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ABSTRACT

NMR measurements have been carried out on stoichiometric β -LiAl samples as a function of temperature and frequency. The ^7Li spin-lattice relaxation was found to be predominantly dipolar. Data were analyzed using several diffusion models. The results show that a fraction of the constitutional Li vacancies in β -LiAl is bound to the vicinity of a Li antisite defect. The remaining free vacancies are responsible for the fact that LiAl is a superionic Li conductor. The spin-spin relaxation results support this picture of two different vacancy environments. The high temperature results demonstrate still another type of Li diffusion related to thermally generated defects.

I. INTRODUCTION

Advanced electrochemical cells with high specific energy and power require electrode materials having large changes in composition and Gibbs free energy with regard to the electroactive ion.^{1,2} Lithium-aluminum alloys

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satisfy the requirement that the anode be a good mixed conductor for both electrons and the electroactive ion. However, the optimization of this material, the understanding of the electrode reactions, and the development of new anode ternary compositions have required a detailed knowledge of the charge and mass transport processes in LiAl at the atomic level.

The most commonly used starting composition is the β -phase alloy of nominal stoichiometry, β -LiAl. The β -phase of LiAl crystallizes in the Zintl structure (B32; prototype NaTl). This structure is built up of two interpenetrating diamond sublattices occupied by Li and Al. The β -phase domain extends from approximately 48 to 54 atom% Li. In this paper, we report careful ^7Li NMR relaxation time measurements in β -LiAl samples over the temperature range between 77K and 680K at 25, 16.8, 7, and 4.3 MHz. We characterize and explain several features of the temperature dependence of the relaxation times, and find the relation between the defect structure and fast Li-ion transport in this material.

Only a few NMR studies of β -LiAl have been done. Schone and Knight³ were the first to point out that the activation energy for the motion of Li in β -LiAl is much smaller than that in lithium metal.⁴ This was concluded from the temperature dependence of ^7Li and ^{27}Al NMR linewidths and was attributed to the existence of constitutional vacancies of a nonthermal origin in the lattice. Brittain and co-workers conducted measurements of ^7Li and ^{27}Al spin-lattice relaxation times (T_1) in stoichiometric β -LiAl over a wide range of temperatures.⁵ Recently, these studies have been extended⁶ to include nonstoichiometric β - $\text{Li}_x\text{Al}_{1-x}$, with $0.48 < x < 0.545$, as well as doped β - $\text{Li}_{0.5}\text{Al}_{0.5-y}\text{M}_y$ where $\text{M} = \text{Ag}$ or In , with $0.0 < y < 0.046$. Their theoretical analysis differs from what we will develop in this paper and the differences will be discussed later.

II. EXPERIMENTAL

The samples used in this study are powders (average diameter $< 42 \mu$) that are sealed in 8-mm O.D. silica tubes under an argon atmosphere. The synthesis and characterization of β -phase lithium aluminum ($\beta\text{-Li}_x\text{Al}_{1-x}$) were described in a previous paper.⁷ The chemical composition of this sample is: $50.0 \pm 0.1 \text{ atom\% } ^7\text{Li}$ and $50.0 \pm 0.1 \text{ atom\% } ^{27}\text{Al}$. We observed an irreversible change of $^7\text{Li } T_1$ values when $\beta\text{-LiAl}$ powders, contained in silica tubes, were kept for several hours at temperatures higher than approximately 200°C . This change is the result of a Li-loss from reaction of LiAl with silica and is evidenced by the formation of color centers in the SiO_2 tubes. To avoid this reaction, sample powders contained in high-purity, hot-pressed boron nitride capsules were used exclusively for all measurements above 200°C .

The determination of $^7\text{Li } T_1$ has been done by using the inversion recovery method ($180^\circ \rightarrow t_{\text{SL}}(\text{variable}) \rightarrow 90^\circ \rightarrow \text{FID pulse sequence}$)^{8,9} at 25, 16.8, 7, and 4.3 MHz with a modified Bruker B-KR 322A pulsed NMR spectrometer, equipped with a computer-controlled data acquisition and processing system.¹⁰ The average experimental error is estimated to be $\pm 3\%$ of $1/T_1$ values for most of the measurements, unless stated otherwise. The $1/T_1$ values shown in the figures are averages of five to ten measurements. ^7Li spin-spin relaxation times (T_2) have also been determined at 25 and 16.8 MHz by using the single echo method ($90^\circ \rightarrow t_{\text{SE}}(\text{variable}) \rightarrow 180^\circ \rightarrow t_{\text{SE}} \rightarrow \text{echo pulse sequence}$)¹¹ as well as the Carr-Purcell-Meiboom-Gill¹² (CPMG) method [$90^\circ \rightarrow [t_{\text{CP}}(\text{variable}) \rightarrow 180^\circ \rightarrow t_{\text{CP}} \rightarrow \text{echo}]_n, n > 12, \text{ pulse sequence}$]. The temperature of the sample was maintained within $\pm 0.5\text{K}$ by employing a temperature-controlled continuous gas flow cryostat.

III. RESULTS

Our results for the ^7Li nuclear signals show that (1) the recovery of ^7Li longitudinal magnetization in the T_1 measurement is exponential over the entire range of temperatures at any Larmor frequency; (2) the decay of ^7Li transverse magnetization in the T_2 measurement by the CPMG method does not fit a single exponential; and (3) the pattern of echo decay in the CPMG experiments depends strongly on the pulse spacing t_{CP} . Because of (2) and (3), we have analyzed the CPMG echo decay assuming the following formula:

$$A(t = nt_{CP}) = A(0)[P'_a \exp(-t/T'_{2a}) + P'_b \exp(-t/T'_{2b})] \quad (1)$$

where P'_i is the apparent fractional population of the i th component and $\sum_i P'_i = 1.0$ must be satisfied. T'_{2i} is the apparent T_2 of the i th component. By applying a nonlinear least squares treatment¹³ to Eq. (1) (as a three-parameter problem), we determined all primed quantities for the CPMG experiments. If $T'_{2a} \gg T'_{2b}$, $P'_a \sim P'_b$ and $0.15 \lesssim t/T'_{2b} \lesssim 1.0$, $A(t)$ is well represented by a single exponential term in Eq. (1). This is actually the case in the single spin echo experiment where the total sweep time was chosen to satisfy the above-mentioned condition for t/T'_{2b} . Thus, the SE experiments yield T'_{2b} .

The ^7Li T_1 and T_2 results obtained at 25 and 16.8 MHz are shown in Fig. 1. One should notice the following features in the temperature dependence of T_1 and T_{2i} : (1) both T_1 curves are asymmetric with respect to a broad T_1 minimum; (2) the T_1 values (25 MHz) at the highest temperatures shown are longer than those at 16.8 MHz; (3) the decrease of both T'_{2a} and T'_{2b} with decreasing temperature is not linear; and (4) the ratio of T_1/T_{2i} at the T_1 minimum is unusually large. In addition to the aforementioned, the

following features should also be noted: (5) T'_{2b} determined by the CPMG method at temperatures higher than about 250K depend on t_{CP} ; and (6) T'_{2a} exhibits a strong dependence on t_{CP} over the entire range of temperatures.

The features exhibited in the temperature dependence of T_1 and T_{21} are rather unusual and strongly suggest that the measurements of T_1 should be extended to lower Larmor frequencies and over a wider temperature range. This is mainly because there are large increments in T_1 vs temperature. The results of T_1 measurements performed at 7 and 4.3 MHz are presented in Fig. 2 together with the results for 25 and 16.8 MHz shown in Fig. 1a. The temperature dependence of T_1 at 7 and 4.3 MHz clearly indicates new features: (a) The broad minimum observed at higher frequencies is resolved into two minima. (b) A new minimum appears at higher temperatures. And (c) the slope of T_1 increases rapidly at $\sim 100K$. In order to analyze and discuss these features, it is convenient to divide the entire temperature range into three regions, A, B, and C, as shown in Fig. 2. Each region has one important question. It is as follows: In region A, what gives rise to a T_1 minimum? In B, what is responsible for the double minimum structure T_1 and the asymmetry? And in region C, what is the reason for the nonlinear behavior?

