

NMR Relaxation Study of Na Cluster in Zeolite NaY

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The spin-lattice relaxation time T_1 of ^{23}Na -NMR in zeolite NaY fully loaded with Na has been measured from 12K to 340K. The nuclear magnetization shows multi-exponential recovery from saturation at all temperatures. The temperature dependence of T_1 of the loaded sample is weaker than that of not loaded one. Below 120K T_1 linearly depends on the temperature. Above 120K an Arrhenius type relaxation with an activation energy of 680K is found.

1. INTRODUCTION

Recently electromagnetic properties of alkali metal clusters in zeolite attract much attention[1]. It is known that in zeolite NaY dilutely loaded with Na, the clusters of Na_4^{3+} is formed in β cage[2]. Then it is expected that further loading causes interaction among them. However the electronic state has not ever been fully clarified. Since the motion of the unpaired electron provides large fluctuation of the local field, the nuclear relaxation should be affected. In this paper, we report ^{23}Na nuclear spin relaxation in NaY highly loaded with Na.

2. EXPERIMENTAL

Two samples, 'NaY fully loaded with Na' and 'not loaded one', were examined. Each sample was prepared from about 0.5g of powder zeolite NaY (TOSO Inc., Si/Al = 2.75) by heating at 500°C for 6 hour with evacuation. Both loaded and not loaded powder were sealed in a quartz glass ampoule without exposure to air. The loading was done as follows: In an evacuated system metal Na was evaporated by heating and trans-

ferred to the reaction tube containing the powder zeolite. The whole of the tube was heated at 150°C for 5 days. During the heating the tube was shaken several times for complete reaction. Eventually the powder became dark black and large amount of Na remained on the inner surface of the reaction tube. Only the powder was collected.

^{23}Na -NMR signal was observed in the field of 7T. The spin echo signal was monitored with $\pi/2$ - τ - π pulse sequence. The spectrum was obtained by measuring the height of the echo with sweeping the frequency. The spin-lattice relaxation time T_1 was determined by measuring the height of the spin echo $M(t)$ at time t after saturation with $\pi/2$ pulse at the center of the resonance line.

3. EXPERIMENTAL RESULTS

3.1. Spectrum

The ^{23}Na -NMR spectrum of fully loaded NaY is shown in Fig. 1. No signal was observed at the frequency corresponding to the Knight shift for bulk Na metal[3]. This indicates that Na almost fully reacted with zeolite.

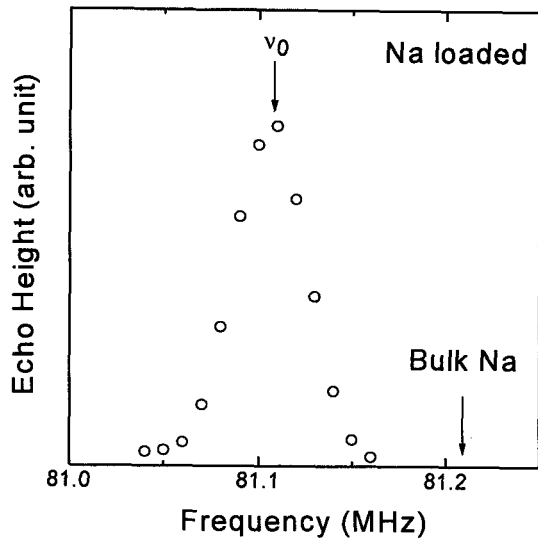


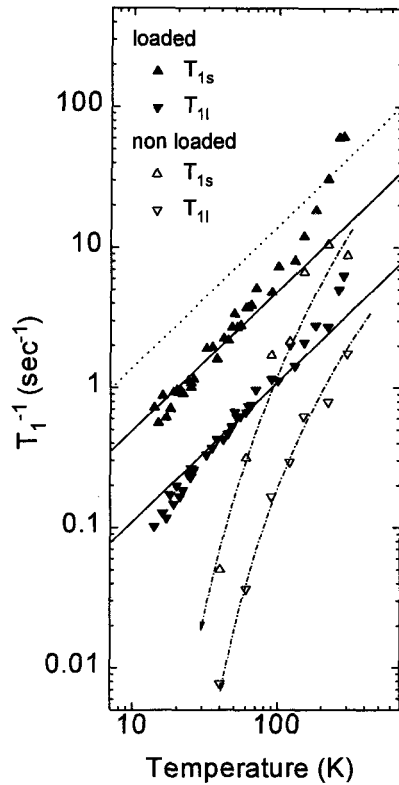
Fig. 1. The spectrum of ^{23}Na -NMR in NaY fully loaded with Na. The arrow with the letter ν_0 indicates the resonance frequency without shift for this field.

