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Diffusion of ^{8}Li short-lived radiotracer in Li ionic conductors of NaTl-type intermetallic compounds

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Abstract. Non-destructive and on-line Li diffusion experiments in Li ionic conductors are conducted using the short-lived α-emitting radiotracer of ^{8}Li. The radiotracers produced as an energetic and pulsed ion beam from TRIAC (Tokai Radioactive Ion Accelerator Complex) are implanted into a structural defect mediated Li ionic conductor of NaTl-type intermetallic compounds (β-LiGa and β-LiIn). The experimental time spectra of the yields of α-particles are compared with simulated results and Li diffusion coefficients in the intermetallic compounds are extracted with an accuracy of ±10%. The diffusion coefficients obtained for β-LiGa with Li content of 43-54 at.% are discussed in terms of the interaction between Li-ion and the structural defects in the specimen, compared with the cases of β-LiAl and β-LiIn. The nonlinear Li-content dependency of Li diffusion coefficients for β-LiGa suggests that the Li diffusion with the Li-deficient region is obstructed by the defect complex composed of vacancies at the Li sites.

Introduction

Over more than half a century, diffusion studies in solids using radioactive tracers [1] have played an important role in understanding the underlying mechanism of atomic transport in solids, which is of great importance in a number of branches of materials science and engineering. Although the conventional radiotracer method for diffusion studies in conjunction with a serial sectioning technique [2] and the conventional non-destructive radiotracer method [3] has yielded the most accurate diffusion coefficients, radioactive isotopes for some elements have not yet been used because of no-availability of radiotracers with adequate lifetimes for the application. Among them, ^{8}Li, the radioactive isotope of Li with a half-life of 0.84s is of special interest for practical issues; how well Li ions could move during the charge- and discharge-processes in the secondary Li ion batteries. Fast Li diffusion is desirable in battery materials, i.e. Li ionic conductors for materials of electrodes and solid electrolyte, which are under development for improving the present capability of the secondary Li ion batteries. When a proper radiotracer is not available, on the other hand, various electro-chemical methods are usually adopted for measuring the macroscopic movement of the constituents of the sample of interest [4]. Depending on the method used for the measurement, however, the diffusion coefficients are scattered over several orders of magnitude. Therefore, the diffusion coefficients measured in different ways, e.g. by using the radiotracer of Li, is highly required to settle down such disagreements, and further such an experimental knowledge on the Li diffusion as developed ingredients for the battery is important in the recent general efforts to design the battery by simulations based on the first principle.

The feasibility of the diffusion tracing by short-lived radioactive ion beams has been simulated in our previous reports [5-7]. Here, the solid material of interest is set at a given temperature and periodically implanted by the energetic tracer beam for a time-duration, order of half-life time of the tracer. Especially when using the α-emitting radiotracer of ^{8}Li, the simulation has shown that the tracer diffusion coefficients in the solid can be measured in a non-destructive and on-line way, completely different from the conventional radiotracer method in conjunction with a serial sectioning technique [2]. The time-dependent yields of α-particles from the diffusing ^{8}Li have been examined as a direct measure of the diffusion of ^{8}Li in the solid material of interest, reflecting the temporal evolution of the concentration-depth profile of the ^{8}Li primarily implanted in the material. The diffusion coefficients in β-LiAl [6] at different temperatures have been obtained with an accuracy of ±13% as a result of the comparisons between the experimental and simulated time-dependent yields of α-particles.

In this study, Li diffusion in β-LiGa with the Li content of 43-54 at.% are examined in detail and the Li content dependency of diffusion coefficients are discussed in terms of the structural defects, i.e. vacancies at the Li sites and antisite Li atoms at the Ga sites.

Experimental

Materials. The crystals of intermetallic compounds were grown by the Tammam-stöber method starting from a mixture of lithium and another metal (Ga, In) in the same way reported previously [8]. Reflection and transmission Laue X-ray analysis showed that the crystal was polycrystal. The content of lithium was determined by the electrical resistivity measurements [9, 10]. The surface of the sample was polished to the roughness less than 1 μm before the experiments.