In order to answer these questions, we must first determine the nuclear relaxation mechanisms which govern the behavior of T_1 . In view of the crystal structure¹⁴ of β -LiAl and the presence of permanent vacancies^{2,7} the important relaxation mechanisms are: (1) the nuclear magnetic dipole-dipole interactions, (2) the nuclear quadrupole interactions; and (3) the interactions between the nuclear spins and the conduction electrons. Since we have not found a leveling off of 7Li T_1 at very low temperatures (in contrast to Li metal),⁴ we must conclude that the contribution from the interactions between the 7Li spins and the conduction electrons (Korringa term)¹⁵ to 7Li T_1 is

negligibly small. This agrees with previous studies.^{5,6} If the quadrupole interaction had been the predominant relaxation mechanism for a 3/2 spin nucleus, it is well known¹⁶ that the recovery of the longitudinal magnetization as well as the decay of the transverse component should exhibit nonexponential behaviors, as shown in Fig. 3. However, this is actually not the case for ${}^7\text{Li}$ T_1 relaxation in $\beta\text{-LiAl}$, strongly suggesting that the nuclear magnetic dipole-dipole interaction is the predominant mechanism for ${}^7\text{Li}$ relaxation.

In support of the above suggestion that ${}^7\text{Li}$ spin-lattice relaxation is predominantly governed by the nuclear magnetic dipole-dipole interactions, we have studied the relaxations in isotopically pure ${}^7\text{LiAl}$ and in isotopically mixed (${}^7\text{Li}$ - ${}^6\text{Li}$)Al samples. Of course, the ${}^7\text{Li}$ quadrupolar interaction is the same in both systems. Because of the crystal structure of $\beta\text{-LiAl}$ (B32 Zintl structure),¹⁴ one must consider the like-spin (${}^7\text{Li}$ - ${}^7\text{Li}$) and the unlike spin (${}^7\text{Li}$ - ${}^{27}\text{Al}$) interactions in the nuclear magnetic dipolar relaxation mechanism for ${}^7\text{Li}$. Thus, one may write the experimentally determined $1/T_1$ for ${}^7\text{Li}$ at ω_0 , $[(1/T_1)_{\text{Li}}]$, in the isotopically-pure $\beta\text{-}{}^7\text{LiAl}$ (sample I) as follows:

$$1) \quad (1/T_1)_{\text{Li}} = (1/T_1)^{\text{DD}}\{{}^7\text{Li} - {}^7\text{Li}\} + (1/T_1)^{\text{DD}}\{{}^7\text{Li} - {}^{27}\text{Al}\} + (1/T_1)^{\text{others}}. \quad (2)$$

Here, the symbols in the brackets designate particular pairs of the nuclear magnetic dipole-dipole interactions. Since there is a significant difference in the nuclear magnetic properties of ${}^7\text{Li}$ and ${}^6\text{Li}$, one can write an expression for $(1/T_1)_{\text{Li}}$ for ${}^7\text{Li}$ at ω_0 in the isotopically-mixed samples $\beta\text{-}{}^7\text{Li}_{0.25}{}^6\text{Li}_{0.25}{}^{27}\text{Al}_{0.5}$ (sample II) as follows:

$$\begin{aligned}
 \text{II)} \quad (1/T_1)_{\text{Li}} &= (1/T_1)^{\text{DD}} \{ {}^7\text{Li} - {}^7\text{Li} \} + (1/T_1)^{\text{DD}} \{ {}^7\text{Li} - {}^6\text{Li} \} + (1/T_1)^{\text{DD}} \{ {}^7\text{Li} - {}^{27}\text{Al} \} + (1/T_1)^{\text{others}} \\
 &= 0.5(1+F)(1/T_1)^{\text{DD}} \{ {}^7\text{Li} - {}^7\text{Li} \} + (1/T_1)^{\text{DD}} \{ {}^7\text{Li} - {}^{27}\text{Al} \} + (1/T_1)^{\text{others}} \quad (3)
 \end{aligned}$$

where

$$F = (16/45) [\gamma({}^6\text{Li})/\gamma({}^7\text{Li})]^2 = 0.05098 \quad (3a)$$

and $\gamma(i)$ is the nuclear magnetogyric ratio of nuclear isotope i . Equation (3) is valid to a high degree of approximation and its validity is discussed in Appendix A. Now, it is possible to determine explicitly $(1/T_1)^{\text{DD}} \{ {}^7\text{Li} - {}^7\text{Li} \}$ from the values of $(1/T_1)_{\text{Li}}$ measured in samples I and II with the aid of Eqs. (2) and (3). Figure 4 shows the temperature dependence of $(1/T_1)^{\text{DD}} \{ {}^7\text{Li} - {}^7\text{Li} \}$ at 7 MHz in the isotopically pure β - ${}^7\text{LiAl}$ (sample I). Once the $(1/T_1)^{\text{DD}} \{ {}^7\text{Li} - {}^7\text{Li} \}$ values are determined, the sum of the second and third terms in Eq. (2) can be easily evaluated. The plot of these terms vs $1/T(\text{K})$ is also shown in Fig. 4.

While there are some contributions from the third term, in Eq. (2), the curves in Fig. 4 reveal a double maximum structure in region B.

In any theory for the nuclear magnetic dipole-dipole relaxation mechanism, the plot of $1/T_1$ vs $1/K$ exhibits a single maximum if there is only one type of motion responsible for relaxation. For simplicity, let us apply Torrey's theory^{17,18} for nuclear relaxation caused by the translational motions of nuclei to ${}^7\text{Li}$ spin-lattice relaxation in β - LiAl . According to this theory, the relaxation rate $1/T_1$ can be expressed as

$$1/T_1 = \frac{C}{\omega_0} \phi(k, y) \quad (4)$$

where C and k are constants and the latter is related to crystal structure. The variable y is defined by $y = \omega_0 \tau / 2$, where ω_0 is the Larmor frequency and τ is the mean time between translational jumps. $1/T_1$ is maximum when $\phi(k, y)$ reaches its maximum. The numerical value of $\phi(k, y)$ depends on the value of k ; namely, crystal structure. Therefore, by rewriting Eq. (4) as

$$\phi(k, y) = \phi(k, y) \Big|_{y = y_{\max}} \cdot \frac{(1/T_1)}{(1/T_1)_{\max}} \quad (5)$$

one can determine the values of $\phi(k, y)$ at various temperatures from the experimental values of T_1 . Once the value of $\phi(k, y)$ is determined, the corresponding value of the variable y , in turn, can be evaluated. If the thermal nature of τ can be represented by

$$1/\tau = 1/\tau_0 \exp(-E_a/kT), \quad (6)$$

where E_a is the Arrhenius activation energy, the plot of $\ln(y)$ vs $1/K$ should be linear. This expectation is based on the assumption that only one kind of thermal motion is responsible for relaxation over the entire range of temperatures. Figure 5 represents such a plot of $\ln(y)$ vs $1/K$ obtained from $^7\text{Li } T_1$ values at 25 MHz in $\beta\text{-}^7\text{LiAl}$. It is apparent that the plot consists of two linear sections with different slopes, even though the plot of experimental T_1 vs $1/K$ shows a smooth curve (Fig. 1). This strongly suggests that at least two different kinds of magnetic dipole-dipole relaxation processes are operative in the middle temperature range. The appearance of a double minimum and a significant asymmetry in the plot of $\ln T_1$ vs $1/K$ at both 7 and 4.3 MHz (Fig. 2) strengthens this suggestion.

Thus, it can be concluded that: (1) the ^7Li nuclear quadrupolar relaxation process is not a major component of the double minimum structure in the temperature dependence of T_1 ; and (2) the double minimum structure and asymmetry of the T_1 curves can be attributed to the nuclear magnetic dipole-dipole relaxations caused by two different kinds of Li motion.

IV. THEORY OF NUCLEAR RELAXATION CAUSED BY TRANSLATIONAL MOTION IN SOLIDS

The theory of nuclear magnetic dipole-dipole relaxation caused by translational motions was first developed by Torrey.^{17,18} Wolf incorporated¹⁹⁻²¹ several different diffusion mechanisms observed in solids into Torrey's theory and obtained significantly modified expressions.

