^{23}Na Nuclear Spin-Lattice Relaxation in Dehydrated Zeolite NaY*

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The spin-lattice relaxation time T_1 of ^{23}Na-NMR in dehydrated zeolite NaY has been measured from 26 to 300 K. The magnetization recovery curve is not single-exponential at all measured temperatures and T_1^{-1} increases in proportion to the square of temperature above 200 K. The result is analyzed with a theory of the Raman process based on covalency. The value of T_1 is compared with that of NaX in which the concentration of Na is about 2 times larger than in NaY.

Key words: Dehydrated Zeolite NaY; ^{23}Na-NMR; T_1; Raman Process; Phonon Spectrum.

1. Introduction

Zeolites have a framework structure consisting of linked SiO_4 and AlO_4^- tetrahedra and contain cations such as Na^+ to compensate the negative charge of the framework [1]. Dehydrated zeolites adsorb external atoms in the open space of the framework to exhibit various properties [2]. For adsorption of Na atoms, at low concentration the formation of clusters Na_4^{3+} in the open space was reported, while at increased concentration metallic sodium was suggested [3]. We found that in dehydrated zeolite NaY loading of Na atoms enhanced the relaxation of the ^{23}Na-NMR and altered the temperature dependence into a Korringa like one [4]. To explain this fact it is required to understand the relaxation in non-loaded NaY. In the preceding paper [5] we reported a result of measurement of the spin-lattice relaxation of ^{23}Na-NMR in dehydrated zeolite NaX. NaX and NaY have the same structure (faujasite, space group Fd3m), but the concentration of Na in NaY is about half that in NaX. In this paper we present the relaxation of ^{23}Na-NMR in dehydrated NaY and discuss it in comparison with that in NaX.

2. Experimental

Powder of NaY (Toso Inc.) was used without further chemical treatment. The composition stated by the company, Si / Al = 2.75, corresponds to chemical formula $Na_{51}[(AlO_2)_{51}(SiO_2)_{141}]$, while the previously examined NaX corresponds to $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]$ [5]. About 0.5 g of the powder was heated at 500°C in a vacuum for 6 hours for dehydration and then sealed in a quartz ampule [6] of 10 mm in diameter without exposour to air. The measurement of ^{23}Na-NMR was done in a field of 7 T. The signal was observed with a standard spectrometer (Matec 5100 pulse power amplifier and 525 receiver) and was recorded after averaging. The temperature of the sample was controlled within 0.1 K. The central transition of ^{23}Na-NMR broadened by the quadrupolar interaction was observed. Since the FID signal could hardly be observed, the spin echo signal was monitored to measure the spin-lattice (T_1) and spin-spin (T_2) relaxation times. The pulse sequence was $\pi/2$ - variable t - $\pi/2$ - τ - π for measurement of T_1 and $\pi/2$ - variable τ - π for T_2. The echo shape was similar to that of NaX.

3. Results and Discussion

3.1. Magnetization Recovery

In general, the magnetization recovery of the spin system of $I = 3/2$ is not single exponential even for

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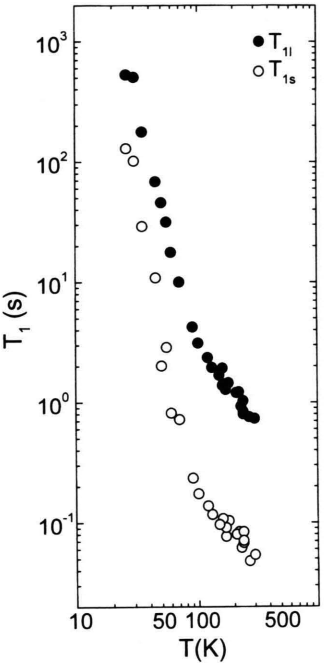

Fig. 1. Temperature dependence of T_1 in zeolite NaY.

one site and one relaxation mechanism, and in fact the observed recovery was not single exponential. Since there are many sites for Na cations in NaY, the magnetization recovery of Na nuclei should be fitted with a multi-exponential function. However, it is difficult to fit with many exponential terms with unknown weights, so that we used a double-exponential function

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

where $M(\infty)$ is the nuclear magnetization at thermal equilibrium.

