

NMR investigation of ionic motion in LiI-KI in the liquid state

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Abstract. The longitudinal relaxation time (T_1), transverse relaxation time (T_2), and chemical shift of ^7Li , and the line width and chemical shift of ^{127}I were measured to study ionic motion in the eutectic LiI-KI mixture in the liquid state. T_1 and T_2 of ^7Li are both very long (more than a few seconds). Motion narrowing is not observed for ^7Li , which gives the lower limit of the correlation time, $\sim 10^{-9}$ s. The relaxation times of ^{127}I nucleus are too short (less than 100 μs) to measure using the standard pulse methods. Although the resonance peak of ^7Li is very narrow and the chemical shift is almost independent of temperature and composition, the resonance peak of ^{127}I is very broad and dependent on temperature and composition, which has been analyzed by assuming two sites of Γ and their rapid exchange. The residence time of Γ is estimated to be about 10^{-5} s.

1 Introduction

Recently, Nozaki and Itami have studied the solidification process of LiI-KI system by measuring the electrical conductivity very precisely [1]. They have found that the electrical conductivity of eutectic composition [2, 3] (LiI 63.1 mol%) has very peculiar behavior; it decreases to the value of solid rather continuously in the small temperature interval of about 30K while it decreases discontinuously in a sample with off eutectic composition even if the difference in composition is only 1 mol%. The results suggest that the dynamics of ionic motion can be dependent on small change in the composition. They also found that similar phenomena in the electrical conductivity occur not only in the LiI-KI but also in many eutectic binary metallic mixtures [4].

To elucidate the ionic motion in the LiI-KI mixture, we measured NMR. The pure alkali halides have served as model substances for understanding of NMR chemical shifts in solids, because their ionic states have been well-understood from theoretical view [5]. However, no systematic study seems to be reported in their mixtures especially in the molten state. The LiI-KI mixture is fitting to NMR measurements. ^7Li and ^{127}I are both good NMR nuclei and it is easy to get a resonance signal. The skin effect which is a major obstacle for metallic specimens does not arise in the ionic materials and then we can use a bulk sample. The major objective of the present work is to investigate ionic motion in the molten ionic halides mixture by measuring the spin lattice relaxation time T_1 , the spin-spin relaxation time T_2 and the peak profile.

2 Experimental procedures

The sample was made by mixing analytical grade of LiI of KI. LiI is highly deliquescent and then handing of specimen was done under dry nitrogen atmosphere. After putting LiI and KI in a Pyrex glass ampoule, the sample was calcined under vacuum at 480K for more than 10 hours to remove adsorbed

Table 1. List of NMR nuclei in LiI-KI mixtures

Nuclei	^7Li	^{127}I
Natural abundance	92.57%	100%
Nucleus spin I	3/2	5/2
Quadruple moment Q (barns)	-0.1	0.454
Gyromagnetic ratio γ_n (MHz/T)	16.546	8.518

water and then sealed. The uncertainty of the concentration is $\pm 1\text{mol}\%$. NMR nuclei in the present investigation are summarized in table 1 [6].

NMR was measured using a Varian Unity-400 spectrometer with 9.4 T superconducting magnet. As resonance references, we used a dilute LiI aqueous solution for ^7Li nuclei and solid KI for ^{127}I nuclei. The resonance frequency was 155.448983 and 80.042770 MHz for respective nuclei. We measured the chemical shift, T_1 and T_2 , the latter two quantities of which were measured using the $2\pi\text{-}\tau\text{-}\pi$ pulse sequences and Meiboom-Gill pulse sequences [7]. The relaxation times of ^{127}I were too short to be measured by the above mentioned pulse method.

We used Doty high temperature NMR probe which uses hot nitrogen gas flow for sample heating and therefore at each temperature measurements were made after sufficiently long time for thermal equilibrium, about 30 minutes.

3 Results and discussion

Fig. 1 shows the summary of the chemical shift of ^7Li . The temperature variation of ^7Li is very small and all the data from the liquidus temperature to 760K fall in a circlet in the

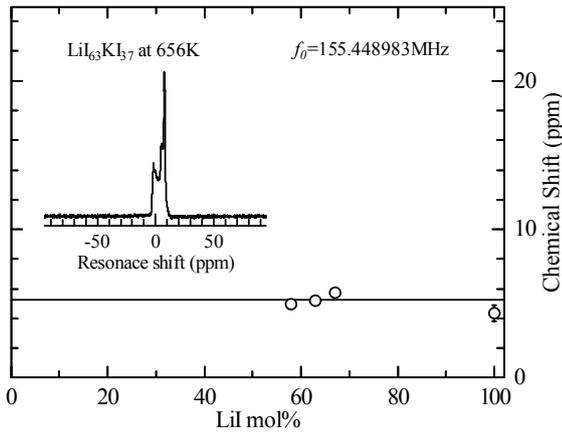


Fig. 1. ⁷Li chemical shift in the liquid Li-KI system. The variation of the respective specimens over the temperature interval of 559–753K is within the circles in the figure. The inset shows the resonance peak in Li₆₃K₃₇ at 656K.