The spin-lattice relaxation rate of the resonant spin I (resonance frequency ω_I) arising from the nuclear magnetic dipole-dipole interactions in a system containing two magnetically different nuclei I (resonant) and S (non-resonant) can be expressed as⁹

$$\begin{aligned} (1/T_1)^{\text{DD}}(\omega_I) = & \frac{3}{2} \gamma_I^4 \hbar^2 I(I+1) [J^{(1)}(\omega_I) + J^{(2)}(2\omega_I)] + \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \left[\frac{1}{12} K^{(0)}(\omega_I - \omega_S) \right. \\ & \left. + \frac{3}{2} K^{(1)}(\omega_I) + \frac{3}{4} K^{(2)}(\omega_I + \omega_S) \right] \end{aligned} \quad (7)$$

Where, γ_I and ω_I are the magnetogyric ratio and Larmor frequency of nucleus I, respectively. $J^{(m)}(\omega)$ and $K^{(m)}(\omega)$ are the spectral densities of the auto correlation functions. The first term in Eq. (7) represents the like-spin interactions while the second term represents the unlike-spin interactions.

The rf 180° pulse is applied exclusively to the resonant nuclei I in the determination of T_1 for spin I by means of the inversion recovery method. However, this will also produce some nuclear polarization of nonresonant spin

S because the amplitudes of the longitudinal magnetizations of the two spin species are coupled together. This polarization of spin S will affect, in turn, the time dependence of the longitudinal magnetization of spin I through cross relaxation effects. In the case of β - $^7\text{LiAl}$, it has been found^{5,6} that ^{27}Al T_1 are shorter than ^7Li T_1 by more than two orders of magnitude. This strongly suggests that ^{27}Al polarization produced by the 180° pulse for ^7Li will dissipate very quickly to an equilibrium value. Therefore, it is a good approximation to assume that cross relaxation effects by ^{27}Al polarization in the ^7Li T_1 measurements are negligibly small and the unlike spin contribution to ^7Li $(1/T_1)^{\text{DD}}(\omega_I)$ is well represented by the second term of Eq. (7).

The final expression of $(1/T_1)^{\text{DD}}(\omega_I)$ rests on the theoretical models which describe the motion of I and/or S nuclei and the corresponding formulae for their spectral densities in Eq. (7). In our study, we have used three different models: (i) Torrey's isotropic diffusion model¹⁷; (ii) Torrey's lattice diffusion model^{17,18} and (iii) Wolf's mono-vacancy encounter model.¹⁹⁻²¹ In the following, we present the final expression applied to a system consisting of spin I and S with brief remarks.

(i) Torrey's Isotropic Diffusion Model

If one assumes that the motion can be described by the solution of the diffusion equation, Eq. (4) must be rewritten as,

$$(1/T_1)^{\text{DD}}(\omega_I) = C' (1/\omega_I) \Psi(\alpha_I, \alpha_S, x_I, x_S) \quad (8)$$

where

$$C' = \frac{4\pi}{5} \gamma_I^4 \hbar^2 I(I+1) n_I a_I^{-3} \quad (8a)$$

and

$$\Psi(\alpha_I, \alpha_S, x_I, x_S) = \sum_j \phi_j(\alpha_I, x_I) + \sum_i \lambda_i' \phi_i'(\alpha_i, x_i) \quad (8b)$$

with

$$\lambda_i' = \left(\frac{\gamma_S}{\gamma_I}\right)^2 \frac{S(S+1)}{I(I+1)} \frac{n_S}{n_I} \quad (8c)$$

Here, $\alpha_I = \langle r^2 \rangle / 12a_I^2$ and $x_I = (\omega_I a_I^2 / D_I)^{1/2}$ where D_I is the self-diffusion coefficient of spin I and a_I is the lower limit of the radial integration. n_J ($J = I$ or S) denotes spin density. α_i and x_i are related to α_I and x_I as shown in a later section and refer to quantities related to the unlike-spin couplings. Here, $\phi(\alpha_I, x_I)$ and $\phi'(\alpha_S, x_S)$ represent the like-spin and unlike spin relaxation functions, respectively, and are given by^{17,22}

$$\phi(\alpha_I, x_I) = f(\alpha_I, x_I) + 2f(\alpha_I, \sqrt{2} x_I) \quad (9a)$$

and

$$\phi'(\alpha_S, x_S) = f(\alpha_S, x_S) + C' f(\alpha_S, x_S') + C'' f(\alpha_S, x_S'') \quad (9b)$$

where

$$C' = (1/3) |1 - R|^{-1}, \quad C'' = 2(1+R)^{-1}, \quad x_S' = |1 - R|^{1/2} x_S, \quad \text{and} \quad x_S'' = |1+R|^{1/2} x_S.$$

Here, $f(\alpha, x)$ is a function of elementary functions and derived by Torrey

(Eq. (55) in Ref. 17) and the constant $R = \omega_S/\omega_I$ or γ_S/γ_I .

The major difference between this model and the lattice diffusion model is that here a nucleus walks randomly not only in direction, but also makes jumps of random magnitude in distance.

(ii) Torrey's Lattice Diffusion Model

$(1/T_1)^{DD}(\omega_I)$ in powdered samples is given by

$$(1/T_1)^{DD}(\omega_I) = (C/\omega_I) \phi(k_I, k_S, y) \quad (10)$$

where

$$C = \frac{8\pi}{5} \gamma_I^4 \hbar^2 I(I+1) n_I (k_I \ell a)^{-3} \quad (10a)$$

and

$$\begin{aligned} \phi(k_I, k_S, y) = [yG(k_I, y) + 4yG(k_I, 2y)] \\ + \lambda [2yG(k_S, 2y) + \frac{2}{3} yG(k_S, 2y') + 4yG(k_S, 2y'')] \end{aligned} \quad (10b)$$

with

$$\lambda = \left(\frac{\gamma_S}{\gamma_I}\right)^2 \frac{S(S+1)}{I(I+1)} \left(\frac{k_I}{k_S}\right)^3 \frac{n_S}{n_I} \quad (10c)$$

Here, variables y , y' , and y'' are defined as $y = \omega_I \tau / 2$, $y' = (1-R)y$, and $y'' = (1+R)y$, respectively. The parameter k_J ($J = I$ or S) is a dimensionless normalization factor introduced by Torrey¹⁷ as follows:

$$k_J = \frac{4}{3} \pi n_J a^{-3} \ell^{-3} / \int r_J^{-6} \quad (11)$$

where ℓ is the nearest neighbor distance for the I or S spin species, a is the lower limit of radial integration and r is the distance from the origin of the coordinate system. n_J denotes the number of I or S spins in the unit cell. The expression for the function $G(k,y)$ is given by Torrey in the following integral form,

$$G(k,y) = \int_0^{\infty} [J_{3/2}(a\rho)]^2 \frac{1 - A(\rho)}{[1 - A(\rho)]^2 + y^2} \frac{d\rho}{\rho}$$

or

$$= \int_0^{\infty} [J_{3/2}(kx)]^2 \frac{1 - A(x)}{[1 - A(x)]^2 + y^2} \frac{dx}{x} \quad (12)$$

where

$$A(x) = \sin(x)/x \quad (12a)$$

$$\text{and } k = a/\ell \text{ with } x = \rho\ell. \quad (12b)$$

$J_{3/2}(kx)$ is the usual Bessel function of rank 3/2. The numerical integration of Eq. (12) was performed by using FORTRAN program ANC4²³. The results calculated by our FORTRAN program were checked with those of Resing and Torrey.¹⁸ A perfect agreement was obtained to at least four significant figures. Equations (12), (12a) and (12b) imply physically that a nucleus walks randomly in allowed directions, but makes jumps of equal magnitude, ℓ , in distance.

