$  and lithium antistructure atoms in the aluminum sublattice  $(\text{Li}_{\text{Al}})$ . The  $V_{\text{Li}}$  concentration  $[V_{\text{Li}}]$  decreases from 3.5 to 0.2 at. % with increasing Li content  $C_{\text{Li}}$  over the range 48–56 at. %, while the Li<sub>Al</sub> concentration  $[\text{Li}_{\text{Al}}]$  varies from 0 to 5.4 at. % with increasing  $C_{\text{Li}}$ .<sup>13,14</sup> Furthermore, the existence of a defect complex  $(V_{\text{Li}}-\text{Li}_{\text{Al}})$  composed of  $V_{\text{Li}}$  and Li<sub>Al</sub> has been suggested by Li diffusion studies; <sup>17,20–22</sup> a vacancy and an impurity tend to form a complex to reduce the strain energy of the matrix, i.e., the atomic size effect.<sup>20,21,23</sup> According to the dependence of  $[V_{\text{Li}}]$  and  $[\text{Li}_{\text{Al}}]$  on  $C_{\text{Li}}$ , the  $V_{\text{Li}}$ -Li<sub>Al</sub> complex concentration is expected to be a maximum at 50.7 at. % Li, where  $[V_{\text{Li}}]$  equals  $[\text{Li}_{\text{Al}}]$ .<sup>13</sup> However, the  $V_{\text{Li}}$ -Li<sub>Al</sub> complex concentration as related to  $C_{\text{Li}}$  is not known yet in detail.<sup>17,20-22</sup>

Increasing resistivity<sup>7,8,10,24-27</sup> with  $C_{\rm Li}$  over the range 48-54 at. % is closely correlated with the increase of  $[{\rm Li}_{\rm Al}]$ , since the Li atom (valence +1) on the Al site (valence -3) is much more effective<sup>24-27</sup> as a scatterer for carriers than  $V_{\rm Li}$  (valence -1) according to Linde's rule.<sup>28</sup> The rule is that the residual resistivity of a metal containing charged impurities is proportional to the square of the valence difference between the impurity atom and the matrix atom. Thus the carrier scattering for the  $V_{\rm Li}$ -Li<sub>Al</sub> complex is expected to be larger than the sum of the carrier scattering for  $V_{\rm Li}$  and Li<sub>Al</sub> defects that exist separately in  $\beta$ -LiAl. In previous work, however, the relation between the resistivity and the  $V_{\rm Li}$ -Li<sub>Al</sub> com-

52

plex has not been considered.

Since the resistivity closely correlates with the defect structure in  $\beta$ -LiAl as mentioned above, we expect that reactor irradiation<sup>29</sup> will change the electrical transport properties of  $\beta$ -LiA1. In a reactor,  $\beta$ -LiA1 is irradiated by  $\gamma$  rays, fast neutrons, and thermal neutrons. As  $\beta$ -LiAl has a unique defect structure, the displacement per atom (DPA) induced by fast neutrons and the recoil of neutron-transmuted atoms must be much larger than those induced by  $\gamma$  rays and thermal neutrons; the main origins of irradiation effects on the electrical transport properties of  $\beta$ -LiAl are the knock on due to fast neutrons and the neutron-transmuted atoms, and also the doping of the neutron-transmuted atoms in  $\beta$ -LiAl. Considering the great difference of the thermal neutron cross section between <sup>6</sup>Li and <sup>7</sup>Li, <sup>30</sup> we expect that reactor irradiation will cause a distinct difference in the electrical transport properties of  $\beta$ -<sup>6</sup>LiAl and  $\beta$ -<sup>7</sup>LiAl.

In a reactor, the dominant nuclear reaction for  $\beta$ -LiAl is only

$${}^{6}\text{Li} + n \rightarrow {}^{3}\text{H} + {}^{4}\text{He} + 4.78 \text{ MeV}$$
 (1)

Tritium (<sup>3</sup>H) is a radioactive isotope of hydrogen and decays through  $\beta$  emission with a half-life of 12.26 yr.<sup>30</sup> The reaction occurs by thermal neutrons (*n*), because the Q value for <sup>6</sup>Li is positive.<sup>30</sup> Since the electronegativity difference between hydrogen (<sup>1</sup>H) and Li is larger than that between <sup>1</sup>H and Al,<sup>31</sup> the ionic interaction between <sup>1</sup>H and Li is stronger than that between <sup>1</sup>H and Al. The chemical properties of <sup>3</sup>H are the same as those of <sup>1</sup>H above room temperature. Accordingly, Li diffusion in  $\beta$ -LiAl will also influence the migration of <sup>3</sup>H produced by neutron irradiation. Indeed, our previous work suggests that there is a strong correlation between the diffusion of <sup>3</sup>H and that of Li in  $\beta$ -<sup>6</sup>LiAl.<sup>6</sup> Thus we examine <sup>3</sup>H diffusion in order to elucidate the Li diffusion mechanism in  $\beta$ -LiAl.

In the present paper, we show that the breakup of the  $V_{\rm Li}$ -Li<sub>Al</sub> complex arises from the knock on of neutrontransmuted <sup>3</sup>H and <sup>4</sup>He atoms produced by the <sup>6</sup>Li( $n, {}^{4}$ He)<sup>3</sup>H reaction. Materials containing <sup>7</sup>Li do not show a transmutation due to thermal neutrons. This breakup of the  $V_{\rm Li}$ -Li<sub>Al</sub> complex induces an important change of electrical resistivity and Li self-diffusion, especially for  $\beta$ -<sup>6</sup>LiAl. We discuss the correlation between the resistivities and the defect structure in  $\beta$ -LiAl as a function of  $C_{\rm Li}$  at 300 K, owing to Linde's rule.<sup>28</sup> Moreover, on the basis of the defect structure in  $\beta$ -LiAl, we also discuss the Li diffusion mechanism in neutronirradiated  $\beta$ -LiAl above room temperature.