Li-8 diffusion experiments. Li-8 decays through β-emission to ^{8}Be with a half lifetime of 0.84s, which immediately breaks up into two α-particles with energies broadly distributed around 1.6MeV with a full width at half maximum (FWHM) of 0.6MeV [11]. The energy resolution of ^{8}Li-beam from TRIAC [12] was improved to be 10 times better than that of ^{8}Li-beam from the recoil mass separator(RMS) [13] as shown in Fig. 1. The ^{8}Li-beam of about 4MeV with an intensity of about 3000 particles/s was periodically implanted to the sample with a following time sequence; 1.6s for implantation (beam-on) and 4.4s for subsequent diffusion (beam-off). With the present energy, the ^{8}Li radiotracer can be implanted into the implantation-depth of about 7μm from the front surface of the sample. The α-particles coming out of the sample were measured as a function of time by an annular solid-state detector (SSD) installed close to the front surface of the sample. The sequence was repeated to obtain good statistics, where the time-zero was always at the beginning of the implantation. More details of the experimental procedure can be found elsewhere [5-7].

Data analysis for diffusion coefficients. The typical normalized time spectra of the yield of α-particles for β-LiAl (Li content, 48.5at.%) at temperatures from 298K to 573K are shown in Fig. 2. The spectra are represented by the ratios, i.e. time-dependent yields of α-particles divided by the α radioactivity of ^{8}Li at the time of interest. If ^{8}Li does not diffuse at all, the values of the ratios should be constant over time. However, with increasing the temperature the experimental values quickly rise and fall down as shown in Fig. 2. On the Basis of this relative time-dependency of α-particle yields (time dependent ratio), a diffusion coefficient was estimated by comparing with the simulation where one-dimensional Fickian (Gaussian) diffusion was assumed. As shown in Fig. 2, the Li diffusion coefficients of β-LiAl increased with increasing the temperature.

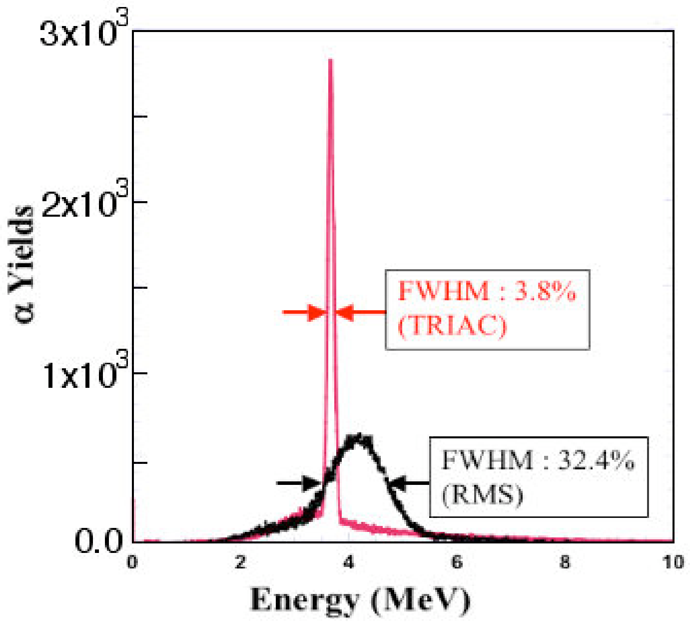

Fig. 1. Li-8 energy spectra for implantation. Theenergy resolution of ^{8}Li-beam of TRIAC is improved compared with that of ^{8}Li-beam of the recoil mass separator in the former work (Ref. 6,7).