(iii) Wolf's Mono-Vacancy Encounter Model

Wolf demonstrated¹⁹ the importance of "temporal correlation," i.e., the correlation between the random motion of the point defect and the motion of the nuclei in the calculation of $J^{(m)}(\omega)$ ²⁴. Following the nomenclature of Eisenstadt and Redfield,²⁴ we call the individual displacements ℓ_j of spin j , "jumps," while the series of jumps of a nucleus produced by the same point-defect is called an "encounter" between the defect and the nucleus. What we observe in a relaxation experiment is an average of the numbers of relative jumps and of the probability $P(\ell_j)$ over the initial distance. This is because there are many encounters of a pair of nuclei with different point defects during the relaxation process. When one incorporates the above aspect, Eq. (12) must be rewritten as follows:

$$G'(k, y) = \int_0^\infty [J_{3/2}(x)]^2 \frac{[1-A(\frac{x}{a})] \cdot \frac{Z(0)}{1-P(0)} \cdot y}{[1-A(\frac{x}{a})]^2 + [\frac{Z(0)}{1-P(0)} \cdot y]^2} \frac{dx}{x} \quad (13)$$

where

$$A(\frac{x}{a}) = \sum_{j>0} P(\ell_j) \frac{\sin(\frac{x}{k} \cdot \frac{\ell_j}{\ell})}{\frac{x}{k} \cdot \frac{\ell_j}{\ell}} \quad (13a)$$

$$\text{and } \frac{1}{\tau_{\text{NMR}}} = \frac{1}{\tau} \frac{1}{Z(0)} [1-P(0)] \quad (13b)$$

Here, Z and τ denote the mean numbers of relative jumps of two spins during an encounter and the mean time between successive jumps, respectively. τ_{NMR} represents the mean time between two encounters. If the last jumps of the encounter bring the nuclei back to the positions that they had before the encounter, one can assume that these encounters do not cause relaxation and

hence do not enter into the correlation function. This is because the time between these jumps is very short.¹⁹ The probability of the occurrence of these encounters is denoted by $P(0)$ in Eq. (13). It should be noted that x and y are defined as $a\rho$ and $\omega\tau_{\text{NMR}}$, respectively. And, C defined in Eq. (10a) must be multiplied by a factor of $Z(0)/[1-P(0)]$.

The calculation of $(1/T_1)^{\text{DD}}$ by this model requires the calculation of $Z(0)$, $P(0)$, and $P(l_j)$ corresponding to various l_j . All these quantities depend on the crystal structure of the substance under investigation.

The expression for spin-spin relaxation rate $[(1/T_2)^{\text{DD}}(\omega_I)]$ corresponding to that for spin-lattice relaxation Eq. (10) and (10b) can be written as follows:^{18,19}

$$(1/T_2)^{\text{DD}}(\omega_I) = C \frac{Z(0)}{1-P(0)} \cdot (1/\omega_I) \Omega(k_I, k_S, y) \quad (14)$$

where

$$\begin{aligned} \Omega(k_I, k_S, y) = & \left[\frac{3}{2} yG'(k_I, 0) + \frac{5}{2} yG'(k_I, y') + yG'(k_I, 2y) \right] \\ & + \lambda \left[\frac{2}{3} yG'(k_S, 0) + \frac{1}{2} yG'(k_S, 2y) + \frac{1}{6} yG'(k_S, 2y') + yG'(k_S, 2y'') + yG'(k_S, 2y''') \right] \end{aligned} \quad (14a)$$

with $y''' = R \cdot y$. The first and second brackets denote the like and unlike spin interactions, respectively.

V. APPLICATION OF THEORY TO ^7Li $(1/T_1)$

First, we turn our attention to $(1/T_1)_{\text{Li}}^{\text{expt}}(\omega_I)$ in the middle temperature region. We apply the three theories described above. The following

assumptions are made in an attempt to deconvolute $(1/T_1)_{Li}^{expt}(\omega_I)$ into two theoretical $1/T_1$ curves: (1) the nuclear magnetic dipole-dipole interactions caused by translational motions of Li are the relaxation mechanisms for two different processes; and (2) the two different motions of Li do not interfere with each other; i.e., the two relaxation processes occur independently. These assumptions lead to the following expression:

$$(1/T_1)_{Li}^{expt}(\omega_I) = (1/T_1)^{DD}(\omega_I, I) + (1/T_1)^{DD}(\omega_I, II) + (1/T_1)^{others}. \quad (15)$$

Here, the Roman numerals in the parentheses denote two relaxation processes and $(1/T_1)^{DD}(\omega_I, I \text{ or } II)$ consists of the like- and unlike-spin interactions. In the three theories described above $(1/T_1)_{Li}^{expt}(\omega_I)$ takes, in general, the form expressed in Eq. (2). In this form, two modes of Li motion can be differentiated by the correlation time τ . Or, through Einstein's relation between τ and the self-diffusion coefficient $D = \langle r^2 \rangle / 6\tau$, the difference in the thermal nature of two Li motions can be represented by the explicit temperature dependence of τ or D through Eq. (6); namely, $1/\tau_0$ (or D_0) and E_a . Thus, the temperature dependence of the relaxation rate for the i th process, $(1/T_1)^{DD}(\omega_I, i)$, can be calculated theoretically with a set of the assumed values for the constant $C(i)$, activation energy $E_a(i)$ and $1/\tau_0(i)$ in Eq. (4) and Eq. (6). While the expressions for $1/T_1$ vary from one model to another, the same relations hold for τ , and thus, the temperature dependence of $1/T_1$ can be calculated.

In order to deconvolute $(1/T_1)_{Li}^{expt}(\omega_I)$ into two theoretical $(1/T_1)^{DD}(\omega_I, i)$ we first calculate $(1/T_1)^{DD}(\omega_I, i)$ with a set of the assumed values for $C(i)$, $E_a(i)$ and $1/\tau_0(i)$ as a function of temperature. By regarding these three quantities as adjustable parameters, we repeat the calculation of

$(1/T_1)^{DD}(\omega_I, i)$ until a satisfactory agreement between the experimental values of $(1/T_1)_{Li}^{expt}(\omega_I)$ and the calculated values of $i = 1, 2 (1/T_1)^{DD}(\omega_I, i)$ is obtained over the middle temperature range. The determination of numerical values for $C(i)$, $E_a(i)$ and $1/\tau_0(i)$ was first performed for experimental values of $(1/T_1)_{Li}^{expt}(\omega_I)$ at 7 MHz over the temperature range $130 < T < 330$ K. Since $(1/T_1)^{DD}(\omega_I, i)$ depends explicitly on the Larmor frequency ω_I and also implicitly on ω_I through the relaxation function $\phi(k, x)$, the numerical values for the six parameters obtained above for $\omega_I = 7$ MHz can be checked by simulating the theoretical $(1/T_1)_{Li}(\omega_I)$ curves at other Larmor frequencies. A good agreement between theoretical and experimental $(1/T_1)_{Li}(\omega_I)$ curves should be regarded as an indication of consistency in our deconvolution of $(1/T_1)_{Li}^{expt}(\omega_I)$.

In model (i), it is assumed that $\langle r^2 \rangle = a^2$ and thus, $\alpha = 1/12$. All like- and unlike-spin interactions must be counted as separate entities for the first and second terms in Eq. (8b). Since the nuclear magnetic dipole-dipole interaction is proportional to r^{-6} in magnitude, it is a good approximation to include only the following interactions in the LiAl lattice system: (1) the Li-Li nearest neighbors, (2) the Li-Al nearest neighbors, and (3) the Li-Al next nearest neighbors. All parameters appearing in the interactions (2) and (3) can be related to those in the interaction (1) and the final expression in the above approximation is given by

$$\Psi(\sigma_I, \alpha_S, x_I, x_S) = \phi(\alpha_I, x_I) + \lambda_1' \phi'(\alpha_{S1}, x_{S1}) + \lambda_2' \phi'(\alpha_{S2}, x_{S2}) \quad (16)$$

where λ_1' and λ_2' are given by Eq. (8c) with $n_S/n_I = 1$ and $n_S/n_I = 3/2$, respectively. Also, it can be shown easily from the crystal structure that $\alpha_{S1} = \alpha_I$, $\alpha_{S2} = (3/4)\alpha_I$, $x_{S1} = x_I$, and $x_{S2} = (2/\sqrt{3})x_{S1}$.

In model (ii), the following numerical values were used for calculation: $k_I = 0.81014a^{-6}$, $k_S = 0.72509a^{-6}$ for the NaTl type lattice system^{5,6} and $l = a\sqrt{3}/4$ with $a = 6.37 \pm 0.01$ Å at room temperature⁷.

