Slow dynamics observed on highly shifted spectral component of ^{23}Na NMR in low silica X zeolite loaded with potassium for saturating level

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Abstract

^{23}Na NMR spectra of Na-K form low silica X zeolite loaded with potassium for saturating level, which corresponds to 9.0 atoms per unit, have been observed. Other than a centered grain of the spectral component, another separated peak component with shift of somewhat larger than bulk Na has been detected. Such the extra peak component shows complex hysteresis on temperature and is accompanied with quite slow dynamics of days-order. It is attributed to atomic re-configurations among sites occurs in the course of melting and re-crystallization process among alloy of sodium and potassium, which possibly is formed on surface or outside of the zeolite crystals.

Keywords: zeolite, sodium-potassium alloy, NMR, ^{23}Na, Knight shift, slow dynamics

1 Introduction

It is known that alkali metal loading introduces metallic property into some kinds of zeolites [1]. In some cases, it is accompanied by magnetic order. Na-K alloy clusters arrayed in zeolite low silica X (LSX) prepared by the alkali metal loading are one of the systems whose conductivity and magnetism have been investigated in detail. The conductivity and magnetism change markedly depending on the Na content, such as an insulating ferromagnetic state [2, 3], a metallic ferrimagnetic state [1, 4–6], and a metallic ferromagnetic state at high pressure [7]. In this study, we report the observation of a strange NMR signal in a paramagnetic metal sample among these many Na-K alloy samples.

LSX is a type of aluminosilicate zeolite whose framework structure type is FAU[8]. Figure 1 shows the schematic illustration of the FAU structure. There are two types of cages: the smaller one is called a β cage (inner diameter $\simeq$ 7 Å) and the larger one is called a supercage (inner diameter $\simeq$ 13 Å). Both are arranged in a diamond structure [9]. Here we define the unit that contains a β cage and a supercage, which is 1/8 of the unit cell of the diamond structure. The framework is formed by a covalent network of Al, Si, and O, and the composition is $Al_{12}Si_{12}O_{48}$ per unit. Since the framework is negatively charged by the number of Al atoms, cations are distributed in the cages. The typical cation sites are shown in Fig. 1. When the system contains monovalent cation M, the chemical formula is written as $M_{12}Al_{12}Si_{12}O_{48}$ per unit. Such the pre-contained cation can be complex one and the formula is rewritten as $Na_xK_{12-x}Al_{12}Si_{12}O_{48}$ for the case that both of Na and K are contained. We write it as Na_xK_{12-x}-LSX . x can vary from 0 to 12 by replacing the cation in aqueous solution.

We here take a case of $x = 4$, where the formula being Na_4K_8-LSX. Na-K alloy clusters can be generated in the cages of it by loading of guest K atoms. Following a previous report[5], we write the system as K_n/Na_4K_8-LSX. n means number of loaded K atoms per unit. This system shows ferrimagnetic transition for narrow range of n around $n = 7.7$[4]. Spectra of ^{23}Na and ^{27}Al NMR have been observed for $n = 7.1$[10], where ferrimagnetic transition occurs at 7 K. It possesses paramagnetic moment above 7 K and multiple components shift through hyperfine interaction between paramagnetic moment and ^{23}Na nuclei have been recognized. As has been reported[6], this system shows metallic property for $n \gtrsim 6$. Studies with variation on n are expected to give hints to resolve the nature of the electron system.

We have studied these materials using NMR. In the ^{23}Na NMR spectrum for $n = 9.0$, where paramagnetic moment exists all through the temperature above 2 K and metallic property is recognized, we found several components. The main component is well coupled to the paramagnetic moments over the wide temperature range between 25 and 300 K, allowing us to estimate the hyperfine coupling constants [11]. Besides such a main component, we found another component around room temperature, which is less coupled with the paramagnetic moment of the sample. This component has hysteresis in its temperature dependence and shows quite slow dynamics. We focus on the strange behavior of this component in this paper.