3.2. Spin Relaxation

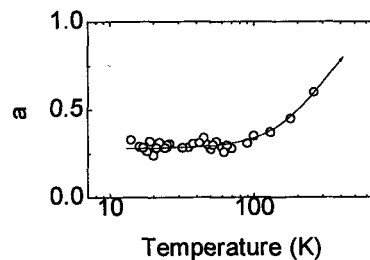
In both samples the magnetization showed multi-exponential recovery from saturation. In spin 3/2 system such as ^{23}Na nuclei, the relaxation of the magnetization has two or three exponential components, depending on the relaxation mechanism[4]. Since the mechanism is not known in the present case, the magnetization $M(t)$ was fitted with two exponential functions for simplicity:

$$M(t) = M(\infty) \left[1 - a \exp\left(-\frac{t}{T_{1s}^{-1}}\right) - (1-a) \exp\left(-\frac{t}{T_{1l}^{-1}}\right) \right] \quad (1)$$

Then T_{1s}^{-1} and T_{1l}^{-1} correspond to the upper and lower limits for the relaxation rates. The temperature dependences of T_{1s}^{-1} and T_{1l}^{-1} are shown in Fig. 2-(a). T_1 's for not loaded sample were too long to be measured below 40K. The temperature dependence of the weight a for fully loaded sample is also shown in Fig. 2-(b). The spin-spin relaxation time T_2 is 3.2 msec for the not loaded NaY at room temperature, whereas 0.8 msec for the fully loaded one. No temperature dependence was observed for the latter.



(a).



(b).

Fig. 2. (a). Temperature dependence of two relaxation rates T_{1s}^{-1} and T_{1l}^{-1} derived with Eq. (1). The dotted line shows T_1^{-1} of bulk metal Na[3]. (b). The weight of T_{1s}^{-1} , a , for fully loaded sample.

4. DISCUSSION

4.1. Spectrum

No observation of the signal corresponding

to the metal Na indicates that Na almost fully reacted with zeolite. The magic angle spinning (MAS) spectrum for the fully loaded NaY[5] consists of sharp line with a small shift of -7 ppm assigned to site I in the literature[6] and broad one ranging over about ± 150 ppm. Our spectrum (Fig. 1) is consistent with MAS spectrum. Since fairly large amount of Na clusters should have neighbouring one in case of heavily doping, electron may be able to move among the clusters. Then Knight shift should be observed for the nuclei in the cluster, whereas the shift is, if any, fairly small compared with that for bulk metal Na. Thus the concentration of the conduction electron at the nuclei is much lower than in bulk Na.

4.2. Spin-Lattice Relaxation

In the not loaded sample T_1^{-1} showed nearly T^2 dependence. This is attributed to the Raman process[7]. The loading with Na changed the temperature dependence drastically as shown in Fig. 2-(a). Since fitting factor a remains constant up to 120K and gradually become large above 120K, We discuss about possible relaxation mechanism with separating into two temperature regions.

4.2.1. Below 120K

For heavily doped NaY zeolite, the ESR of the clusters showed significant narrowing. This was regarded as an evidence of occurrence of the metallic state through the doubled six membered ring (D6R)[8]. As seen in Fig. 2-(a), T_1^{-1} for the doped sample linearly depends on T . This suggests the relaxation through Fermi contact interaction with conducting electron. For s electron, T_1^{-1} obeys the Korringa relation.

$$(T_1 T)^{-1} \propto K^2 \left[\frac{\rho(E_F)}{\chi_e^s} \right]^2, \quad (2)$$

where K means the Knight shift and χ_e^s the electron susceptibility. $\rho(E_F)$ is the density of state at the Fermi level. Since K for the loaded sample is quite small, the relation (2) means that $(T_1 T)^{-1}$ for the loaded sample is also quite small. However, the observed value is as large as about 1/3 of that for bulk Na. Therefore in highly loaded NaY the density of state at the Fermi level may be much larger than bulk or the electronic susceptibility is much smaller than metallic Na,

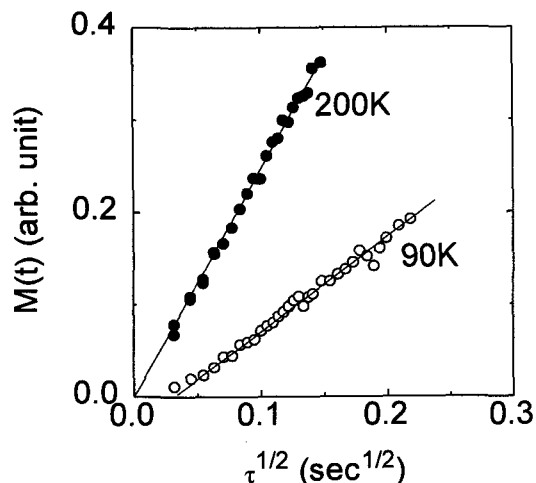


Fig. 3. Initial growth of magnetization $M(t)$ plotted versus $t^{1/2}$ at two temperatures. $M(t)$ for 90K shows a point of inflection at $t^{1/2} \simeq 0.07$. The solid lines are for eye guides.

if the relaxation process can be explained by Korringa relation. Moreover, there is the deviation from the constancy of $T_1 T^{-1}$ below 50K. This fact requires other mechanism.