# **II. EXPERIMENT**

The chemical purities of <sup>6</sup>Li (95.5% in isotopic purity) and <sup>7</sup>Li (99.9% in isotopic purity) metals were both 99.9% and that of Al over 99.999%. Samples of  $\beta$ -<sup>6</sup>LiAl and  $\beta$ -<sup>7</sup>LiAl were prepared in the range 48.2–54.0 at. % Li by the same method<sup>32,33</sup> reported previously, in which the crystals were grown in a closed atmosphere of argon by slow cooling from a temperature above the melting point<sup>2,25</sup> of 966 K. The estimated error of Li content was confirmed to be 0.1% by both atomic absorption spectroscopy and lattice-parameter measurements.<sup>33</sup>

The samples were formed in dimensions of  $4 \times 4 \times 1$ mm<sup>3</sup> and their surfaces were polished with abrasive paper in paraffin oil. The samples wrapped with Al foil were enclosed in quartz tubes under  $10^{-5}$  Torr. The samples in the quartz tubes were irradiated for 120 min below 350 K in the Japan Research Reactor 4 (JRR-4). The thermal and fast neutron fluxes were  $8.0 \times 10^{13}$  and  $1.2 \times 10^{12}$  cm<sup>-2</sup> s<sup>-1</sup>, respectively. Tritium (<sup>3</sup>H) and <sup>4</sup>He atoms were produced by nuclear reaction between thermal neutrons and <sup>6</sup>Li (cross section<sup>30</sup> 953 b) only in  $\beta$ -<sup>6</sup>LiAl, but scarcely produced by nuclear reaction between fast neutrons and <sup>7</sup>Li (cross section<sup>30</sup> 0.037 b) in  $\beta$ -<sup>7</sup>LiAl. Although <sup>27</sup>Al (natural abundance, 100%; cross section, <sup>34</sup> 0.002 24 b) was transmuted to <sup>28</sup>Al by captur-ing thermal neutrons and <sup>28</sup>Al (half-life<sup>34</sup> 2.30 min) decayed immediately to the stable atom <sup>28</sup>Si, the amount of <sup>28</sup>Si was negligibly small. The decay product <sup>3</sup>He of <sup>3</sup>H (half-life<sup>30</sup> 12.26 yr) in  $\beta$ -<sup>6</sup>LiAl is also negligible, because the electrical measurements were carried out in one or two months after neutron irradiation.

Hall coefficients for  $\beta$ -<sup>6</sup>LiAl with 49.3 at. % Li and  $\beta$ -<sup>7</sup>LiAl with 48.5 at. % Li were measured with a modified ac method<sup>24</sup> at 300 K. The resistivities of  $\beta$ -<sup>6</sup>LiAl with 48.2, 49.3, and 51.8 at. % Li were measured from 300 to 800 K under neon gas flow (60 ml/min) with the Van der Pauw technique.<sup>35</sup> The temperatures of the samples were increased at the rate of about 1 K/min. Simultaneously, the amount of <sup>3</sup>H released from the sample was measured by an ionization chamber.<sup>6,36</sup> The ionization chamber system uses neon carrier gas for the convenience of other experiments,<sup>6,36</sup> and the kind of inert carrier gas is not essential in this study.

### **III. RESULTS AND DISCUSSION**

## A. Defect structure of $\beta$ -LiAl at 300 K

### Neutron-irradiation effect on the resistivity of β-LiAl

The resistivities of unirradiated  $\beta$ -<sup>6</sup>LiAl and  $\beta$ -<sup>7</sup>LiAl increase with increasing  $C_{Li}$  as shown in Fig. 2(a). There is no difference in the resistivities of unirradiated  $\beta$ -<sup>6</sup>LiA1 and  $\beta$ -<sup>7</sup>LiAl. Thus the isotope dependence of the resistivity in  $\beta$ -<sup>6</sup>LiAl and  $\beta$ -<sup>7</sup>LiAl is negligible. Accordingly, it is reasonable that the relation between  $C_{Li}$  and the resistivity of  $\beta$ -LiAl (natural Li contains<sup>30</sup> 7.5 at. % <sup>6</sup>Li and 92.5 at. % <sup>7</sup>Li) determined in previous works<sup>7,8,10,24-27</sup> is the same in this work. However, the number of determinations of resistivity in previous work was not enough to determine the relation between the resistivity and the defect structures in  $\beta$ -LiAl. The resistivities of irradiated  $\beta$ -<sup>6</sup>LiAl and  $\beta$ -<sup>7</sup>LiAl are shown in Fig. 2(b). The percentage change of resistivity in  $\beta$ -<sup>6</sup>LiAl neutron-irradiated and  $\beta$ -<sup>7</sup>LiAl,  $\Delta \rho_p = (\Delta \rho / \rho_{un}) \times 100$ , is summarized as a function of  $C_{Li}$ in Fig. 3. Here,  $\Delta \rho$  is the difference between the resistivity of irradiated  $\beta$ -LiAl ( $\rho_{irr}$ ) and that of unirradiated  $\beta$ -



FIG. 2. Li-content dependence of resistivities for unirradiated  $\beta$ -LiAl (a) and neutron-irradiated  $\beta$ -LiAl (b).

LiAl  $(\rho_{un})$ .  $\Delta \rho_p$  is almost zero for  $\beta$ -<sup>7</sup>LiAl through the range of  $C_{Li}$  examined. Since there is scarcely any nuclear reaction of <sup>7</sup>Li with thermal and fast neutrons, the above fact means that knock on due to fast neutrons has no effect on the resistivity of  $\beta$ -<sup>7</sup>LiAl. The knock on due to fast neutrons has no effect on the resistivity of  $\beta$ -<sup>6</sup>LiAl either. Nevertheless, an apparent decrease of  $\Delta \rho_p$  is observed for  $\beta$ -<sup>6</sup>LiAl and  $\Delta \rho_p$  shows a minimum (about



FIG. 3. Decreasing percentage  $[(\Delta \rho / \rho_{un}) \times 100]$  of resistivities for neutron-irradiated  $\beta$ -<sup>6</sup>LiAl and  $\beta$ -<sup>7</sup>LiAl as a function of Li content.  $\Delta \rho$  is the difference between the resistivity of neutron-irradiated  $\beta$ -LiAl ( $\rho_{irr}$ ) and that of unirradiated  $\beta$ -LiAl ( $\rho_{un}$ ).

50%) around a  $C_{\rm Li}$  of 50 at. %. In general, radiation damage increases the resistivity of a conductor owing to the increase of scatterers. Thus the resistivity decrease in neutron-irradiated  $\beta$ -<sup>6</sup>LiAl does not arise from simple radiation damage, but from the decrease of effective scatterers induced by the knock on due to the neutrontransmuted atoms arising from the <sup>6</sup>Li(*n*, <sup>4</sup>He)<sup>3</sup>H reaction as discussed later.