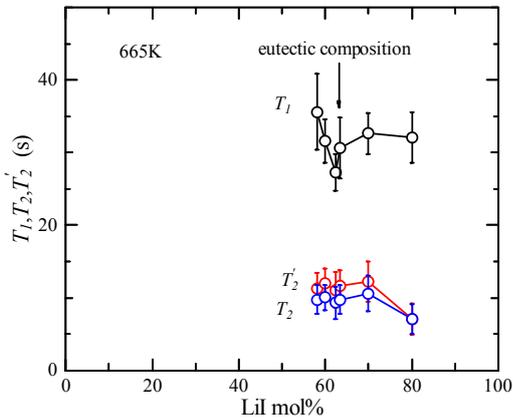


Fig. 2. The composition dependence of T_1 , T_2 , and T_2' of ⁷Li nuclei at 665K, where $1/T_2' = 1/T_2 - 1/2T_1$. Arrow indicates the eutectic composition.

figure. The composition dependence is also very small and almost constant. The inset shows the NMR spectra of ⁷Li in Li₆₃K₃₇ at 656K. The resonance spectrum is not a single Lorentzian curve, but has fine structures. The persistence of structures in the resonance peak indicates that the motional narrowing does not take place even in the liquid state.

Fig. 2 shows the relaxation times at 665K. They are as long as those in a reference aqueous solution in which the resonance peak is a single Lorentzian curve. A minimum appears around the eutectic composition. The increase in the relaxation rates or the shortening of the relaxation times implies that the hopping time of Li ion increases around the eutectic composition. However, the absence of the motional narrowing prevents to use the Redfield's theory to estimate the magnitude of the hopping time [7]. The condition for the motional narrowing is given by [7],

$$\tau\omega < 1, \tag{1}$$

where τ and ω are hopping time and the Larmor frequency respectively. From this equation the lower limit of the hopping time of Li ion in the molten Li-KI mixtures can be estimated. Using the resonance frequency of ⁷Li, the lower limit of the