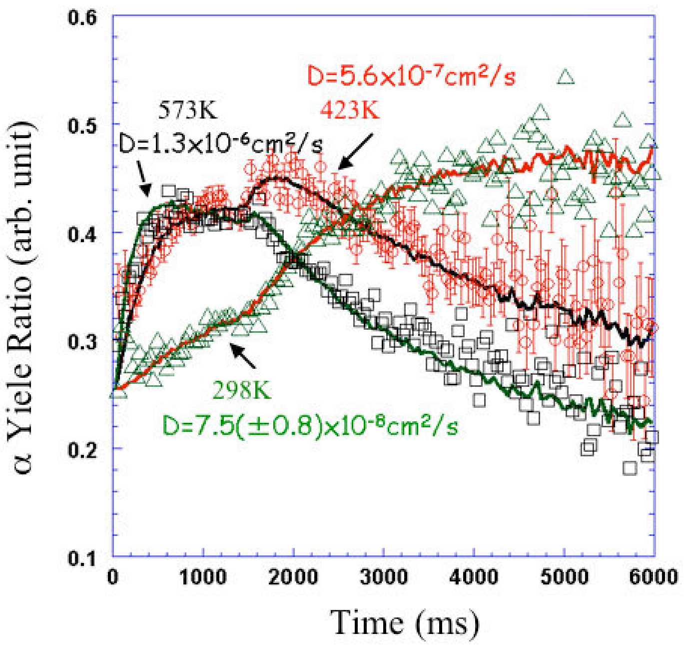

Fig. 2. Normalized time spectra of α yields from β-LiAl. The results from the simulation (solid line) are also shown with the coefficients. Open triangles mean the normalized α yields for 298K (the diffusion coefficient D = 7.5×10^{-8}cm^{2}/s), open circles for 423K (D = 5.6×10^{-7}cm^{2}/s), and open squares for 573K (D = 1.3×10^{-6}cm^{2}/s).

In the simulation, as described in detail in Ref. 6, we first determined the incident energy and energy spread of the ^{8}Li beam from the energy spectrum measured at the instant of implantation. Using the incident condition of the beam, we simulated the concentration-depth profile of ^{8}Li implanted in the sample and the time-evolution of the profile when a certain diffusion coefficient of Li in the sample was assumed. And then were simulated the energies of α-particles emitted from the time-dependent (diffusing) profiles of ^{8}Li, by taking into account the energy loss and straggling on their passage from the emitted position to the sample surface. Finally, integrated over the energies larger than 400keV, the time-dependent α-particle yields depending on the diffusion coefficients assumed in the simulation were obtained and then compared with the experimental time spectrum, after being normalized in the same way as preformed for the experimental data. The Li diffusion coefficients were extracted with an accuracy of ±10%. The parameters (mean and FWHM) describing the concentration-depth profile and the energy loss and straggling of α-particles were estimated by using the SRIM-2003 code [14], which is widely used in this kind of application with high reliability.

The χ^2 (*Chi-square*) test was performed for the likelihood test between the experimental and simulated time spectra. During the test of likelihood, two input parameters, i.e. diffusion coefficients and implantation depth, were examined in the simulation. As the reference spectrum for normalization, an experimental time spectrum of the α-radioactivity of ^{8}Li implanted in pure Cu was used. It allows us to avoid the systematic errors caused by the beam on/off operations, since no measurable diffusion effects were observed in the case.

Results and discussion

The crystal structure of β-phase (β-LiAl, β-LiGa and β-LiIn) is NaTl-type (or Zintl phase) [15], which is composed of two interpenetrating diamond sublattices such that each atom has eight nearest neighbors: four like and four unlike atoms, as shown in Fig. 3. The characteristic defect structure [16] of the compound consists of two types of defects at room temperature, i.e. vacancies in the Li sublattice (V_{Li}) and Li antistructure atoms in the Ga sublattice (Li_{Ga}). The concentrations of the point defects, [V_{Li}] and [Li_{Ga}], strongly depends on Li content; with increasing the Li content from 43 to 54%, [V_{Li}] decreases from 11.4 to 2.8%, while [Li_{Ga}] increases from 0 to 5.1%. V_{Li} is the dominant defect for the Li-deficient region, Li_{Ga} is the dominant defect for the Li-rich one. The coexistence V_{Li} of Li_{Ga} is expected to form V_{Li}- Li_{Ga} complex defects [10] as reported for the defect structure of β-LiAl [9], which would play an important role in reducing the strain energy caused by the point defects in the real cystal. Especially, almost the same amounts of V_{Li} and Li_{Ga} exist around the content of 51 at.% Li. Althoug β-LiAl has been studied as an electrode material for secondary batteries [19] because of its high diffusivity of Li, the Li diffusion cefficients of β-LiGa are also much larger than those of β-LiAl as reported in this study.