In model (iii), the numerical values of l_j , $P(l_j)$, $P(0)$, and $Z(0)$ are needed in the calculation of $(1/T_1)^{DD}(\omega_I, I \text{ or } II)$. Table I lists the values of these parameters calculated for the diamond lattice system.²⁵⁻²⁷

The values of the six parameters determined for each of the three models in the deconvolution of $(1/T_1)_{Li}^{expt}(\omega_I = 7 \text{ MHz})$ are summarized in Table II. Figure 6 demonstrates excellent agreement between the experimental and theoretical $(1/T_1)_{Li}(\omega_I)$ values obtained by Wolf's theory (Model (iii)) at 7 MHz in the middle temperature range. All the calculations were performed by using the values listed in Tables I and II for model (iii). In addition, Fig. 6 shows deviations at the high and low temperature ranges from the theoretical values. Good agreement between the experimental and theoretical $(1/T_1)_{Li}(\omega_I)$ values at frequencies other than 7 MHz was obtained for all three models. The best agreement was obtained with model (iii).

Once the deconvolution of $(1/T_1)_{Li}^{expt}(\omega_I)$ has been completed in the middle temperature region, the theoretical $(1/T_1)_{Li}(\omega_I)$ values are generated in the high and low temperature regions by using the values in Table II. By subtracting the theoretical $(1/T_1)_{Li}(\omega_I)$ from the experimental one in the high temperature region, the $(1/T_1)^{DD}(III)$ values were determined where III represents the third relaxation process which is effective only at higher temperatures (see Fig. 2). The activation energy for this relaxation process was estimated from the slope of $(T_1)^{DD}(III)$ plot vs. $1/K$, to be $E_a = 0.30$ eV. The experimental T_1 in $\beta\text{-}^7\text{Li}_{0.25}\text{}^6\text{Li}_{0.25}\text{Al}_{0.5}$ are longer than the corresponding T_1 in $^7\text{LiAl}$ in the high temperature region. This clearly eliminates the possibility of explaining the third T_1 minimum by the paramagnetic impurity

effect.²⁸ The magnetization relaxes through nuclear magnetic dipolar interactions. Besides, the total amount of paramagnetic impurity in the sample was less than 1 ppm as determined from chemical analyses⁷. This amount is too small to account for the third T_1 minimum as observed in some fluorides²⁸.

The theoretical evaluation of $(1/T_1)^{DD}(\text{III})$ was also attempted by using Torrey's isotropic diffusion model.¹⁷ One of the important differences in the temperature dependence of $(1/T_1)^{DD}$ between process III and either process I or II is the fact that the absolute value of the former is only about a third of either of the latter. This implies a larger value of a_I in Eq. (8) and also, more importantly, suggests changes in both α_I and x_I values. In a manner similar to the deconvolution of $(1/T_1)_{Li}^{expt}(\omega_I)$ in the middle temperature region, we calculated $(1/T_1)^{DD}(\text{III})$ over the temperature range $380 < T < 670$ K by adjusting the values of α , D_0 , E_a , and $C(\text{III})$ until a satisfactory agreement between the experimental and calculated $(1/T_1)^{DD}(\text{III})$ values was obtained. Agreement could only be obtained for $\alpha > 1/12$. Physically, this means that the mean jump distance is longer than the nearest neighbor distance. The values determined for process III are also listed in Table II.

At temperatures between 125 and 143 K, there is some disagreement between the experimental and theoretical $(1/T)_{Li}(\omega_I)$ values at 7 MHz. This may be explained by the small contribution from ^7Li quadrupole relaxation as suggested by Kishio et al.^{5,6} The $(1/T_1)_{Li}^{expt}(\omega_I)$ measured at 7 MHz at temperatures below 125 K reveal a somewhat unusual trend; i.e., there is a gradual transition near 100 K (Fig. 2). This anomaly is characterized by the following: (1) The absolute values of $(1/T_1)_{Li}^{expt}(\omega_I)$ below 100 K are considerably smaller than those extrapolated from the values in the temperature range $150 < T < 115$ K and; (2) the experimental values are, of

course, smaller than the values of $\sum_{i=1,2} (1/T_1)^{DD}(i)$ calculated with the values listed in Table I. A possible explanation will be presented in the following section.

Figure 1 includes a T_2 curve at 25 MHz calculated by Wolf's mono-vacancy encounter model¹⁷ with the values listed in Tables I and II. A comparison of the curve with the experimental T'_{2A} and T'_{2B} values leads to the following: (1) the non-linear nature of the temperature dependence of T_2 stems from the existence of two dipolar relaxation processes; and (2) only T'_{2A} values fall in the vicinity of the calculated T_2 values and, therefore, the relaxation mechanism for T'_{2B} is not attributable to the nuclear dipole-dipole interactions. Further discussion will be found in the following section.

VI. DISCUSSION

Precision density and x-ray lattice constant measurements^{7,29} have led to a two-defect model for β -LiAl. In this model, two types of constitutional point defects coexist over the entire β -phase field at room temperature. These defects are: (a) vacancies on the Li sublattice, V_{Li} , which are dominant in the Li-poor side of the phase field; (b) Li antisite defects on the Al sublattice, Li_{Al} , which are dominant defects in the Li-rich side. The existence of Li-vacancies for Li-poor compositions of β -LiAl has been confirmed directly in a neutron diffraction study³⁰ that showed an ordering of the vacancies on the Li sublattice below 100 K. The relatively low ordering temperature suggests that Li vacancies are very mobile for Li-poor compositions.

Chemical diffusivity measurements³¹ by Wen et al. have demonstrated that β -LiAl is a good Li conductor over the entire phase field at elevated temperatures. At the lower phase boundary, Li is transported by the very

mobile vacancies. Since the concentration of vacancies at the upper phase boundary is very low, mobile Li vacancies cannot be responsible for the Li diffusion in Li-rich alloys. However, the mechanism of rapid Li transport at the upper phase boundary is not known.

A. T_1 in the High Temperature Range

A recent study of the crystal structure by the powder neutron diffraction method in the temperature range between 300 and 940 K has revealed that:²

(1) the lattice constant increases linearly with temperature and the thermal expansion coefficient $\Delta a/a$ is $2.57 \times 10^{-5} \text{deg}^{-1}$; (2) the lithium root mean square displacements derived from the thermal parameter B_{Li} are not anomalously large; (3) there is no phase transformation in β -LiAl upon heating from room temperature up to the melting point; however, β -LiAl disorders at high temperatures.² This last fact implies that both types of anti-site defects, Al_{Li} and Li_{Al} , are present in large concentrations at elevated temperatures. Based on these neutron diffraction results, relaxation process III (Table II) is associated with the nuclear motion related to the disordering process. One question arising from this conclusion is whether there are rapid Al motions involved at elevated temperatures in terms of the NMR time scale. Schone and Knight found³ that ^{27}Al NMR linewidths were constant (5 kHz) over the temperature range between 170 and 300 K and much broader than those of 7Li (200 Hz). On this basis, they concluded that Al nuclei do not move rapidly in this temperature range. We have extended the ^{27}Al linewidth measurements from 300 to 670 K by using a Varian CW spectrometer operated at 8.5 MHz. We have also found a temperature-independent 5 kHz linewidth. This result implies that ^{27}Al motions are slower than several kilohertz. Since there is a substantial increase of both kinds

of anti-site defects at elevated temperature, Al must leave the Al sublattice system, and the resultant interchange with Li must give the average equilibrium distribution obtained by the neutron diffraction experiment.

B. Middle Temperature Range

As shown in earlier sections, the unusual behavior of ${}^7\text{Li } T_1$ as a function of temperature in the middle temperature range has been successfully analyzed by the deconvolution of experimental $(1/T_1)$ curves into two dipolar relaxation processes. We now wish to compare the deconvolution results obtained by the three different models. (See Table II and Fig. 6.)