hopping time is calculated to be 10^{-9} s. It is very long as

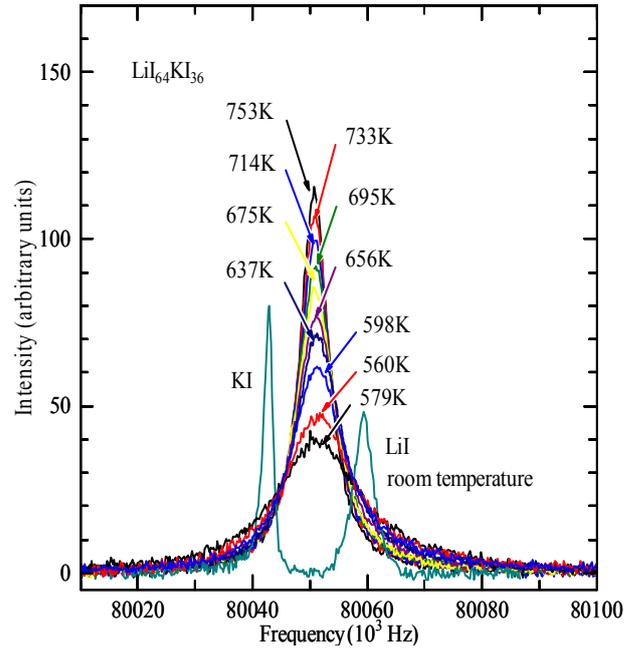


Fig. 3. NMR spectra of ¹²⁷I in Li₆₄KI₃₆

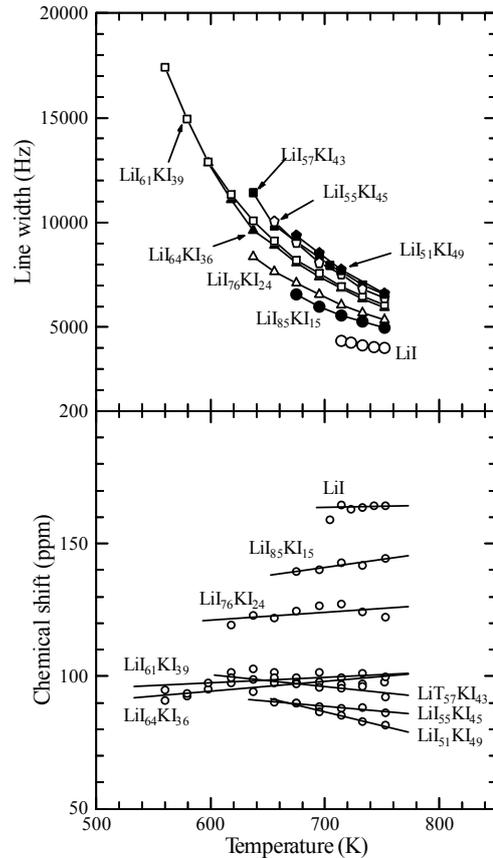


Fig. 4. ¹²⁷I resonance width and chemical shift as a function of temperature.

compared with the value, $\sim 10^{-12}$ s, in a usual monatomic liquid. The reason for the absence of the motional narrowing is that

the Larmor frequency for ${}^7\text{Li}$, 9.767×10^8 rad/s in the present NMR experiments, was too high to study atomic motion of Li ion in the molten LiI-KI mixture with a conventional NMR theory.

Fig. 3 shows the temperature evolution of resonance peak of ${}^{127}\text{I}$ nuclei in $\text{LiI}_{64}\text{KI}_{36}$. The resonance width is very broad and temperature dependent. With decreasing temperature the breadth increases rapidly and the resonance peak splits to two peaks upon solidifying, while the position of the resonance peak has only very small temperature dependence. LAM14

Fig. 4 shows the line width and chemical shift as a function of temperature. It is interesting note that temperature coefficient of the chemical shift changes from positive to negative around the eutectic composition (63.1 LiI mol%) though uncertainty is large.

To interpret the present NMR results, we deal with a very simple model. The local ionic configuration around Li^+ and I^- ions are visualized in Fig. 5, which shows plausible local atomic arrangement around Li^+ and I^- ions. While Li^+ ions take only one site, I^- ions take two kinds of site, A-type and B-type, that can exchange each other after a characteristic time interval. Mixing of Li^+ and K^+ in the nearest coordination shell can be neglected to a crude approximation because of the eutectic interaction in a mixture. With this model, the resonance position, ω , and the line width, $1/\pi T_2$, can be written as [6],

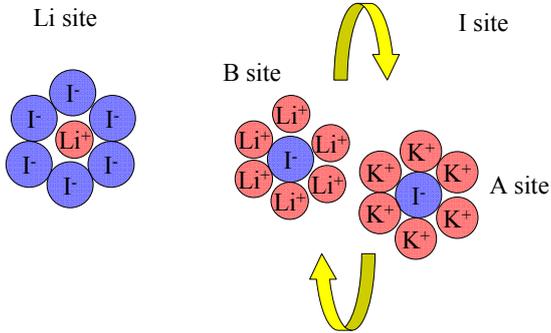


Fig. 5. Simplified local ionic arrangements in liquid LiI-KI mixture

$$\omega = P_A \omega_A + P_B \omega_B \quad (1)$$

$$1/T_2 = P_A/T_{2A} + P_B/T_{2B} + P_A P_B \delta\omega^2 / (1/\tau_A + 1/\tau_B). \quad (2)$$

In these equations, τ_i is the resident time at site i , and the resident probability is written as,

$$P_{AorB} = \tau_{AorB} / (\tau_A + \tau_B) \quad (3)$$

Here two definite resonances are assumed, respectively, to A-type site and B-type site, for which the difference in resonance frequencies is $\delta\omega = \omega_A - \omega_B$. With increasing exchange rate of two sites, two resonances merge into a single resonance.

To a very crude approximation, we assume $\tau_A = x_A \tau$ and $\tau_B = x_B \tau$, where x_A (x_B) is the mol% of LiI (KI) and $x_A + x_B = 1$. With these simplifications, the resonance occurs at,