3.2. Temperature Dependence of T_1

The magnitude of a was almost constant at every measured temperature and equal to 0.35 ± 0.1. The temperature dependence of the determined T_1's is shown in Figure 1. At every measured temperature, T_1 of NaY is about 10 times longer than the corresponding T_1 of NaX. Since the electric field gradient (EFG) at the cation sites is large, the spin-lattice relaxation of the Na nuclei is expected to be dominated by the quadrupolar interaction [5]. With increasing temperature, T_1^{-1} gradually becomes proportional to the

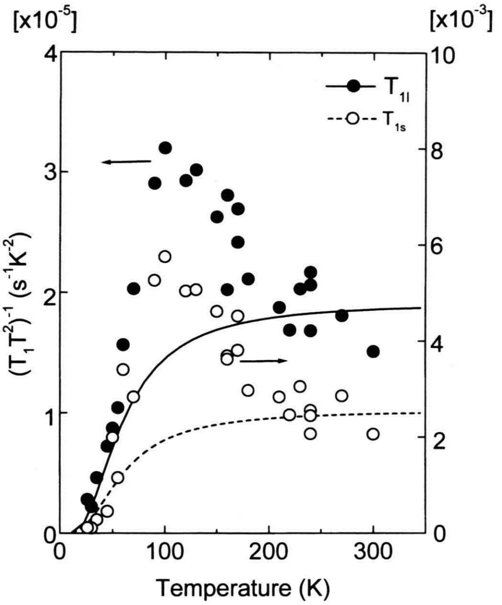

Fig. 2. Temperature dependence of $(T_1T^2)^{-1}$. The curves show the result of fitting of (2).

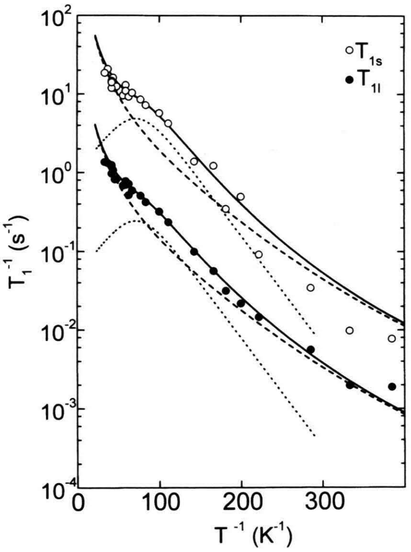

Fig. 3. Temperature dependence of T_1. Dashed curves represent the contribution of the Raman process and the dotted ones the contribution of the BPP mechanism. Solid curves are their sums. Instead of $T^{-1}(K^{-1})$ read $10^4{\cdot}T^{-1}(K^{-1})$.

square of temperature, as in NaX. This suggests that the spin-lattice relaxation is caused through the Raman process[7]. Thus $(T_1T^2)^{-1}$ was plotted against T for T_{1s} and T_{1l} (Figure 2). Then an unexpected hump appeared between 80 K and 200 K. This indicates that another mechanism contributes to the relaxation. This may be seen in a plot of $\log(T_1^{-1})$ versus T^{-1} in Figure 3. So we treated the relaxation below 80 K and above 200 K as due only to the Raman process and that between 80 K and 200 K as due to two mechanisms.

3.2.1. Raman Process

Yosida and Moriya showed that the contribution to the relaxation from the Raman process based on covalency is overwhelmingly greater than that based on an ionic model [8]. Their theory could explain the relaxation of NQR in several kinds of metal halides [9]. When we also apply the theory to Na nuclei in NaY, we must consider which bonds are effective to the relaxation. In the faujasite structure, four or six atoms (Al or Si) are linked through O atoms to form a 4- or 6-membered ring, and there are one or two sites for Na$^+$ per one ring (see Fig. 1 in [5]). However, it is suggested that the position of the site is displaced from the center axis of the ring, and the distances between Na and other atoms are not determined exactly. For simplicity we assume that Na$^+$ forms a weak covalent bond with effectively one partner atom. Then the transition probability W for spin $I = 3/2$ is expressed as follows [10]:

$$WT^{-2} = (\tau\theta_D^2)^{-1}\sum_{\nu=1}^{3} D_\nu(T^*) \qquad (2)$$

with

$$\tau^{-1} = \frac{3e^4Q^2\langle r^{-3}\rangle_{\mathrm{Na}}^2 c^3}{100\pi^3 a^7 d^2 v_s^3} N_{11}(0), \qquad (3)$$

where $N_{11}(0) = 705\lambda^2$. In calculating $N_{11}(0)$, the distance between Na and O, 2.24 Å [11], has been used for a, and the measure of degree of covalency λ has been assumed to depend on the repulsive range parameter ρ as $\lambda \propto e^{-r/\rho}$ with $\rho = 0.345$Å, as was assumed before [8, 12]. $D_\nu(T^*)$ is given by

$$D_\nu(T^*) = T^*\int_0^{1/T^*} \frac{x^2e^x}{(e^x-1)^2} L_\nu(cT^*x)\mathrm{d}x, \qquad (4)$$