As discussed in a review article³² treating various models for NMR relaxation processes caused by translational motions, there are some characteristic differences between Torrey's models and Wolf's mono-vacancy encounter model. In Torrey's models, the theories do not take the discrete character of the crystal structure into account. The role of vacancy motions followed by nuclear motions is not explicitly formulated in the relaxation theories. Furthermore, the lattice diffusion model, which describes the motion of a particle in an empty lattice, can have the interacting particles occupying the same position as the spin with which they interact. This rather unrealistic situation is solved by Wolf's mono-vacancy encounter model applied to NMR relaxation theory. The Torrey isotropic diffusion model may fit rather well to motions in the liquid state and also (perhaps) to interstitial diffusion in solids. For the latter, this model has been successfully used for hydrogen diffusion in metal hydrides.³³

The deconvolution results reveal that: (1) the activation energies for relaxation process I and relaxation process II are virtually model independent; and (2) the D_0 values are model dependent. While the Torrey

isotropic diffusion model gives almost the same values for both D_0 's, the other two models provide distinctly different D_0 values for the two processes. A considerable difference between Wolf's mono-vacancy encounter model and Torrey's lattice diffusion model can be seen from the derivation of the $1/T_1$ formula. Smaller τ_0 values are needed for the encounter model in order to compensate for restrictions on the direction of jumps as compared to jumps appearing in Torrey's models; i.e., Wolf's model takes correlation effects into account. The description of translational motions used in Torrey's isotropic diffusion model is similar to an unlimited continuum diffusion model; nevertheless, it seems to offer a rather realistic description of the diffusion process in superionics. The D_0 values presented in Table II tend to support this argument. All three models have been successfully used to deconvolute the experimental $1/T_1$ curves in the middle temperature range. However, a close examination of both experimental and theoretical $1/T_1$ curves around the double maximum indicates that Wolf's model fits best. Throughout the deconvolution process, we experienced a more sensitive behavior of Wolf's relaxation function Eq. (13) vs temperature near the $1/T_1$ maximum than those in Torrey's models.

In any models used in this study, Li motions are characterized by τ_0 and E_a . One question naturally arises: which mode of Li motion is associated with which relaxation process? Since the nuclear motions under study are induced by the random motion of the point defects, it would be reasonable to seek some relationship between the defect structure of $\beta\text{-Li}_x\text{Al}_{1-x}$ and the two relaxation processes that we have observed in region B.

Previous studies²⁹ on the defect structure of $\beta\text{-Li}_x\text{Al}_{1-x}$ led to a two-defect model. Vacancies on the lithium sublattice (V_{Li}) and lithium antisite defects on the aluminum sublattice (Li_{Al}) co-exist over the entire β -phase

domain. If a V_{Li} is trapped in the local field of Li_{Al} , one may call this a defect complex ($V_{Li} \cdot Li_{Al}$). Then, the concentration of so-called free vacancies on the lithium sublattice $[V_{Li}^f]$ is given by $[V_{Li}] - [Li_{Al}]$. In the stoichiometric β -LiAl, $[V_{Li}^f]$ and $[V_{Li} \cdot Li_{Al}]$ [or equivalently (Li_{Al})] were determined as 0.9 and 1.5%, respectively. Fast ion motion over a long-range distance (on an atomic scale) in β -LiAl may be achieved through the constitutional free vacancy population on the lithium sublattice. As shown in our preliminary study³⁴ of 7Li T_1 in β - Li_xAl_{1-x} with $x = 0.486, 0.50, 0.513$, we have assigned process I to the more rapid Li motions of V_{Li} bound near the antisite Li_{Al} defect and process II to the slower Li motions caused by the free V_{Li} . As Table II shows, the activation energy for jump of a free vacancy is greater than that for a bound vacancy.

Now we turn our attention to the temperature dependence of 7Li spin-spin relaxation times. We have shown that there are two relaxation times, and that the long relaxation times T_{2A}' obtained in the CPMG experiments have exhibited distinct t_{CP} dependences in the middle temperature range. This dependence is also observed for T_{2B}' at temperatures higher than 250 K.

First of all, let us consider the t_{CP} dependence of T_{2A}' . If there are no time-dependent processes other than relaxation processes, T_2 is independent of t_{CP} . But, certain time-dependent processes can produce random, irreversible dephasing of the transverse magnetizations. T_2 exhibits a distinct t_{CP} dependence when the time scale of time-dependent processes becomes comparable to t_{CP} . This effect has been well studied for chemical exchange in liquids.³⁵⁻³⁷ Based on the Bloch equations modified to include nuclear transfer effects, Allerhand and Gutkowsky^{35,36} performed a rather detailed numerical simulation of T_2^0/T_2 as a function of t_{CP} , transfer rate $1/\tau$ and spectral frequency difference between two sites $\delta\omega$. Here, T_2 and

T_2^0 refer to spin-spin relaxation time in the presence and absence of nuclear transfer, respectively. The results present a quite complicated behavior of T_2^0/T_2 . It is important to note that T_2^0/T_2 is not a single-valued function. Because of several conditions imposed in the calculation, the quantitative application of this approach to our T_{2A}' data is not feasible. However, a general trend may be useful to interpret our results. If we regard the two defects as a dynamic entity, one type of defect will become another type and vice versa at a given rate. This will cause a switching of the characteristics of the Li motions. When this switching rate is much faster than $1/T_2^0$, the above calculation indicates that T_2^0/T_2 does not change significantly with t_{CP} . When t_{CP} and $1/\tau$ are comparable in magnitude, T_2^0/T_2 exhibits oscillatory variations with t_{CP} . The behavior seems to begin at smaller T_2^0/t_{CP} with decreasing $\delta\omega T_2^0$. This situation seems to fit our observations; i.e., the ^7Li linewidth is constant and narrow (<200 Hz) at temperatures between 150 and 300 K, and the variation of T_{2A}' with t_{CP} is not linear (it is oscillatory at some temperatures). Therefore, the switching frequency becomes comparable to the inverse of the t_{CP} values used in the CPMG experiment (100-2000 Hz).

Now turning to the temperature dependence of T_{2B}' , it should be recognized first that the T_{2B}' values are too short to be explained by the nuclear dipole relaxation. One possible explanation for such short relaxation times may require the active participation of the nuclear quadrupole relaxations. It has been shown^{5,6} that ^{27}Al quadrupole relaxation in $\beta\text{-LiAl}$ arises from V_{Li} motion. The same Li-vacancy motion should give rise to ^7Li quadrupole relaxation. Since T_{2B}' becomes shorter with decreasing temperature in a way similar to T_{2A}' , we assume that the ^7Li quadrupole relaxation is associated with the motion of two different defects.

We now attempt to estimate ${}^7\text{Li } T_{2B}'$ from ${}^{27}\text{Al } T_1$. Although previous investigators^{5,6} have not observed the two-component relaxation behavior for ${}^7\text{Li}$ (probably due to higher Larmor frequency) they have observed a nonexponential decay for the ${}^{27}\text{Al}$ spin-lattice relaxation. By using the same equation as Eq. (1), they⁶ have obtained two constants, $(1/T_1)_s^Q$ and $(1/T_1)_l^Q$. The values of $(1/T_1)_s^Q$ range from 6×10^2 to $9 \times 10^2 \text{ sec}^{-1}$ at temperatures between 100 K and 250 K and exhibit a maximum ($9.0 \times 10^3 \text{ sec}^{-1}$) at ~ 150 K. The corresponding values of $(1/T_1)_l^Q$ are from 1×10^2 to $2.2 \times 10^2 \text{ sec}^{-1}$ with a maximum ($1.76 \times 10^3 \text{ sec}^{-1}$) at the same temperature. Theoretically, the longitudinal quadrupole relaxation of an $I = 5/2$ spin consists of the sum of three $(I + 1/2)$ decaying exponentials if the correlation time is not so short.^{16,38,39} While the analytic form for the longitudinal relaxation is not obtainable, Bull et al.³⁹ have reached the following conclusion from the detailed numerical analysis of $I = 5/2$ quadrupole relaxation: the longitudinal relaxation can be regarded as a simple exponential decay when $\omega_0 \tau < 0.2$. This is mainly because the contribution from the second and third decaying components are negligibly small for this condition. This particular condition holds for ${}^{27}\text{Al}$ spin-lattice relaxations at temperatures above ~ 150 K as shown below.