The calculated concentrations of <sup>3</sup>H and <sup>4</sup>He atoms neutron transmuted from  ${}^{6}Li_{Li}$  and  ${}^{6}Li_{Al}$  in  $\beta$ - ${}^{6}LiAl$  are shown in Fig. 4 together with the calculated concentration of  $\text{Li}_{\text{Li}}$  [Li<sub>Li</sub>] and the reported values<sup>13</sup> of  $[V_{\text{Li}}]$  and [Li<sub>Al</sub>]. As shown in Fig. 4, the number of  ${}^{6}\text{Li}(n, {}^{4}\text{He}){}^{3}\text{H}$ reactions mainly depends on  $[Li_{Li}]$  and is almost constant in the whole  $\beta$ -phase region. In contrast, as shown in Fig. 3, the resistivity in  $\beta$ -<sup>6</sup>LiAl were reduced greatly by the  ${}^{6}\text{Li}(n, {}^{4}\text{He}){}^{3}\text{H}$  reaction in the stoichiometric region of the  $\beta$  phase. This resistivity change must be strongly correlated to the reduction of effective scatterers. Thus the  $C_{\rm Li}$  dependence of the effective scatterers in  $\beta$ -<sup>6</sup>LiAl should have a maximum in the stoichiometric region. Since the  $V_{\rm Li}$ -Li<sub>Al</sub> complex in  $\beta$ -LiAl, which acts as the most effective scatterer, also has a maximum concentration in the stoichiometric region [see Fig. 5(a)], it is expected that the origin of the resistivity decrease in the neutron-irradiated  $\beta$ -<sup>6</sup>LiAl is the breakup of the  $V_{Li}$ -Li<sub>Al</sub> complex induced by the knock on due to particles arising from the  ${}^{6}Li(n, {}^{4}He){}^{3}H$  reaction.

The Hall coefficient  $(R_H)$ , the hole concentration  $(N_h)$ , and the hole mobility  $(\mu_h)$  at room temperature for irradiated and unirradiated  $\beta$ -LiAl are tabulated in Table I. Although  $\beta$ -LiAl is a semimetallic compound, in this work the hole concentration was evaluated using the one-carrier model.<sup>9,25</sup> As shown in Table I,  $N_h$  was not affected by neutron irradiation in  $\beta$ -LiAl, but  $\mu_h$  increased. This supports the hypothesis that the origin of the resistivity decrease in neutron-irradiated  $\beta$ -<sup>6</sup>LiAl is



FIG. 4. The calculated concentration of neutron-transmuted <sup>3</sup>H and <sup>4</sup>He atoms from <sup>6</sup>Li<sub>Li</sub> and <sup>6</sup>Li<sub>Al</sub>, the concentration of  $V_{Li}$  and Li<sub>Al</sub> (Ref. 13), and the calculated concentration of Li<sub>Li</sub>, as a function of Li content in  $\beta$ -LiAl.

Sample	at. % Li	$R_H (10^{-3} \text{ cm}^3 \text{C}^{-1})$		$N_h \ (10^{21} \ {\rm cm}^{-3})$		$\mu_h \ (\mathrm{cm}^2 \ \mathrm{V}^{-1} \mathrm{s}^{-1})$	
		unirradiated	irradiated	unirradiated	irradiated	unirradiated	irradiated
β-⁰LiAl	49.3	0.9	1.0	6.9	6.3	26	47
$\beta$ - <sup>7</sup> LiAl	48.5	1.2	1.3	5.2	4.8	59	58

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TABLE I. Hall coefficient  $(R_H)$ , hole concentration  $(N_h)$ , and hole mobility  $(\mu_h)$  for unirradiated and irradiated  $\beta$ -LiAl.

the breakup of the  $V_{\text{Li}}$ -Li<sub>Al</sub> complex which is an effective scatterer.

# 2. Carrier-scattering model for the defect structure of β-LiAl

In this section, we discuss the relation between the resistivity and the defect structure in  $\beta$ -LiAl according to Linde's rule.<sup>28</sup> Hereafter, a vacancy at the Li site and a Li antisite atom at the Al site, which are not part of the  $V_{\rm Li}$ -Li<sub>Al</sub> complex, are denoted as  ${}^{f}V_{\rm Li}$  and  ${}^{f}{\rm Li}_{\rm Al}$ , respectively. That is,  ${}^{f}V_{\rm Li}$  is a free vacancy<sup>21</sup> and  ${}^{f}{\rm Li}_{\rm Al}$  a free antisite atom. Thus the concentration of net Li vacancies is

$$[{}^{n}V_{\text{Li}}] = [{}^{f}V_{\text{Li}}] + [V_{\text{Li}} - \text{Li}_{\text{Al}}]$$
(2)

and the concentration of net Li antisite atoms is

$$[{}^{n}\text{Li}_{Al}] = [{}^{j}\text{Li}_{Al}] + [V_{Li}\text{-}Li_{Al}], \qquad (3)$$



FIG. 5. Defect concentration deduced from previous work (Ref. 13) (a) and that estimated in this work (b) as a function of Li content in  $\beta$ -LiAl.

where  $[{}^{f}V_{Li}]$  is the concentration of  ${}^{f}V_{Li}$ ,  $[V_{Li}-Li_{Al}]$  the concentration of the  $V_{Li}$ -Li<sub>Al</sub> complex, and  $[{}^{f}Li_{Al}]$  the concentration of  ${}^{f}Li_{Al}$ . The  $C_{Li}$  dependence of  $[{}^{n}V_{Li}]$  and  $[{}^{n}Li_{Al}]$ , which are derived from the reported data<sup>13</sup> using the least-squares method, is shown in Fig. 5(a).

When Coulomb scattering is dominant for carriers, the resistivity due to the ionic impurity atoms per unit volume  $(n_{imp})$  is given by the first Born approximation<sup>28</sup>

$$\rho_0 = R n_{\rm imp} Z^2 , \qquad (4)$$

where Z is the valence difference between the impurity atom and the host material and R a constant which depends on the screening radius in the scattering potential of the impurity and also on the effective mass of the carriers, the charge, the Fermi velocity, and the initial wave number. Equation (4) is the theoretical explanation of Linde's rule.<sup>28</sup>

From Eq. (4), the resistivity due to each defect is derived as a function of  $C_{Li}$ :

$$\rho_{0v}(C_{\rm Li}) = R_v [{}^f V_{\rm Li}](-1)^2 , \qquad (5)$$

$$\rho_{0a}(C_{\rm Li}) = R_a [{}^f {\rm Li}_{\rm A1}](-2)^2 , \qquad (6)$$

$$\rho_{0c}(C_{\rm Li}) = R_c [V_{\rm Li} - {\rm Li}_{\rm Al}](-3)^2 .$$
<sup>(7)</sup>

Here, the net charge of  $V_{\rm Li}$ -Li<sub>Al</sub> composed to  $V_{\rm Li}^{-}$  and  ${\rm Li}_{\rm Al}^{2^{-}}$  is assumed as -3 in a neutral background. The subscripts v, a, and c in Eqs. (5), (6), and (7) mean vacancy, antisite, and complex, respectively. Thus the residual resistivity due to the structural defects in  $\beta$ -LiAl is given as

$$p_{0SD}(C_{Li}) = \rho_{0v} + \rho_{0a} + \rho_{0c}$$
  
=  $R_v [{}^f V_{Li}] + 4R_a [{}^f Li_{Al}] + 9R_c [V_{Li} - Li_{Al}].$ 
(8)

Here, the subscript "SD" in Eq. (8) means the structural defect.