As mentioned in the former paragraph, the concentration of the native Li vacancy in β-LiGa even at the Li-deficient region attained to 2.8% (10^{21}cm^{-3}). Therefore, the concentration of the radiation-induced defects like a frenkel pair is several order of magnitude smaller than that of the native defects and the effects of the radiation-induced defects are negligibly small [10].

As shown in Fig. 4, the Li diffusion coefficients of β-LiGa around the Li content of 48 at.% have maximum. The results is quite different from those observed for β-LiAl and β-LiIn (the Li-content of β-phase: 48-54at.%) [17] which are iso-structural with the β-LiGa. In the cases of β-LiAl and β-LiIn, the Li diffusion coefficients, the corresponding diffusion constants and activation energies, decrease monotonically with increasing the lithium content with a minor modification due to the coexistence of V_{Li} and Li_{Ga}. Since the vacancy concentration in the Li sublattice decreases with increasing lithium content, this monotonic behavior can be associated with the Li vacancy, i.e. the Li diffusion path, concentration increase. The motion of Li is slightly suppressed or assisted depending on the kinds of anti-site atoms; Li diffusion rather slows down in β-LiAl, while becomes rather faster in β-LiIn around the stoichiometric region. Such a slight modification in the monotonic behavior of Li diffusion has suggested the possibility of an interaction between vacancies and lithium anti-structure atoms; the interaction must be attractive in β-LiAl and repulsive in β-LiIn [17]. The difference in the interactions has been understood by the atomic size effect [17]. The lithium anti-structure atom, Li_{Al}, in β-LiAl produces compressional strain (expanded lattice), since the radius (0.68Å) for the Li ion in a closed shell configuration [20] is larger than that (0.50 Å) for the Al ion, while the anti-structure atom, Li_{In}, in β-LiIn induces dilatational strain (contracted lattice) because of ionic radius (0.8 Å) for In larger than that of the substitutional Li ion. On the other hand, the vacancy, V_{Li}, always produces dilatational strain [21]. On the basis of the atomic size effect, the interaction between V_{Li} and Li_{Ga} in β-LiGa is supposed to be attractive as in β-LiAl, because the radius (0.62 Å) of Ga ion is slightly smaller than that of Li ion. The strength of the interaction can be considered to be weaker than observed in β-LiAl and β-LiIn, since the radii of the constituent ions are quite close to each other.

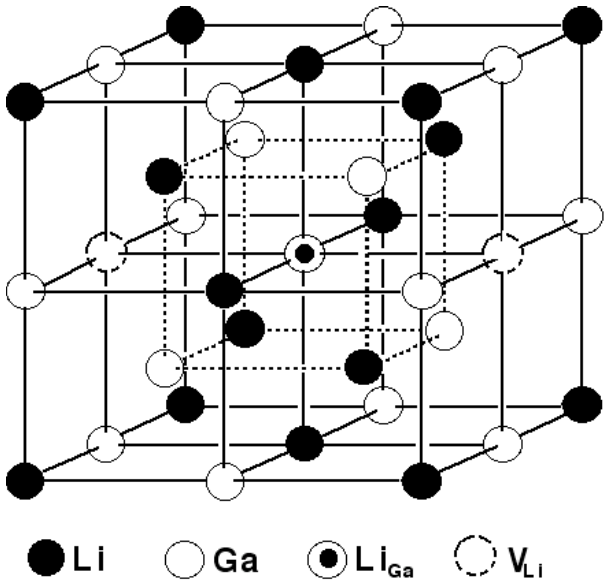

Fig. 3. Crystal Structure of NaTl type (Ref. 15) containing defects in β-LiGa (Ref. 9). A possible example of the defects complex is composed of two vacancies at the Li sites and an antisite Li atom at the Ga sites in the nearest neighbor; the triple defects complex is a juxtaposition of two Li vacancies and one Li antisite defect.