Since ${}^{27}\text{Al}$ spin-lattice relaxation arises from the electric field gradient fluctuations caused by vacancy diffusion, the correlation time τ_v associated with this diffusion can be used to evaluate the $\omega_0 \tau$ values at various temperatures. Kishio et al.⁶ have obtained τ_{0v} associated with $(1/T_1)_s^Q$ and $(1/T_1)_l^Q$ as 1.03×10^{-12} and $1.97 \times 10^{-12} \text{ sec}$, respectively. The corresponding activation energies are 0.109 and 0.104 eV. The calculation of $\omega_0 \tau$ at 12.5 MHz by Eq. (6) with these values shows clearly that the $\omega_0 \tau$ values are less than 0.2 at >150 K. Therefore, the two constants

$(1/T_1)_s^Q$ and $(1/T_1)_l^Q$ determined by Kishio et al.⁶ should be regarded as the ^{27}Al spin-lattice relaxation rates arising from two different relaxation processes.

For a spin $I = 3/2$ species such as ^7Li , the analytical expression for the longitudinal and transverse components of the nuclear quadrupole relaxation have already been derived.^{16,40} Both relaxations consist of two exponentially decaying components with two different time constants. There is no unambiguous definition of either $(1/T_1)^Q$ or $(1/T_2)^Q$. Thus, it is not possible to estimate ^7Li $(1/T_1)^Q$ or $(1/T_2)^Q$ from ^{27}Al $(1/T_1)^Q$. It is well known, however, that $(1/T_1)^Q$ can be explicitly defined for an arbitrary spin I in the case of extreme narrowing.⁴⁰ At higher temperatures ($\omega\tau \ll 1$)

$$(1/T_1)^Q = \frac{3}{40} \frac{2I+3}{I^2(2I-1)} \left(1 + \frac{\eta^2}{3}\right) (e^2 Q_q / \hbar)^2 \tau^Q. \quad (18)$$

As shown in Fig. 1, the calculated ^7Li T_2 values attributable to the dipolar relaxations approach the T_1 values at temperatures between 330 and 400 K. Since the correlation times, τ_V , are shorter than the dipolar correlation times by more than an order of magnitude,^{5,6} the extreme narrowing condition holds for the ^7Li quadrupole relaxation in the above temperature range. If the field gradients eQ at ^{27}Al and ^7Li produced by vacancies in $\beta\text{-LiAl}$ are of similar magnitude, the ratio of $(1/T_1)^Q$ of ^7Li vs that of ^{27}Al becomes 0.33 from Eq. (18) (asymmetry parameter η is assumed to be zero). Thus, ^7Li $(1/T_2)^Q$ can be estimated from the sum of ^{27}Al $(1/T_1)_s^Q$ and $(1/T_1)_l^Q$. The values obtained at 25 MHz are 9.5 and 5.4 msec at 286 and 250 K, respectively. These values can be favorably compared with the experimental T_{2B} values (see Fig. 1c).

Finally, one comment is in order as to why the ^7Li longitudinal

relaxation does not have an appreciable contribution from the ${}^7\text{Li}$ quadrupole relaxation. This arises from a difference in the experimental setup for measuring T_1 and T_2 rather than a difference in physics between longitudinal and transverse relaxations in the system of interest. In solids, it is well known that T_1 is always longer than T_2 . Therefore, the time domain for T_1 measurement is much longer than that for T_2 measurement - in general, 10 to 20 times longer. In other words, the initial (short) time period for the first few t_{SL} values in the inversion recovery experiment for T_1 actually corresponds to the whole time span for T_2 measurement by the CPMG method. This latter time period is also more than ten times the whole time span for T_2 measurement by the SE method. Because of this experimental setup for T_1 measurement, there is no appreciable contamination from $(1/T_1)_{Li}^Q$ into $(1/T_1)_{Li}^{expt}$ determined by the inversion recovery method in the middle temperature range. The time span of the CPMG experiment just falls in the middle of the inversion recovery and SE method and thus, there are contributions from both $(1/T_2)_{Li}^Q$ and $(1/T_2)_{Li}^{DD}$.

C. T_1 in the Low Temperature Range

A brief account of the anomalous behavior of ${}^7\text{Li}$ T_1 in the temperature range between 80 and 125 K is now in order. If there is an additional relaxation mechanism operative at low temperature, the resultant T_1 must be less than that given by the dipolar relaxation processes I and II. This is actually not the case, as demonstrated in Fig. 2. Therefore, the anomaly in $(1/T_1)_{Li}^{expt} (\omega_I = 7 \text{ MHz})$ must be attributed to a considerable increase in the correlation time corresponding to a slowing down of Li motion. Recent measurements of the resistivity of $\beta\text{-Li}_x\text{Al}_{1-x}$ with $0.480 < x < 0.515$ as a function of temperature reveal⁴¹ an anomaly at ~ 100 K when x is less than or equal to

0.507. The anomaly indicates a phase transition in which the number of scattering centers is reduced more than that extrapolated from high temperature. The recent neutron diffraction study on a Li-deficient single crystal of β - $^7\text{LiAl}$ as a function of temperature has demonstrated that the "100 K" anomaly in the resistivity is associated with the ordering of vacancies at low temperatures.³⁰ The T_1 anomaly in the NMR experiment shows that the diffusion rate of vacancies in the ordered state (< 100 K) is very small. These experiments demonstrate for the first time that upon warming to 100 K, substoichiometric β -LiAl undergoes a transition into a superionic phase.

VII. SUMMARY

NMR measurements have been carried out on stoichiometric β -LiAl samples as a function of temperature and frequency. The ^7Li spin-lattice relaxation was found to be predominantly dipolar. Data were analyzed using several diffusion models. The results show that a fraction of the constitutional Li vacancies in β -LiAl is bound to the vicinity of a Li antisite defect. The remaining free vacancies are responsible for the fact that LiAl is a superionic Li conductor. The spin-spin relaxation results support this picture of two different vacancy environments. The high temperature results demonstrate still another type of Li diffusion related to thermally generated defects.

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APPENDIX

In a system containing two magnetically different nuclei I and S, there are like-spin and unlike-spin dipolar interactions. The terms in the first and second square brackets in Eq. (7) represent the spectral densities for like and unlike interactions, respectively. In the extreme narrowing case, i.e., $\omega\tau \ll 1$ (or less precisely at higher temperatures), it is easy to show that the entities in both brackets are identical.⁴⁰ This is valid irrespective of the theory for molecular or atomic motions applied to Eq. (7). In sample II, there are $^7\text{Li}-^7\text{Li}$ and $^7\text{Li}-^6\text{Li}$ interactions corresponding to the above two brackets. Thus, it is quite valid to write Eq. (3) for $(1/T_1)_{\text{Li}}$ by scrambling these terms together, with the aid of Eq. (3a), in the extreme narrowing case. However, the discussion is not, in general, valid in the cases of $\omega\tau \gg 1$ and also of $\omega\tau \sim 1$ (i.e., in lower temperature ranges). Naturally, a question arises with regard to the validity of the final form of Eq. (3) in the low temperature range. In order to examine this non-trivial problem over a wide range of $\omega\tau$ or temperature, certain numerical calculations must be performed using explicit expressions for the spectral densities.