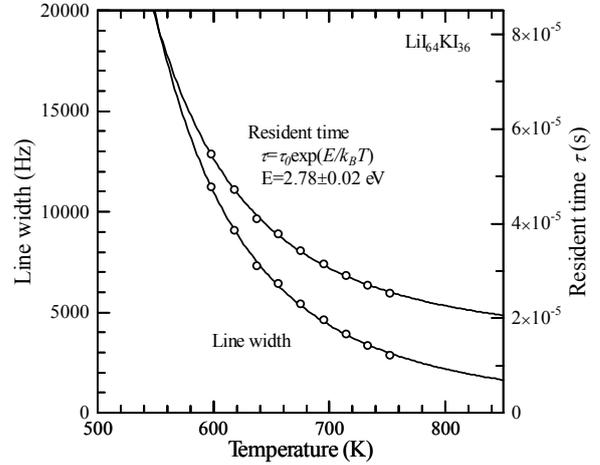


Fig. 7. Line width and resident time, τ , of ${}^{127}\text{I}$ in liquid $\text{LiI}_{64}\text{KI}_{36}$ as a function of temperature.

$$\omega = x_A \omega_A + \omega_B x_B, \quad (4)$$

and

$$1/T_2 = x_A/T_{2A} + x_B/T_{2B} + (x_A x_B)^2 \delta\omega^2 / \tau \quad (5)$$

Equations (4) and (5) predict that the resonance position (or chemical shift) changes linearly with composition between those for LiK and LiI, respectively, while the line breadth changes like $(x_A x_B)^2$. Fig. 6 compares equations (4) and (5) with the results at 753K.

By adopting the difference in the resonance frequencies in the solid (see in Fig. 3) as $\delta\omega$, we can estimate the magnitude of the residence time, τ , as plotted in Fig.7. The temperature dependence of τ can be fitted to an activation type, $\tau = \tau_0 \exp(E/k_B T)$,

where $\tau_0 = (4.1 \pm 0.34) \times 10^{-9}$ s and $E = 2.43 \pm 0.041$ eV. As can be seen in the figure, the residence time is very long, $\sim 1 \times 10^{-5}$ s in the liquid state as compared with the hopping time of ion in a monatomic liquid, $\sim 10^{-12}$ s [8]. However, the present conclusion is resulted from the observation, large peak width of a few thousands of Hz, and its rapid temperature dependence. The order of characteristic time scale is not dependent on a model used in this investigation. It is the consequences of the formal theory of NMR [7]

4 Conclusions

Molten LiI-KI mixtures have been investigated by measuring ${}^7\text{Li}$ and ${}^{127}\text{I}$ NMR. Temperature dependences of ${}^7\text{Li}$ and ${}^{127}\text{I}$ chemical shifts are very small. Some unusual behavior has been observed in the NMR measurements, which correlates with

other physico-chemical properties associated with the eutectic binary system: the temperature coefficient of ^{127}I chemical shift changes its sign around the eutectic composition, $\sim 63\text{mol}\%$ LiI. The relaxation of both nuclei increases around the eutectic composition as well. The origin of the phenomena remains, however, open to further investigations. Motion narrowing is not observed for ^7Li , which gives the lower limit of the correlation time, $\sim 10^{-9}$ s. The width of ^{127}I resonance peak shows large temperature dependence. The results have been analyzed using a very simple model of exchange narrowing. The resident time, τ , of I $^-$ ion in molten LiI-KI mixture has been obtained for the first time. It is $\sim 10^{-5}$ s and is very long.

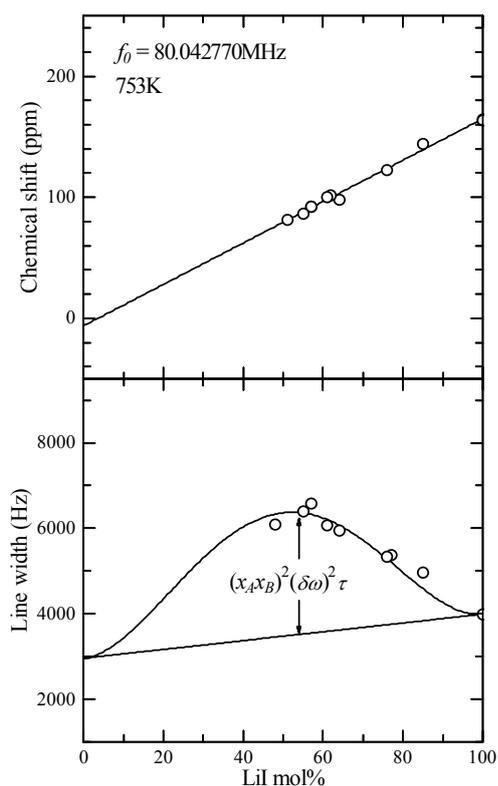


Fig. 6. Chemical shift (circlets in the upper figure) and line width (circlets in the lower figure) of ^{127}I at 753K as a function of mol% LiI are compared with equations (4) and (5), respectively. Although uncertainty in the fitting is large, the predictions in the text can be seen.

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