2 Experimental

Sample preparation has been done with the same procedure as before[4]. Vapor of K atom is thermally absorbed in vacuum environment up to the saturation level. The loading level was estimated as 9.0 K atoms per unit using chemical analysis. We express, by similar manner with the previous report[5], the sample as $K_{9.0}/Na_4K_8$-LSX, where 9.0 means number of loaded K atoms per unit. X-ray diffraction analysis has not been done for it but, taking into account an analysis on the case of Na_n/Na_{12}-LSX[12], it is quite natural to consider that there are several variations of sites for cations. No magnetic transition is observed above 2 K in spite that previously reported sample, $K_{7.1}/Na_4K_8$-LSX, shows ferrimagnetic transition at 7 K.

NMR spectra of ^{23}Na have been measured at 6.3 T at several points of temperature below 300 K. Another magnetic field of 9.4 T has been utilized for part of the observation such as long time one. References for the frequency shift are taken as the resonance frequency of ^{23}Na in NaCl aqueous solution for both magnetic fields. NMR spectrum is obtained by Fourier transformation of the spin echo signal. In order to establish thermal equilibrium state of the nuclear magnetization, waiting time between each pulse was set effectively long enough. Typical value of it has been several 10 seconds.

3 Results and Discussion

^{23}Na spectrum of $K_{9.0}/Na_4K_8$-LSX at 300 K is shown in Fig. 2. In the region around zero shift there is a structured component similar to the one which is previously reported for $K_{7.1}/Na_4K_8$-LSX[10]. In addition to it, a separated component with somewhat large shift is seen. The shift value of this component is ∼1400 ppm. The reason why the shape of such the component looks as out of phase is that one shot pulse with narrow Fourier component around zero shift has been adopted for this observation.

Such the sharp component with large shift is not seen for $n = 7.1$. There should be some certain reasons for an appearance of this component. It looked coming from metallic nature of the sample itself, since shifted component in metallic materials often corresponds to Knight shift and, moreover, the value of the shift is different from that of bulk metal sodium, ∼1100 ppm[13]. Therefore trial efforts had been made for measurements of the spin-lattice relaxation time T_1 down to lower temperature from room temperature to obtain additional information about the metallic property of the sample. Several measurements, however, have shown that as the waiting time of the RF pulse is extended, the tail part of the magnetization recovery becomes progressively longer up to several tens of minutes.

Then we decided to follow temperature variation of the spectrum with taking long pause between each measurement. An example of the spectral variation on temperature is shown in Fig. 3 (a). Cooling steps had been taken continuously in the first sequence of the measurements from 290 K until 215 K. Heating steps had successively been taken in the second sequence of the measurements from 215 K until 270 K. Between each step of data acquisition, long time pause more than one hour had been taken. As seen in the figure, the process has hysteresis. Such the behavior is observed not only for the shift value of the peak but also for the signal intensity. Peak height is

plotted in the bottom of Fig. 3 (b). The peak height decreases from 290 K to 215 K, in spite of cooling process. If the spectrum is given by nuclei with steady environment, nuclear paramagnetic moment obeys Curie law and the intensity simply follows inverse of temperature. On the other hand, heating process from 215 K until 250 K does not give recovering to the signal intensities of the previous cooling process as before but, after branched behavior around 260 K, partial recover happens at 270 K. Such the observation suggests clearly that there is a somewhat strange hysteresis in the temperature range of 220 K to 260 K. Moreover the behavior such as time duration for an appearance of peak split depends on the temperature history of the sample. Such the fact may corresponds to first order transition. Multiple phases may coexist in the course of the change.

In order to grasp the nature of this behavior, a trial observation through long term has been done. The result is shown in Fig. 4 (a). At first to prepare a uniform thermal equilibrium condition for nuclear magnetization, the temperature of the sample had been kept constant at 319 K for 1 hour, where no hysteresis is recognized. After such the preparation stage, rapid cooling down to 225 K had been done. Just after such the cooling treatment, the signal intensity is higher than that at 319 K. This behavior qualitatively follows Curie law for nuclear magnetism of ^{23}Na. Other than such the basic feature, small deviation to lower side of the shift has been recognized. Keeping constant temperature after such the rapid cooling, the spectrum had repeatedly been recorded many times with intervals around one hour. Shift of the peak gradually goes to the higher side as time passing and a shoulder like structure appears on the less shift side of the peak. We did not make a precise examination for an appearance of such the shoulder, since we rather focused on overall behavior. Thick curves in the figure among many spectra are representative ones. In order to present more the behavior, the intensity at each peak is plotted in the bottom of Fig. 4 (b). Through more than a few days, it continuously decreases. Although behavior after keeping the temperature for 100 hours is unknown, we terminated this experiment. We think it is not natural that regrowth of the spectrum up to the one similar to starting time occurs, even if we had continued the measurement. Disappeared signal must exist somewhere on the spectrum but we did not search for it.