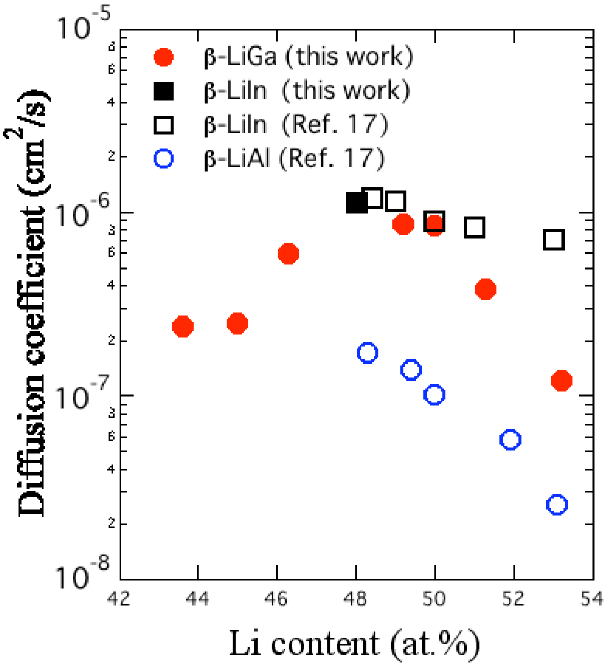

Fig. 4. Li-content dependence of the diffusion coefficients for β-LiGa (this work), β-LiIn (a closed square, this work; open squares, Ref. 17) and β-LiAl (Ref. 17).

What observed in the present measurement goes the other way contrary to the consideration of former paragraph; the Li diffusion around the stoichiometric region is faster than in the most Li-rich region and Li-deficient one, demonstrating that the Li diffusion through the vacancies on the Li atomic site seems to be strongly promoted by the coexistence of V_{Li} and Li_{Ga}. This suggests that the interaction between V_{Li} and Li_{Ga} would be unexpectedly large and repulsive as same as observed in β-LiIn [17]. On the other hand, it is also suggested that the motion of Li ion for the Li-deficient region could be quenched by the formation of the defects complex such as V_{Li}-Li_{Ga}-V_{Li} and /or V_{Li}-V_{Li} as shown in Fig. 3, since the concentration of V_{Li} defects is much (almost three times) larger in the Li-deficient side as compared to the cases in β-LiAl and β-LiIn. It should be noted that the number of vacant Li sites in a unit cell volume (8 for Li and 8 for Ga) is about two for the most Li-deficient β-LiGa [9], whereas there exist about one vacant Li site in every two unit cells for the most Li-deficient β-LiAl and β-LiIn [17] by assuming the random distribution of the vacancies over the entire volume.

Summary

We measured the Li diffusion coefficients in the intermetallic compound β-LiGa with a accuracy of ±10% as a function of the Li content of 43-54 at.%. The Li content dependency of diffusion coefficents showed a convex shape and a maximum around 48-50 at.%. This feature of the Li diffusion coefficients suggests that the Li diffusion with the Li-deficient region is obstructed by the defect complexes composed of vacancies at the Li sites and antisite defects at the Ga sites.