The resistivity of  $\beta$ -LiAl with  $C_{\text{Li}}$  at a temperature  $T, \rho(C_{\text{Li}}, T)$ , is composed of the temperature-independent residual resistivity  $\rho_{0 \text{ SD}}(C_{\text{Li}})$  and the temperature-dependent resistivity  $\rho_{l}(T)$  as follows:<sup>26</sup>

$$\rho(C_{\mathrm{Li}}, T) = \rho_{\mathrm{OSD}}(C_{\mathrm{Li}}) + \rho_{l}(T) .$$
(9)

Here, the subscript l in Eq. (9) means lattice, and  $\rho(C_{\rm Li}, T)$  equals  $\rho_{\rm OSD}(C_{\rm Li})$  below 30 K as shown in previous work.<sup>26,27</sup> Since  $\beta$ -LiAl contains a very large concentration of constitutional defects (approximately 3 at. %) below room temperature,<sup>13,14</sup>  $\rho_{\rm OSD}(C_{\rm Li})$  originates from the structural defects, but not from the impurities.  $\rho_l(T)$ 

is due to both the thermal vibration of the lattice and the disordered arrangement of  $V_{\rm Li}$  which acts as a scattering center. The contribution of the disorder arrangement of  $V_{\rm Li}$  to  $\rho_l(T)$  is negligible at room temperature (RT).<sup>26,27</sup> Thus in Eq. (8), we regard  $\rho_l(\rm RT)$  as constant within experimental error  $(\pm 7\%)$  in the whole  $\beta$ -phase region. According to previous work,<sup>26,27</sup> we estimate  $\rho_l(\rm RT)$  as

$$\rho_l(\mathbf{RT}) = 17.3 \ \mu\Omega \ \mathrm{cm} \ . \tag{10}$$

From Eqs. (8) and (9), the resistivity of  $\beta$ -LiAl at room temperature is given by

$$\rho_0(C_{\mathrm{Li}}, \mathrm{RT}) = R_v[{}^{f}V_{\mathrm{Li}}] + 4R_a[{}^{f}\mathrm{Li}_{\mathrm{AI}}] + 9R_c[V_{\mathrm{Li}} - \mathrm{Li}_{\mathrm{AI}}] + \rho_l(\mathrm{RT}) .$$
(11)

On the basis of Eqs. (2), (3), (10), and (11), the relation between the resistivity and the defect structure in  $\beta$ -LiAl is discussed as follows. First, we consider the simplest dependence of  $[V_{\text{Li}}-\text{Li}_{\text{Al}}]$  on  $C_{\text{Li}}$ , i.e., the case that  $[V_{\text{Li}}-\text{Li}_{\text{Al}}]$  equals  $[{}^{n}\text{Li}_{\text{Al}}]$  at  $C_{\text{Li}}$  of less than 50.7 at. % and  $[{}^{n}V_{\text{Li}}]$  at  $C_{\text{Li}}$  of more than 50.7 at. % as shown in Fig. 5(a). From Eqs. (2) and (3),

$$[{}^{f}V_{\rm Li}] = [{}^{n}V_{\rm Li}] - [{}^{n}{\rm Li}_{\rm Al}] \quad (C_{\rm Li} \le 50.7 {\rm at.} \%)$$
(12)

and

$$[{}^{f}\mathrm{Li}_{\mathrm{Al}}] = [{}^{n}\mathrm{Li}_{\mathrm{Al}}] - [{}^{n}V_{\mathrm{Li}}] \quad (C_{\mathrm{Li}} \ge 50.7 \mathrm{at.} \ \%) \ . \tag{13}$$



FIG. 6. Comparison of the calculated resistivities of unirradiated (a) and neutron-irradiated (b)  $\beta$ -LiAl with the experimental ones (Fig. 2) as a function of Li content.

The values of  $R_v$ ,  $R_a$ , and  $R_c$  are determined by the best fit of Eq. (11), which is indicated as the solid line in Fig. 6(a), using the  $[{}^{f}V_{Li}], [{}^{f}Li_{Al}]$ , and  $[V_{Li}-Li_{Al}]$  of Fig. 5(a).

$$R_v = 0.311 \ \mu\Omega \ \text{cm/at.} \ \%$$
, (14)

$$R_a = 3.93 \ \mu\Omega \ \text{cm/at.} \ \%$$
, (15)

and

$$R_c = 3.42 \ \mu\Omega \ \text{cm/at.} \ \%$$
 (16)

As shown in Fig. 6(a), the experimental resistivity between 49.4 and 51.9 at. % Li is smaller than the resistivity simulated in the case of Fig. 5(a). This fact means that



FIG. 7. Residual resistivities of  $\beta$ -LiAl due to each defect in the three kinds of carrier-scattering models: (a) the case of Fig. 5(a), (b) the case of Fig. 5(b), and (c) the case of no  $V_{\rm Li}$ -Li<sub>Al</sub> complex.

the actual concentration of the  $V_{\text{Li}}$ -Li<sub>Al</sub> complex between 49.4 and 51.9 at. % Li is smaller than that expected in the case of Fig. 5(a). Figure 7(a) indicates that the origin of the residual resistivity based on the above simulation is only  ${}^{f}V_{Li}$  at the Li-deficient  $\beta$ -phase boundary. The dominant origins of the residual resistivity are the  $V_{\rm Li}$ -Li<sub>Al</sub> complex in both the Li-deficient and stoichiometric regions, and <sup>f</sup>Li<sub>Al</sub> in the Li-rich region. Though the lattice distortion around the impurity  $atoms^{37}$  is not considered for Linde's rule [Eq. (4)],<sup>28</sup> the experimentally obtained values for  $R_v$ ,  $R_a$ , and  $R_c$  contain the correction for the lattice distortion. We can evaluate the resistivity per each defect in  $\beta$ -LiAl using Eqs. (10), (11), and (14)–(16), as 0.3  $\mu\Omega$  cm/at. % for  ${}^{f}V_{Li}$ , 15.7  $\mu\Omega$  cm/at. % for  ${}^{f}Li_{Al}$ , and 30.1  $\mu\Omega$  cm/at. % for the  $V_{Li}$ -Li<sub>Al</sub> complex. These values reveal that the carrier scattering of  ${}^{f}Li_{Al}$  and the  $V_{Li}$ -Li<sub>Al</sub> complex is much larger than that of  ${}^{f}V_{Li}$ . The reason is that the lattice strain around  ${}^{f}Li_{Al}$ and  $Li_{Al}$  in the  $V_{Li}$ -Li<sub>Al</sub> complex is much larger than that around  ${}^{f}V_{\text{Li}}$ , since the crystal radius of the  $\text{Li}^{-}$  ion (0.60 Å) is larger than that of the  $\text{Al}^{3+}$  ion (0.50 Å).<sup>21,38</sup> Indeed, for the example of a small lattice strain, the theoretical value of the resistivity per 1 at. % vacancy in pure Li metal is 0.759  $\mu\Omega$  cm.<sup>39</sup> The carrier scattering of the  $V_{\text{Li}}$ -Li<sub>Al</sub> complex is about twice larger than that of  $^{f}$ Li<sub>Al</sub>, as predicted by Linde's rule.<sup>28</sup>