After 23 hours it can be seen by eye that a shoulder component appears to the left of the main peak in the spectrum. Its peak intensities are estimated by eye and plotted in Fig. 4 (b). If the spectrum is fitted with two Lorentzian components, such a small component can be picked up for the period prior to 23 hours. However, since we are not aiming for a clear separation of these two components, but simply hoping to describe the phenomenon, we have not performed such a fitting. To indicate the possibility of a left shoulder component before 17 hours, a dotted line is drawn in Fig. 4 (b) as a guide.

The above behaviors must be certainly an appearance of some thermal dynamics other than phenomena of electromagnetism, which in usual does not contribute to quite slow dynamics. Taking into account the fact that the shift value $\sim$ 1400 ppm is similar but different to that of metallic sodium $\sim$ 1100 ppm[13], it may be attributed to Na-K alloy. Melting point of eutectic compound of Na an K is 260 K[14], which just corresponds to the upper limit temperature where the strange hysteresis starts

in our data. The starting point temperature 260 K of the hysteresis is well preserved. This correspondence is not accidental. Since, in general, melting point is expected to decrease when such the alloy is formed in quite small pore of supercage whose diameter is $\sim$ 13 Å. Although Na-K alloy nanoclusters are formed in LSX, they are not expected to have exactly the same melting point as the bulk alloy.

There is small amount of excess K atoms in the purpose to guarantee the condition of saturation for loading K atoms fully into the cages. Therefore Na-K alloy in the outside space of zeolite particles can be provided with such the K atoms. It is consisted with the fact that a shifted component similar to the case of $n = 9.0$ does not appear on the spectrum of $n = 7.1$. Excess K atoms correspond to Na-K alloy located outside of zeolite particle. As described in the experimental section, however, the mother substance has not ever been exposed to Na vapor. Na atoms must come from somewhere. Unique source to provide with Na to the environment of zeolite particle is restricted within the original substance of zeolite itself, where Na cations are included as the charge compensation ions. Although there is no way to confirm the pass to give such the component to the environment, diffusion process of the cation during the sample preparation can be supposed as an origin. Heating above 423 K is necessary there to promote diffusion of the cations in the time of loading external K atoms. Since such the process is performed in much higher temperature than the melting point of Na-K alloy $\sim$ 260 K [14], Na-K alloy liquid possibly distributes on the surface of LSX micro-crystal of ~ 2 μm. Although there are some reports on ^{23}Na NMR of Na-K alloy[14], such the slow dynamics has not been reported so far. The environment of the zeolite surface possibly gives a special condition to Na-K alloy to have the slow dynamics.

Here we estimate thickness of Na-K alloy distributed on the surface of zeolite crystal. Integral intensity of this shifted component is estimated to be at most 10% of the whole spectrum. If we suppose that each particle of zeolite is just sphere, thickness of such the Na-K alloy is estimated as less than $\sim$ 30 nm. Such the thin film can be supposed to have no influence on optical spectra, which are adopted to estimate properties of K clusters in the cages. When analyzing the NMR signal associated with the Na-K clusters in the cages of LSX, the $\sim$ 1400 ppm shift component, which is the focus of this paper, can be ignored.

Despite the above discussion, the possibility still remains that the focused spectral component is given by ^{23}Na nuclei in the cage of LSX. Whether outside or inside the crystal is more likely to be determined by observing the precise loading level dependence on the external K atom just below the saturation condition.