References

[1] C. Tujin: Defect and Diffusion Forum, Vol. 141-142 (1997) , p. 1

[2] F. Wenwer, A. Gude, G. Rummel, M. Eggersmann, T. Zumkley, N.A. Stolwijk and H. Mehrer: Meas. Sci. Technol., Vol. 7 (1996), p. 632

[3] For example, H. Sugai: Solid State Ionics, Vol. 177 (2007), p. 3507

[4] H. Sato, D. Takahashi, T. Nishina and I. Uchida: J. Power Sources, Vol. 68 (1997), p. 540

[5] S.C. Jeong, I. Katayama, H. Kawakami, H. Ishiyama, H. Miyatake, M. Sataka, A. Iwasse, S. Okayasu, H. Sugai, S. Ichikawa, K. Nishio, Y. Sugiyama, M. Yahagi, K. Takada and M. Watanabe: Jpn. J. Appl. Phys., Vol. 42 (2003) p. 4576

[6] S.C. Jeong, I. Katayama, H. Kawakami, Y. Watanabe, H. Ishiyama, H. Miyatake, M. Sataka, S. Okayasu, H. Sugai, S. Ichikawa, K. Nishio, T. Nakanoya, N. Ishikawa, Y. Chimi, T. Hashimoto, M. Yahagi, K. Takada, B.C. Kim, M. Watanabe, A. Iwase, Takashi Hashimoto and T. Ishikawa: Nucl. Instr. and Meth., Vol. B 230 (2005) p. 596

[7] S.C. Jeong, I. Katayama, H. Kawakami, Y. Watanabe, H. Ishiyama, N. Imai, Y. Hirayama, H. Miyatake, M. Sataka, S. Okayasu, H. Sugai, S. Ichikawa, K. Nishio, S. Mitsuoka, T. Nakanoya, M. Yahagi, T. Hashimoto, K. Takada, M. Watanabe, T. Ishikawa and A. Iwase: Journal of Phase Equilibria and Diffusion, Vol. 26 (2005), p. 472

[8] M. Yahagi: J. Cryst. Growth, Vol. 49 (1980), p. 396

[9] K. Kuriyama, H. Hamanaka, S. Kaido and M. Yahagi: Phys. Rev., Vol. B 54 (1996), p. 6015

[10] H. Sugai, M. Tanase, M. Yahagi, T. Ashida, H. Hamanaka, K. Kuriyama and K. Iwamura: Phys. Rev., Vol. B 52 (1995), p. 4050

[11] T. W. Bonner, J. E. Evans, C. W. Malichard and J. R. Risser: Phys. Rev., Vol. 73 (1948), p. 885

[12] Information on http://triac.kek.jp/

[13] H. Ishiyamaa, , T. Ishikawa, T. Hashimoto, Y.X. Watanabea, Y. Hirayama, N. Imai, H. Miyatake, M.H. Tanaka, Y. Fuchi, N. Yoshikawa, S.C. Jeong, H. Kawakami, I. Katayama, T. Nomura, S. Mitsuoka, K. Nishio, M. Matsuda, P.K. Saha, H. Ikezoe, S.K. Das, Y. Mizoi and T. Fukuda: Nucl. Instr. And Meths., Vol. A 560 (2006), p. 366

[14] Information on http://www.srim.org/

[15] E. Zintl and G. Brauer: Z. Phys. Chem. Abt., Vol. B 20 (1993), p. 245

[16] K. Kishio and J.O. Britain: J. Phys. Chem. Solids, Vol. 40 (1979), p. 933

[17] J.C. Tarczon, W.P. Halperin, S.C. Chen and J.O. Brittain: Mater. Sci. and Eng., Vol. A 101 (1988), p. 99.

[18] T. Tokuhiro, S. Susman, T.O. Brun and K.J. Volin: J. Phys. Soc. Jpn., Vol. 58 (1989), p. 2553.

[19] C.J. Wen and R.A. Huggins: J. Electrochem. Soc., Vol. 128 (1981), p. 1636

[20] For example, C. Kittel: Introduction to Solid State Physics, 8-th ed. (Wiely, New York, 2005), p. 71

[21] For example, J.I. Pankove: Optical Process in Semiconductors (Dover, New York, 1971), Chap.1