4.2.2. Above 120K

The temperature dependence of T_1^{-1} gradually increase above 120K associated with the increase of a . This indicates that other mechanism becomes dominant above 120K.

When dilutely dissolved paramagnetic impurities exist in nonmagnetic materials, the impurities often become the relaxation center. The thermal equilibrium of the nuclear spin system is established by the energy flow toward the thermally fluctuating impurities[9]. In such a case the initial growth of the magnetization $M(t)$ from the saturation is governed by the following equation:

$$M(t) \simeq (4\pi^{3/2}/3) N C^{1/2} t^{1/2}, \quad (3)$$

where N is the concentration of the paramagnetic impurities and C is a function of the temperature. The observed $M(t)$ for small t at two temperatures is shown in Fig. 3. The initial $M(t)$ for 200K can be well approximated by linear line passing the origin, while $M(t)$ for 90K has a point of inflection, which is characteristic of the exponential

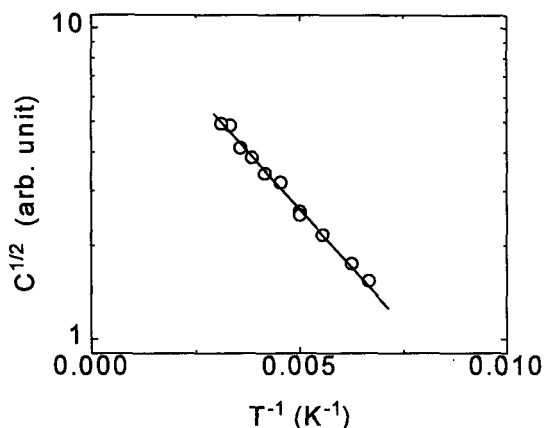


Fig. 4. Temperature dependence of $C^{1/2}$. The solid line corresponds to an activation energy of 680K.

function. Thus the relaxation above about 120K is attributed to some fluctuation of paramagnetic species such as Na_4^{3+} . Since the factor C in the Eq.(3) originates from the interaction between the paramagnetic spin and the neighboring nuclear spin, it is proportional to the Fourier component of the fluctuation of the local field[8]:

$$C \propto \frac{\tau}{1 + (\omega\tau)^2}, \quad (4)$$

where ω is the resonance frequency of the nuclear spin and τ is the correlation time of the fluctuation of the local field. When $\omega\tau \gg 1$, C is proportional to $1/\tau$. If Arrhenius type relation $\tau = \tau_0 \exp(E_a/kT)$ is assumed for τ , C has the following temperature dependence:

$$C \propto \exp\left(-\frac{E_a}{kT}\right), \quad (5)$$

where E_a is the activation energy for the motion of the paramagnetic species. From the plot of $C^{1/2}$ versus T shown in Fig. 4, a value of $680 \pm 40\text{K}$ was obtained for E_a . It is fairly smaller than the typical value of the activation energy (several thousand K) reported for Na as charge compensate ion[10]. Therefore the observed activation energy may be attributed to the motion of the clusters formed by external Na atoms. Since the size of Na_4^{3+} is larger than the diameter of the window of the β cage, the motion should be

confined within the cage. If there are several local minima of the potential for the position of the cluster and the barrier between them is quite lower than that for Na ion in the not loaded sample, the motion over the barrier may be the source of the nuclear relaxation. Alternatively, since the melting point of small cluster is lower than that of bulk, extra Na loaded in NaY may be in a state like liquid and be able to self-diffuse even below the melting point of Na, 370K. If this process is dominant for the nuclear relaxation, similar property should be observed in other zeolites. Then NMR has advantages to investigate self-diffusion process of excess alkali atoms in zeolites.

5. CONCLUSION

For T_1^{-1} of ^{23}Na -NMR in zeolite NaY fully loaded with Na, two mechanisms have been discussed. For T_1^{-1} below 120K, it is difficult to explain the magnitude only by the conventional Korringa relation in spite of the linear dependence on the temperature. Above 120K an activated motion of some paramagnetic species was found. The activation energy of the motion is quite smaller than that for charge compensate ions.

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REFERENCES

1. Y. Nozue, et. al., Phys. Rev., **48**(1993)12253.
2. M. R. Harrison, et. al., J. Solid State Chem., **54**(1984)330.
3. A. Narath and H. T. Weaver, Phys. Rev., **175**(1968)175.
4. E. R. Andrew and D. P. Tunstall, Proc. Phys. Soc., **78**(1961)1.
5. H. Nakayama, et. al., J. Am. Chem. Soc., **116**(1989)9777.
6. H. A. M. Verhulst, et. al., J. Phys. Chem., **98**(1994)7056.
7. M. Igarashi, et. al., Z. Naturforsch., in press.
8. P. A. Anderson and P. P. Edwards, J. Am. Chem. Soc., **114**(1992)10608.
9. W. E. Blumberg, Phys. Rev., **119**(1960)79.
10. G. Kelemen and G. Schön, J. Mater. Sci., **27**(1992)6036.