4 Conclusion

^{23}Na NMR spectra for zeolite low silica X loaded with K for saturating level has been observed. Other than grain of spectrum around the zero shift, a separated peak at $\sim$ 1400 ppm has been recognized. It shows strong hysteresis between 260 K and 220 K and slow dynamics with the time scale up to days-order. Possible candidate for the source of such the component is Na-K alloy formed on the surface of zeolite micro-crystals.

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Declarations

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- Availability of data and materials: not applicable

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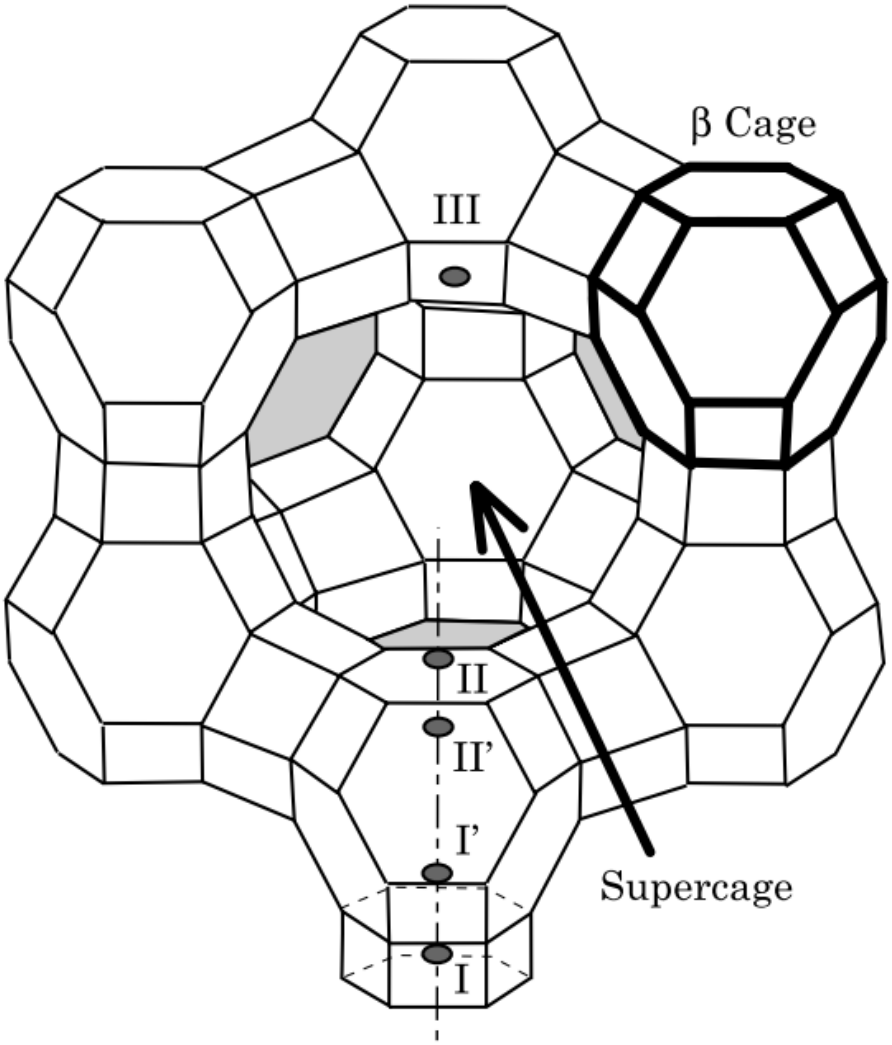

Fig. 1 Schematic illustration of the framework of zeolite low silica X (LSX), which has the FAU structure [8]. The sites for Al and Si atoms correspond to crossing points on the framework in the figure. The Si and Al atoms are alternatively ordered in the framework through the Si-O-Al bonds. Typical cation sites I, I', II, II', and III are shown with the small circles.