Next, inversely, we estimate the actual defect concentrations in  $\beta$ -LiAl from the experimental resistivity of Fig. 6(a) using Eqs. (10), (11), and (14)-(16). The estimated defect concentrations of Fig. 5(b) are different from the concentrations of Fig. 5(a) considered in the above paragraph. In particular,  $[V_{\text{Li}}\text{-Li}_{\text{Al}}]$  in Fig. 5(b) increases linearly with increasing  $C_{\text{Li}}$  between 49.4 and 51.9 at. %. As discussed in Secs. III B and III C, the Li diffusion mechanism of  $\beta$ -LiAl also supports the  $C_{\text{Li}}$  dependence of defect concentration in the case of Fig. 5(b). The residual resistivity due to each defect concentration is shown in Fig. 7(b); the resistivity of  $\beta$ -LiAl is predominantly due to the  $V_{\text{Li}}\text{-Li}_{\text{Al}}$  complex in the stoichiometric region and  ${}^{f}\text{Li}_{\text{Al}}$  in the Li-rich region.

If all of the  $V_{\text{Li}}$ -Li<sub>Al</sub> complexes in  $\beta$ -<sup>6</sup>LiAl are broken up by the <sup>6</sup>Li(*n*, <sup>4</sup>He)<sup>3</sup>H reaction,

$$[V_{\rm Li}-{\rm Li}_{\rm Al}]=0$$
 . (17)

From Eqs. (2) and (3)

$$\begin{bmatrix} {}^{f}\boldsymbol{V}_{\mathrm{L}i} \end{bmatrix} = \begin{bmatrix} {}^{n}\boldsymbol{V}_{\mathrm{L}i} \end{bmatrix}$$
(18)

and

$$[{}^{f}\mathrm{Li}_{\mathrm{Al}}] = [{}^{n}\mathrm{Li}_{\mathrm{Al}}] .$$
<sup>(19)</sup>

This case is identical to the two-point-defects model<sup>13,26</sup> with no  $V_{\text{Li}}$ -Li<sub>Al</sub> complex. Substitution of Eqs. (17)–(19) in Eq. (11) gives the resistivity

$$\rho_0(C_{\rm Li}, RT) = R_v[{}^nV_{\rm Li}] + 4R_a[{}^n{\rm Li}_{\rm Al}] + \rho_l(RT) .$$
 (20)

The resistivity predicted from Eqs. (14), (15), and (20) is shown as the dash-dotted line in Fig. 6(b) together with the experimental resistivity in neutron-irradiated  $\beta$ -LiAl. The resistivity estimated from the two-point-defects model increases with increasing  $C_{\rm Li}$  and shows a negative deviation from linearity (a concave shape). The resistivity is similar to the experimental one in neutron-irradiated  $\beta$ -<sup>6</sup>LiAl, but not to that in  $\beta$ -<sup>7</sup>LiAl. This fact supports our hypothesis that the origin of the resistivity decrease in neutron-irradiated  $\beta$ -<sup>6</sup>LiAl is the breakup of the  $V_{\text{Li}}$ -Li<sub>Al</sub> complex induced by the <sup>6</sup>Li(n, <sup>4</sup>He)<sup>3</sup>H reaction. When the residual resistivity arises from only the two kinds of defects <sup>f</sup> $V_{\text{Li}}$  and <sup>f</sup>Li<sub>Al</sub>, <sup>f</sup>Li<sub>Al</sub> is the dominant origin of the resistivity as shown in Fig. 7(c).

# 3. Breakup mechanism for the defect complex of neutron-irradiated $\beta^{-6}$ LiAl

The concentration of displacement atoms  $[N_{DA}]$  induced by the  ${}^{6}\text{Li}(n, {}^{4}\text{He}){}^{3}\text{H}$  reaction was estimated to be  $9.3 \times 10^{20}$  cm<sup>-3</sup> by the NRT (Norgett, Robinson, and Torrens) model.<sup>40</sup> The number of nuclear reactions induced by neutrons was calculated using the neutron energy spectrum of the JRR-4,<sup>41,42</sup> and the neutron crosssection library ENDF/B-IV (Evaluated Nuclear Data File, Version-IV).<sup>43,44</sup> The damage energy used in the NRT model was calculated by the extended EDEP-1 computer code.<sup>45</sup> The recoil events for the energetic <sup>3</sup>H and <sup>4</sup>He atoms produced by the  ${}^{6}Li(n, {}^{3}H){}^{4}He$  reaction are 73 and 121 per reaction, respectively. In the EDEP-1 calculation, the mean mass number of <sup>6</sup>Li and <sup>27</sup>Al was used as the mass of the irradiated material. On the other hand,  $[N_{DA}]$  induced by the knock on of fast neutrons was estimated to be  $9.3 \times 10^{18}$  cm<sup>-3</sup> using the method mentioned above. The exact calculation of the DPA for the cascade in two components was not done at present, but the above approximations are enough for order-ofmagnitude estimation. 46