We have carried out the detailed calculation of $1/T_1$ for ^7Li in samples I and II using Torrey's isotropic diffusion model. Since $(1/T_1)_{\text{Li}}$ for ^7Li in samples I and II are given by Eq. (2) and Eq. (3), respectively, their difference can be written as

$$\begin{aligned}
[(1/T_1)_{Li}(I) - (1/T_1)_{Li}(II)] &= (1/T_1)^{DD}({}^7Li-{}^7Li)(I) \\
&- [(1/T_1)^{DD}({}^7Li-{}^7Li)(II) + (1/T_1)^{DD}({}^7Li-{}^6Li)(II)]
\end{aligned}
\tag{A-1}$$

By applying Eq. (8), (8a), (8b), and (8c) to the r.h.s. of Eq. (A-1), together with the fact that n_I in Eq. (8a) as well as n_S in Eq. (8c) for sample II become $0.5 n_I$ for sample I, the l.h.s. of Eq. (A-1) can be rearranged as follows:

$$\text{l.h.s. [Eq. (A-1)]} = \frac{4\pi}{5} \gamma^4({}^7Li) \hbar^2 (0.5n_I/a_I^3 \omega_I) .$$

$$\{I(I+1)\phi(\alpha_I, x_I) - S(S+1)[\gamma^2({}^6Li)/\gamma^2({}^7Li)]\phi'(\alpha_I, x_I)\} \tag{A-2}$$

or

$$\text{l.h.s. [Eq. (A-1)]} = C'(1/2\omega_I)\phi(\alpha_I, x_I)[1-\beta L] \tag{A-3}$$

$$\text{with } \beta = \frac{S(S+1)}{I(I+1)} \frac{\gamma^2({}^6Li)}{\gamma^2({}^7Li)} = 7.647 \times 10^{-2} \tag{A-4}$$

$$\text{and } L = \frac{\phi'(\alpha_I, x_I)}{\phi(\alpha_I, x_I)} = \frac{2}{\sum_{i=1}^2} \lambda_i' \phi_i'(\alpha_i, x_i) / \sum_{j=1}^2 \phi_j(\alpha_j, x_j) \tag{A-5}$$

Here, I and S refer to 7Li and 6Li , respectively, and ϕ_j , ϕ_i' , and λ_i are already defined in Eq. (8b) and (8c).

Now we have generated L values as a function of temperature by using the numerical values for the six parameters given in Table II for β -LiAl. The L values represent the ratio of Torrey's relaxation functions for hetero and homo-nuclear dipole-dipole interactions. It was found that the L values vary from about 1.4 to 0.7 in the middle temperature range. Since β is only 7.647×10^{-2} , the correction factor $[1-\beta L]$ in Eq. (A-3) varies only $\pm 6\%$ at temperatures between 125 and 400 K. Therefore, the final form of Eq. (3) is valid to a high degree of approximation.

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TABLE I. Diffusion parameters for Wolf's mono-vacancy mechanism
of self-diffusion in the diamond lattice.*

Shell number	Radius of shell	Number of Atoms in shell j	$W(r_j)$ for atoms in shell j**	$P(1_j)$	$Z(0)$
j	$ r_j $	N		$N \times W(r_j)$	
1	0	1	$W(0)=0.243$	0.243	1.68
2	1	4	$W(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})=0.1755$	0.702	
3	1.63299	12	$W(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})=0.0043$	0.0516	
4	1.91485	12	$W(\frac{1}{4}, \frac{1}{4}, \frac{3}{4})=0.0003$	0.0036	

* The diamond lattice system is subdivided into shells j with radius $|r_j|$ around the origin $j = 1, |r_j| = 0$.

** $W(|r_j|)$ denotes the geometrical probabilities due to encounters with mono-vacancies.²⁵

Table II. Relaxation parameters determined

Model	(i)		
Theory	Torrey's Isotropic Diffusion		
Relaxation Process (i)	I	II	III
$(1/T)_{\max}(i) (7 \text{ MHz}) (\text{sec}^{-1})$	7.56	7.31	2.78
at Temp (K)	175.4	227.3	615.4
$E_a(i)$			
(ev)	0.112 ± 0.001	0.141 ± 0.002	0.369
(Kcal/mole)	2.59 ± 0.01	3.25 ± 0.05	8.51
$\tau_0(i) \times 10^{11} (\text{sec})$	$1.14_3 \pm 0.005$	$1.09_3 \pm 0.05_0$	1.26
$\tau_{\text{ONMR}}(i) \times 10^{11} (\text{sec})$			
$D_0(i) \times 10^5 (\text{cm}^2/\text{sec})^{**}$	1.10	1.15	1.0
$C(i) \times 10^{-8} (\text{sec}^{-2})$	$1.29_8 \pm 0.040$	$1.28_1 \pm 0.07_1$	2.08

* $\tau_0(i)$ was obtained from τ_{ONMR} by using Eq. (13b) and Table I. $(1-P(0))$

** $D_0(i)$ were calculated by using Einstein's relation, $D = \langle r^2 \rangle / 6\tau$ and τ

ained by deconvolution of ${}^7\text{Li}(1/T_1)^{\text{expt}}$ in $\beta\text{-}{}^7\text{LiAl}$

(ii)			(iii)	
Torrey's Lattice Diffusion			Wolf's Mono-vacancy Encounter	
III	I	II	I	II
2.78	8.73	6.45	9.13	6.82
15.4	178.6	227.3	178.6	232.6
0.369	0.111 ± 0.002	0.127 ± 0.002	0.111 ± 0.001	0.125 ± 0.002
3.51	2.57 ± 0.04	2.94 ± 0.06	2.55 ± 0.003	2.88 ± 0.07
1.26	1.55 ± 0.05	$2.92_5 \pm 0.02_5$	$0.322 \pm 0.007^*$	$0.744 \pm 0.04^*$
			0.715 ± 0.015	1.65 ± 0.07
1.0	0.811	0.430	3.90	1.69
2.08	5.40 ± 0.05	3.85 ± 0.10	5.375 ± 0.025	3.870 ± 0.190

$-P(0))/Z(0) = 0.4506.$

and r is the jump distance to the nearest neighbor.

Figure Captions

Fig. 1(A). Temperature dependence of ^7Li spin-lattice relaxation times (T_1) in $\beta\text{-}^7\text{LiAl}$. Closed and open circles denote T_1 determined at 25 and 16.8 MHz, respectively.

(B) Temperature dependence of apparent ^7Li spin-spin relaxation times (T_{2a}') determined at 25 MHz by the CPMG method. Closed circles, open circles, open triangles, closed triangles, and downward triangles denote values determined with $t_{CP} = 2010, 810, 210, 110, \text{ and } 99 \text{ } \mu\text{sec}$, respectively. Solid line denotes the T_2 values calculated by Wolf's mono-vacancy encounter model [Eqs. (14)] with parameters listed in Table I at 25 MHz.

(C) Temperature dependence of apparent ^7Li spin-spin relaxation times (T_{2b}') determined at 25 MHz by the CPMG and single echo methods. Symbols are the same as (B) and open squares denote the values determined by the latter method. Solid line as above.

Fig. 2. Temperature dependence of ^7Li spin-lattice relaxation times in $\beta\text{-}^7\text{LiAl}$ determined at 25, 16.8, 7, and 4.3 MHz.

Fig. 3. Time dependence of the nuclear magnetization components caused by nuclear quadrupole relaxation for spin $I = 3/2$. The calculation was done by using Eqs. (24-27) in Ref. 16. Both axes are in arbitrary units. (A) Longitudinal, $\omega^2 \tau^2 \gg 1$. (B) Longitudinal, $\omega^2 \tau^2 = 1$. (C) Transverse, $\omega^2 \tau^2 = 1$.

Fig. 4. Temperature dependence of ^7Li spin-lattice relaxation rate exclusively arising from ^7Li - ^7Li nuclear magnetic dipole-dipole interactions (closed circles). Open circles denote the contribution from ^7Li - ^{27}Al dipole-dipole interactions and others.

Fig. 5. Temperature dependence of parameter y ($= \omega_0 \tau / 2$) in Torrey's lattice diffusion model applied to ^7Li spin-lattice relaxation time determined at 25 MHz in β - $^7\text{LiAl}$. (A) $E_a = 0.09$ eV/Li, $1/\tau_0 = 1.1 \times 10^{10} \text{ sec}^{-1}$. (B) $E_a = 0.11$ eV/Li, $1/\tau_0 = 3.0 \times 10^{10} \text{ sec}^{-1}$.

Fig. 6. Comparison of experimental $1/T_1$ data at 7 MHz with Model (iii).
 Open circle: Experimental data
 Open square: Theoretical fit to data in Region B.
 Cross: Deconvoluted process I.
 Open triangle: Deconvoluted process II.
 The experimental points are obtained from the smoothed 7 MHz curve of Fig. 2.

Fig. 1. Tokuhiko, Phys. Rev. B1

Fig. 2. Tokuhiro, Phys. Rev. B1

Fig. 3. Tokuhiro, Phys. Rev. B1

Fig. 4. Tokuhiro, Phys. Rev. B1

Fig. 5. Tokuhiko, Phys. Rev. B1.

Fig. 6. Tokuhiko, Phys. Rev. B1