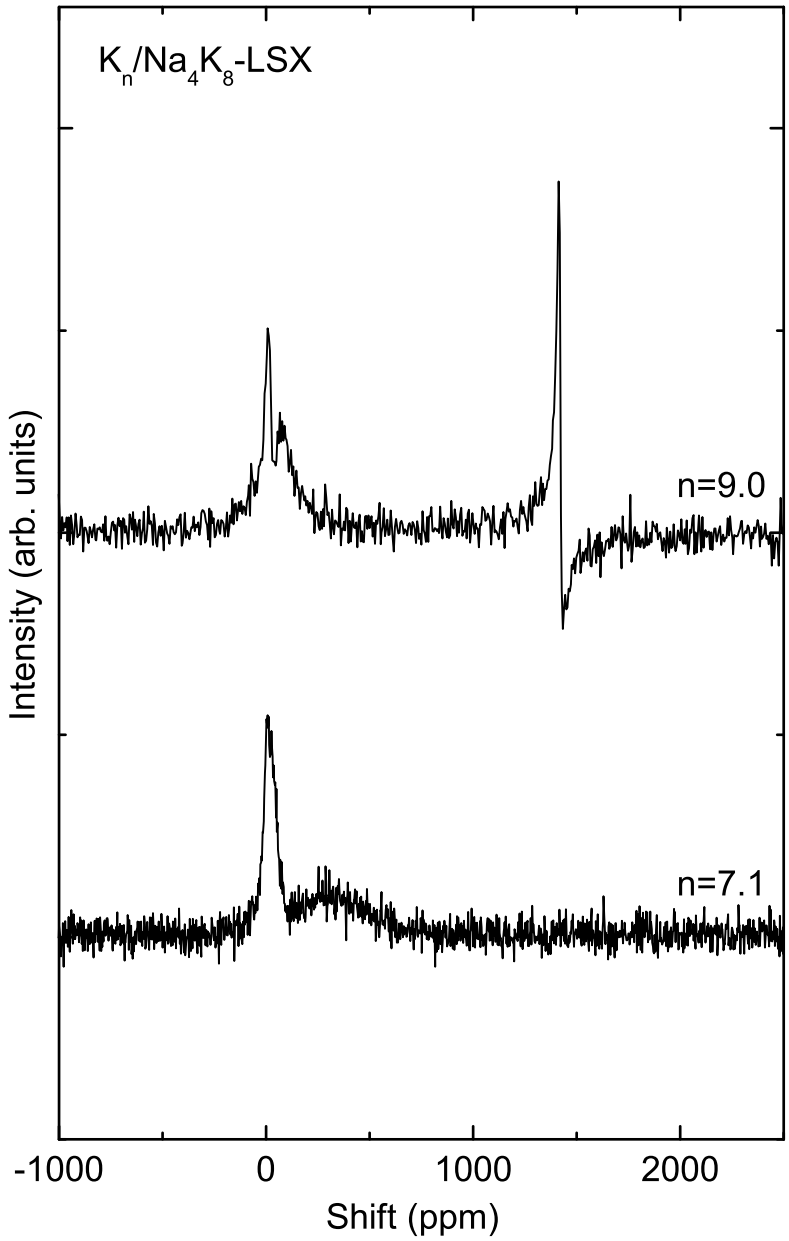

Fig. 2 ^{23}Na NMR spectra of K_n/Na_4K_8-LSX at 300 K in a field of 6.3 T for $n = 7.1$ and $n = 9.0$.