On the basis of the above DPA calculation, we discuss the possible mechanism for the breakup of the  $V_{Li}$ -Li<sub>Al</sub> complex by the  ${}^{6}\text{Li}(n, {}^{4}\text{He}){}^{3}\text{H}$  reaction in  $\beta {}^{-6}\text{LiAl}$ .  ${}^{6}\text{Li}$ atoms at both Li and Al atom sites transmute to <sup>3</sup>H and <sup>4</sup>He atoms through the <sup>6</sup>Li(n, <sup>4</sup>He)<sup>3</sup>H reaction in  $\beta$ -<sup>6</sup>LiAl. Tritium (<sup>3</sup>H) and <sup>4</sup>He atoms recoil with kinetic energies of 2.7 and 2.0 MeV, respectively; the energies are derived from the Q value of the <sup>6</sup>Li(n, <sup>4</sup>He)<sup>3</sup>H reaction. <sup>30,47</sup> Consequently, <sup>6</sup>Li<sub>Li</sub><sup>0</sup> and <sup>6</sup>Li<sub>Al</sub><sup>2-</sup> change to  $V_{Li}^{-}$  and  $V_{Al}^{3-}$ , respectively. Successively, the recoil <sup>3</sup>H and <sup>4</sup>He atoms collide with the constituent atoms of  $\beta$ -<sup>6</sup>LiAl and lose their energy through multiscattering with the constituent atoms. The recoil atoms produce vacancies and interstitial atoms to disturb the defect structure of  $\beta$ -<sup>6</sup>LiAl. Although the recoil atoms produce Frenkel pairs, the interstitial atoms of the Frenkel pairs migrate and combine with vacancies of the same kind of atoms to disappear on annealing during and after irradiation. In particular, the activation energy for Li diffusivity in  $\beta$ -LiAl is so small<sup>21</sup> (0.09-0.13 eV) that Li atoms easily diffuse through  ${}^{f}V_{\text{Li}}$ (as mentioned in Sec. III B) to occupy the vacancy sites even at room temperature. Here, it must be noticed that the interstitial Li atom hardly migrates to  $V_{\rm Li}$  in the  $V_{\rm Li}$ -Li<sub>Al</sub> complex, because there is a repulsive interaction between the interstitial Li atom and the defect complex due to the atomic size effect<sup>20,21,23</sup> of Li<sub>Al</sub>. Since  $[N_{DA}]$  of 9.3×10<sup>20</sup> cm<sup>-3</sup> induced by the <sup>6</sup>Li(*n*, <sup>4</sup>He)<sup>3</sup>H reaction in  $\beta$ -<sup>6</sup>LiAl is four times larger than the  $[V_{Li}-Li_{Al}]$  of 2.4×10<sup>20</sup> cm<sup>-3</sup> in the stoichiometric region [see Figs. 4 and 5(b)], it is possible to break up the defect complex by the rearrangement of atoms in  $\beta$ -<sup>6</sup>LiA1. The above speculation is supported by the facts that the resistivity of neutron-irradiated  $\beta$ -<sup>6</sup>LiA1 was not increased in either Li-deficient or Li-rich  $\beta$ -phase boundaries, and decreased in the stoichiometric region of the  $\beta$  phase as shown in Fig. 3.

After room-temperature annealing, most of the recoil <sup>3</sup>H and <sup>4</sup>He atoms occupy constituent vacancy sites, because the number of  $V_{\rm Li}$  is  $10^2$  times larger than those of <sup>3</sup>H and <sup>4</sup>He atoms as shown in Fig. 4. The transmuted atoms trapped in the vacancy sites are more stable than those trapped in the interstitial sites. Then the constituent vacancy sites  $(V_{Li}^{-})$  change to  ${}^{3}H_{Li}^{0}$  and  ${}^{4}He_{Li}^{-}$  by trapping the  ${}^{3}H$  and  ${}^{4}He$  atoms, respectively. Two vacancy sites,  $V_{\rm Li}^{-}$  and  $V_{\rm Al}^{3-}$ , are created by the recoil of the neutron-transmuted atoms as mentioned in the previous paragraph. The valence change at the constituent vacancy sites trapping <sup>3</sup>He atoms [0-(-1)=1] compensates the change at the Li sites (-1-0=-1) and the Al sites [-3-(-2)=-1]. On the other hand, the valence of the constituent vacancy sites trapping <sup>4</sup>He atoms, which have a closed shell, does not change. Consequently, the net valence in  $\beta$ -<sup>6</sup>LiAl is not altered by the neutrontransmuted <sup>3</sup>H and <sup>4</sup>He. Thus, according to Linde's rule,<sup>28</sup> the neutron-transmuted <sup>3</sup>H and <sup>4</sup>He do not alter the resistivity of  $\beta$ -<sup>6</sup>LiAl not containing the  $V_{\text{Li}}$ -Li<sub>Al</sub> complex. The resistivity of  $\beta$ -<sup>6</sup>LiAl at both Li-deficient and Li-rich  $\beta$ -phase boundaries is not affected by neutron irradiation as shown in Fig. 3. In the stoichiometric region, the concentration of the neutron-transmuted <sup>3</sup>H and <sup>4</sup>He atoms in  $\beta$ -<sup>6</sup>LiAl is 10<sup>2</sup> times smaller than [ $V_{Li}$ - $Li_{A1}$ ] as shown in Fig. 4. Thus the occupation of  $V_{Li}$ with neutron-transmuted <sup>3</sup>H and <sup>4</sup>He atoms is not dominant for the breakup of the  $V_{\rm Li}$ -Li<sub>Al</sub> complex in  $\beta$ -<sup>6</sup>LiAl, but the knock on due to the recoil <sup>3</sup>H and <sup>4</sup>He atoms must be essentially important. [ $N_{DA}$ ] of 9.3×10<sup>18</sup> cm<sup>-3</sup> estimated for fast neutrons is

 $[N_{\rm DA}]$  of  $9.3 \times 10^{18}$  cm<sup>-3</sup> estimated for fast neutrons is 30 times smaller than  $[V_{\rm Li}-{\rm Li}_{\rm Al}]$  of  $2.4 \times 10^{20}$  cm<sup>-3</sup> in the stoichiometric region of the  $\beta$  phase [see Figs. 4 and 5(b)]. This supports the fact that a resistivity change was not observed in neutron-irradiated  $\beta$ -<sup>7</sup>LiAl as shown in Fig. 3. The difference in recoil between fast neutrons and neutron-transmuted atoms must be the same as that in mass between neutrons and atoms. We conclude that the knock on due to neutron-transmuted <sup>3</sup>H and <sup>4</sup>He atoms causes the decrease of the  $V_{\rm Li}$ -Li<sub>Al</sub> complex concentration.

# B. Relation between Li self-diffusion constant and the defect structure of $\beta$ -LiAl

In the previous section, we suggested that the existence of the  $V_{\text{Li}}$ -Li<sub>Al</sub> complex is very important for the electrical transport properties in  $\beta$ -LiAl. In this section, we also suggest that the  $V_{\text{Li}}$ -Li<sub>Al</sub> complex plays an important role for Li diffusion in  $\beta$ -LiAl. In order to verify the path of Li diffusion in the defect structure, we discuss the relationship between  $V_{\text{Li}}$  concentrations ([ $V_{\text{Li}}$ ]) and Li selfdiffusion constants  $D_0(\text{Li})$  in  $\beta$ -LiAl.  $D_0(\text{Li})$  for a simple vacancy diffusion mechanism is given by<sup>20,21,48</sup>

$$D_{0}(\text{Li}) = \begin{cases} f(l^{2}/6)\tau_{0}[{}^{f}V_{\text{Li}}] & \text{for } C_{\text{Li}} \leq 51.9 \text{ at. }\%, \\ f(l^{2}/6)\tau_{0}[V_{\text{Li}}\text{-}\text{Li}_{\text{Al}}] & \text{for } C_{\text{Li}} \geq 51.9 \text{ at. }\%, \end{cases}$$
(21)

where  $f(=\frac{1}{2}$  for a diamond lattice<sup>49</sup>) is the correlation factor, l the nearest-neighbor distance  $(l = \sqrt{3}/4a)$ , where a is the lattice constant), and  $\tau_0$  is the time when Li<sub>Li</sub> atoms jump into  ${}^{f}V_{Li}$  or  $V_{Li}$  in the  $V_{Li}$ -Li<sub>Al</sub> complex.  $C_{\rm Li} \sim 51.9$  at. % is the Li concentration at  $[{}^{f}V_{\rm Li}] = 0$ at. %. Figure 8 shows the experimental data of  $D_0(Li)$ for  $[{}^{f}V_{Ii}]$  or  $[V_{Ii}-Li_{A1}]$  and the lines calculated using Eq. (21).  $D_0(\text{Li})$  increases linearly with  $[{}^fV_{\text{Li}}]$  or  $[V_{\text{Li}}-\text{Li}_{\text{Al}}]$ .  $D_0(\text{Li})$  values used here were taken from a recent study<sup>20,21</sup> of Li self-diffusion by pulsed-field gradient NMR at temperatures below 500 K. Here, we estimated the  $\tau_0$  to be  $8.2 \times 10^{-14}$  s from Eq. (21) using  $D_0$ (Li) and  $[{}^{f}V_{Li}]$  for near the Li-deficient  $\beta$ -phase boundary where  ${}^{f}V_{\rm Li}$  is dominant in  $C_{\rm Li} \sim 48.2$  at. %, and  $\tau_0$  for a region where the  $V_{\rm Li}$ -Li<sub>Al</sub> complex is dominant in  $C_{\rm Li} \sim 51.9$ at. % is estimated as  $2.8 \times 10^{-13}$  s. The calculated lines are consistent with the experimental data as shown in Fig. 8. Therefore, the Li self-diffusion mechanism in  $\beta$ -LiAl evaluated here supports the defect concentrations estimated in Sec. III A 2. On the other hand, Chen and co-workers<sup>20,21</sup> claimed that the relation between  $D_0$ (Li) and  $[{}^{n}V_{Li}]$  is nonlinear from the Li self-diffusion model using two mean jump times for  ${}^{f}V_{Li}$  and  $V_{Li}$  in the  $V_{Li}$ -Li<sub>Al</sub> complex. They suggested that the nonlinear behavior arises from an attractive interaction between  $V_{\text{Li}}$  and  $\text{Li}_{A1}$  due to the atomic size effect.<sup>20,21,23</sup> However, using  $[{}^{J}V_{\text{Li}}]$  or  $[V_{\text{Li}}\text{-}\text{Li}_{A1}]$ , we found that Li selfdiffusion in  $\beta$ -LiAl can be explained easily with the conventional diffusion model.



FIG. 8. Li diffusion constant as a function of free vacancy  $({}^{f}V_{Li})$  and  $V_{Li}$ -Li<sub>Al</sub> complex concentrations. The solid and broken lines are calculated by Eq. (21). The experimental data are taken from Ref. 20.

### C. Li out-diffusion mechanism for neutron-irradiated β-LiAl

In this section, we discuss the Li out-diffusion behavior below 800 K on the basis of the Li self-diffusion mechanism in  $\beta$ -LiAl, which is made clear in Sec. III B. The Li out-diffusion behavior is examined in the three defect regions of  $\beta$ -LiAl where  ${}^{f}V_{\text{Li}}$  and the  $V_{\text{Li}}$ -Li<sub>Al</sub> complex coexist (the stoichiometric region),  ${}^{f}V_{\text{Li}}$  is dominant (the Li-deficient region), and the  $V_{\text{Li}}$ -Li<sub>Al</sub> complex is dominant (the Li-rich region), as shown in Fig. 5(b).

### 1. Free-vacancy and defect-complex region

Figure 9 shows the resistivity before and after neutron irradiation and <sup>3</sup>H release after neutron irradiation in near-stoichiometric  $\beta$ -<sup>6</sup>LiAl. In the unirradiated samples, anomalous resistivity is observed around 600 K as in our previous work.<sup>10</sup> This irreversible behavior in the electrical resistivity is interpreted as follows. Above 500 K,  $V_{Al}$ is formed by Li diffusion from  $Li_{Al}$  to  $V_{Li}$  in the  $V_{Li}$ - $Li_{Al}$ complex, and  $V_{Al}$  is filled up successively by Al migration from Al<sub>Li</sub> sites at elevated temperatures. As a result, Li out diffusion from Li<sub>Al</sub> bound to a Li vacancy (in the  $V_{\text{Li}}$ -Li<sub>Al</sub> complex) creates  ${}^{f}V_{\text{Li}}$  and the  $V_{\text{Li}}$ -Li<sub>Al</sub> complex disappears. The electrical resistivity decreases with increasing  ${}^{f}V_{Ii}$ , showing the lower scattering effect. An oxide layer is formed by the reaction of the out-diffused Li with oxygen in the atmosphere. The presence of a thin layer of Li<sub>2</sub>O was observed on the surface of  $\beta$ -LiAl after resistivity measurement.  $^{10,50}$  This was confirmed to be mainly Li<sub>2</sub>O by Rutherford backscattering and x-ray diffraction.<sup>10,50</sup>

We remark that the  $\beta$ -LiAl crystal in an appropriate equilibrium pressure of Li vapor is grown with each Li content.<sup>32,33</sup> On the other hand, as mentioned in the above paragraph, Li in Li-rich  $\beta$ -LiAl diffuses out as a result of heating in the atmosphere to high temperatures. Thus  $\beta$ -LiAl is a novel intermetallic compound which



FIG. 9. Curves A: Temperature dependence of electrical resistivity (heating, closed circles; cooling, open circles) and <sup>3</sup>H release (open squares) for neutron-irradiated  $\beta$ -LiAl with 49.3 at. % Li. Curves B: Temperature dependence of electrical resistivity (heating, closed triangles; cooling, plus) for unirradiated  $\beta$ -LiAl with 50.1 at. % Li.

reaches a more stable Li-deficient phase containing only  $V_{\rm Li}$  through a Li out-diffusion process at higher temperatures.