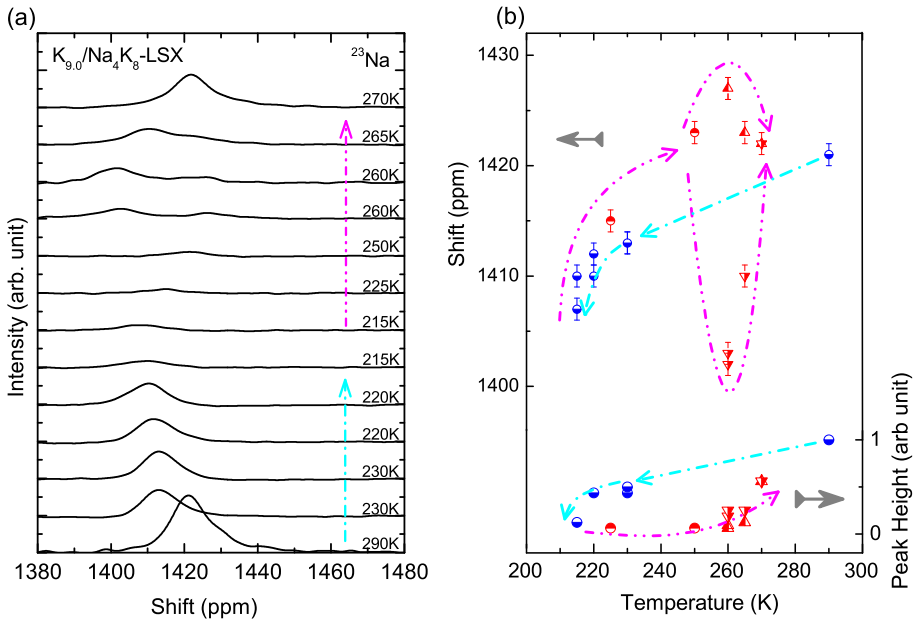

Fig. 3 An example of temperature variation of the separated component on ^{23}Na NMR spectra of $K_{9.0}/Na_4K_8$-LSX taken in a field of 9.4 T. (a) Spectra observed every one hour in the course of cooling from 290 K down to 215 K (process of the blue-colored dash-dotted arrow) and successive heating from 215 K up to 270 K (process of the red-colored dash-doubledotted arrow). (b) The shift and the height of each peak versus temperature. The height is normalized to the value at the starting temperature, 290 K.

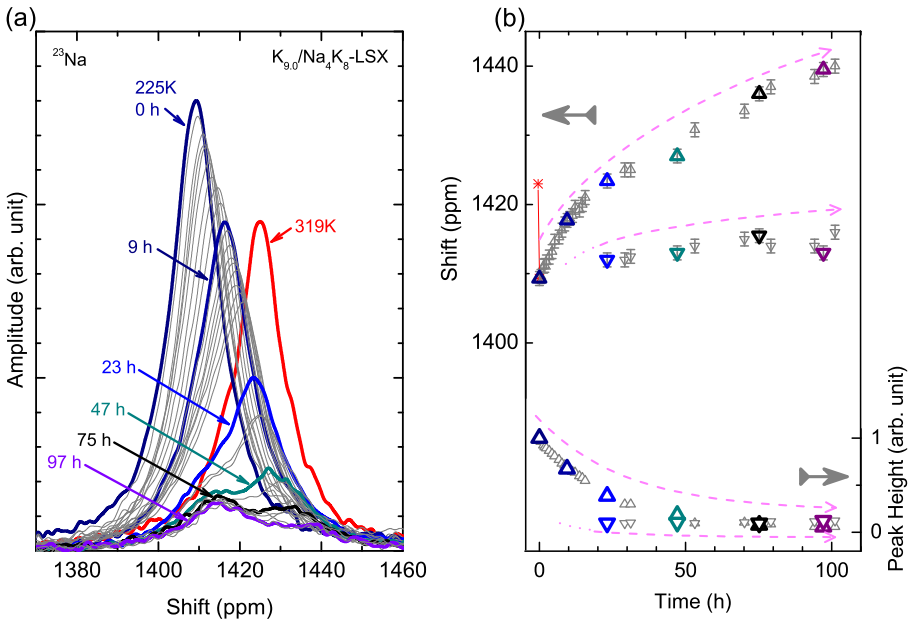

Fig. 4 Long term observation of the separated component on ^{23}Na NMR spectra of $K_{9.0}/Na_4K_8$-LSX with constant temperature. The sample had been held at 319 K for one hour to prepare an initial thermal equilibrium condition and forced to be cooled until 225 K as rapid as possible. Observation of the spectrum at 225 K started with such the condition. (a) Spectra at each time. Representative ones are emphasized with thick lines. (b) The shift and the height of each peak versus temperature. The height is normalized to the value at the starting time of measurement at 225 K. Trends of their behavior are shown with dashed lines. Two points are plotted at each time point after 23 hours, since it can be confirmed by eye that the spectrum is composed of two parts. On the other hand, for the period prior to 23 hours, where it looks like one component, plots were made only for the peaked component. Although fitting the spectrum can possibly extract two components from such a single peaked shape, we did not perform such a fitting. To indicate the possibility of a left shoulder component for such a period, dotted lines are drawn as a guide.