In the irradiated samples, the remarkable irreversible behavior in the electrical resistivity around 600 K is only slight (see Fig. 9). These facts suggest that breakup of the  $V_{\rm Li}$ -Li<sub>Al</sub> complex as a large scatterer is caused by neutron irradiation. Conversely, the Li out diffusion does not occur if  $V_{\rm Li}$  and  ${\rm Li}_{\rm Al}$  are distributed separately in  $\beta$ -LiAl since the irreversible change in the resistivity is not observed in neutron-irradiated  $\beta$ -<sup>6</sup>LiAl. Moreover, the resistivity of neutron-irradiated  $\beta$ -<sup>6</sup>LiAl does not approach the value for the Li-deficient  $\beta$ -phase boundary with decreasing temperature, showing a slight increase in resistivity, because the remaining <sup>f</sup>Li<sub>Al</sub> act as scattering centers.<sup>51</sup> We also suggest that the release of <sup>3</sup>H occurs through  ${}^{f}V_{Li}$  from  ${}^{3}H_{Li}$  sites rather than from  ${}^{3}H_{Al}$  sites because the  ${}^{3}H$  release shows the same tendency as in the Li-deficient  $\beta$  phase containing only  ${}^{f}V_{\text{Li}}$ , as shown in the next section.

### 2. Free-vacancy region

Figure 10 shows the resistivity and the <sup>3</sup>H release after neutron irradiation in Li-deficient  $\beta$ -<sup>6</sup>LiAl. A resistivity change is not observed in  $\beta$ -<sup>6</sup>LiAl containing only  ${}^{f}V_{\text{Li}}$ . In the Li-deficient region, the Li diffusion is caused simply by Li exchange between  ${}^{f}V_{\text{Li}}$  and Li<sub>Li</sub>. Thus the <sup>3</sup>H release in the Li-deficient  $\beta$  phase shows similar behavior to that in neutron-irradiated stoichiometric  $\beta$ -<sup>6</sup>LiAl, where the  $V_{\text{Li}}$ -Li<sub>Al</sub> complex has already been broken up by neutron irradiation.

### 3. Defect-complex and Li-antisite-defect region

Figure 11 shows the resistivity and the <sup>3</sup>H release after neutron irradiation in Li-rich  $\beta$ -<sup>6</sup>LiAl. Irreversible behavior in the resistivity is observed clearly in this region. This suggests that the  $V_{\text{Li}}$ -Li<sub>Al</sub> complex exists in this region at room temperature because, after the breakup of the defect complex due to neutron irradiation, in order to relax the lattice strain due to the atomic size



FIG. 10. Temperature dependence of electrical resistivity (heating, closed circles; cooling, open circles) and <sup>3</sup>H release (open squares) for neutron-irradiated  $\beta$ -LiAl with 48.2 at. % Li.



FIG. 11. Temperature dependence of electrical resistivity (heating, closed circles; cooling, open circles) and <sup>3</sup>H release (open squares) for neutron-irradiated  $\beta$ -LiAl with 51.8 at. % Li.

effect, <sup>20,21,23</sup> which is stronger in the Li-rich region of the  $\beta$  phase than in either the Li-deficient or the stoichiometric region, the defect complex is recreated by the combination of  ${}^{f}V_{\text{Li}}$  and  ${}^{f}\text{Li}_{\text{Al}}$ . The recreation of defect complexes is also suggested by the fact that the resistivity of neutron-irradiated  $\beta$ -<sup>6</sup>LiAl is much the same as that of unirradiated  $\beta$ -<sup>6</sup>LiAl above 51.5 at. % Li as shown in Fig. 6(b). On the other hand, <sup>3</sup>H begins to be released through  ${}^{f}V_{\text{Li}}$  sites attributed to the thermally decomposed complex, accompanied by a decrease in resistivity as mentioned in Sec. III C 1.

# **IV. CONCLUSION**

Thermal neutron irradiation of stoichiometric  $\beta$ -<sup>6</sup>LiAl drastically decreased the resistivity at room temperature,

but not that of  $\beta$ -<sup>7</sup>LiAl. The phenomena are consistently explained in terms of the breakup of the  $V_{\rm Li}$ -Li<sub>Al</sub> complex acting as the most effective scatterer in  $\beta$ -LiAl. The present studies strongly support the conclusion that the breakup of the complex defect arises from the knock on of neutron-transmuted <sup>3</sup>H and <sup>4</sup>He atoms produced by the  ${}^{6}\text{Li}(n, {}^{4}\text{He}){}^{3}\text{H}$  reaction. We also demonstrated that the RT resistivity of  $\beta$ -LiAl depends on the concentration of  ${}^{f}V_{Li}$ ,  ${}^{f}Li_{Al}$ , and the  $V_{Li}$ -Li<sub>Al</sub> complex. The relation between the RT resistivity and the concentrations of the three kinds of defects  $({}^{f}V_{Li}, {}^{f}Li_{Al}, and the V_{Li}-Li_{Al} com$ plex) was derived from the carrier-scattering model based on Linde's rule. The evaluated values of the residual resistivities for each defect are 0.3  $\mu\Omega$  cm/at. % for  ${}^{f}V_{Li}$ , 15.7  $\mu\Omega$  cm/at. % for <sup>f</sup>Li<sub>Ab</sub>, and 30.1  $\mu\Omega$  cm/at. % for the  $V_{\rm Li}$ -Li<sub>Li</sub> complex.

The Li self-diffusion constant showed a linear relationship for  $[{}^{f}V_{\text{Li}}]$  (Li content  $\leq 51.9$  at. %) and  $[V_{\text{Li}}-\text{Li}_{Al}]$ (Li content  $\geq 51.9$  at. %) using a conventional diffusion model. This strongly suggests that the defect concentrations estimated in the present work are reasonable. We also found that the Li out diffusion is obstructed by the breakup of the  $V_{\text{Li}}$ -Li<sub>Al</sub> complex due to neutron irradiation.

# ACKNOWLEDGMENTS

We acknowledge R. Nakasima of Hosei University for encouragement and Y. Kazumata of the Japan Atomic Energy Research Institute (JAERI) for support in the Hall measurement. One of the authors (H.S.) is grateful to T. Aruga, H. Maeta, and H. Naramoto of JAERI for valuable discussions on this work. This work was supported by the cooperative research program between JAERI and Hosei University.

- \*Present address: Department of Electronics and Information Engineering, Faculty of Engineering, Aomori University, Aomori 030, Japan.
- <sup>†</sup>Present address: Power Reactor and Nuclear Fuel Development Corporation, Tokai, Ibaraki, 319-11, Japan.
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