where

$$L_1(ka) = \left[-\frac{1}{2}f(\sqrt{2(1+\cos\phi)}ka) + \frac{1}{2}f(\sqrt{2(1-\cos\phi)}ka)\right]^2,$$

$$L_2(ka) = \left[1 - 2f(ka) + \frac{1}{2}f(\sqrt{2(1+\cos\phi)}ka) + \frac{1}{2}f(\sqrt{2(1-\cos\phi)}ka)\right]^2,$$

$$L_3(ka) = 2\left[-\frac{1}{2}f(\sqrt{2(1+\cos\phi)}ka) + \frac{1}{2}f(\sqrt{2(1-\cos\phi)}ka)\right] \cdot \left[1 - 2f(ka) + \frac{1}{2}f(\sqrt{2(1+\cos\phi)}ka) + \frac{1}{2}f(\sqrt{2(1-\cos\phi)}ka)\right],$$

and

$$f(y) = \frac{\sin y}{y}.$$

The notation is the same as in [10]. When the central transition ($+\frac{1}{2} \leftrightarrow -\frac{1}{2}$) is observed in the system of the quadrupole relaxation, $1/2W_1$ and $1/2W_2$ are obtained as T_1's [13], where W_1 and W_2 mean the transition probabilities corresponding to $\Delta m = \pm 1$ and $\Delta m = \pm 2$, respectively. Since for the Raman process in powder NMR, $W_1 = W_2 = W$ [10], we can use $(2T_1)^{-1}$ for W. A value of 1.44×10^3 kg/m^3 is used for d. $k_D = (6\pi^2N/V)^{1/3}$ is calculated to be 1.06×10^{10} /m from $N = 662$ atoms/unit cell and $V = 1.55 \times 10^{-26}$ m^3 [14]. For $e^2Q\langle r^{-3}\rangle_{\mathrm{Na}}/h$, $5/4 \times (-5.16)$ MHz [15] is used. The results of fitting of (2) with θ and τ as parameters to be determined is shown by solid lines in Figure 2. The values of θ_D and those of λ calculated through (3) from τ are summarized in Table 1.

If the principal z axis of the EFG is directed toward the partner atom, λ itself should be compared with $f = e^2Qq_{\mathrm{mol}}/e^2Qq_{\mathrm{at}}$, where e^2Qq_{mol} is the coupling constant in the molecule and $e^2\,Qq_{\mathrm{at}}$ is that in the

Table 1. θ_D and λ in NaY and NaX.

Zeolite		θ_D (K)	λ
NaY	(T_{1s})	230 ± 20	4.41
	(T_{1l})	230 ± 20	1.21
NaX	(T_{1s})	250 ± 20	6.39
	(T_{1l})	250 ± 20	3.70

Table 2. e^2Qq_{mol}[15] and f in NaY and NaX. The asymmetry parameter η is assumed to be zero.

Site	e^2Qq_{mol} (MHz)	f
I	0.4	0.077
I′	2.3	0.44
II	4.2	0.81
II′	2.3	0.44
III	4.7	0.90

free atom [15]. The value of f, calculated using the value determined from double rotation NMR [16] for e^2Qq_{mol} and the value of -5.16 MHz for e^2Qq_{at}, is shown in Table 2.

The obtained $\theta_D = (230 \pm 20)$ K of NaY is close to that of NaX, as expected from the same structure, whereas the λ's are much smaller than those of NaX, corresponding to much longer T_1's. Moreover, the values of λ are by far greater than the corresponding value of f. Since zeolites contain open spaces, called sodalite cage, D6R and supercage, the phonon spectrum may be much different from the normal one in the bulk which is assumed in the theory. To the author's knowledge, the phonon spectrum in these zeolites is not reported.

3.2.2. Another mechanism between 80 and 200 K

In the BPP type relaxation, the temperature dependence of T_1 is roughly expressed as [17]

$$T_1^{-1} \propto \frac{\tau}{1 + (\omega\tau)^2}, \tag{5}$$

where E_a is the activation energy of the motion and τ is the correlation time of the fluctuation of the local field assumed to have the temperature dependence of $\tau = \tau_0 \exp\left(E_a/k_BT\right)$. T_1^{-1} has a maximum around at T, where $\omega\tau \sim 1$. Thus, tentatively we fitted (5) to the remainder of the subtraction of the contribution of the Raman process (2) from the whole data. The result is shown in Figure 3. The obtained values are (330±20) K for E_a and 2×10^{-10} s for τ_0. The activation energy reported from the experimental conductivity is about 3eV [18]. This value is more than two orders of magnitude larger than the above one. Since the cations are bound loosely in the open space, there may be more than one site of potential minimum for them. Then jumping among these minima can be an effective relaxation mechanism. In NaX, a similar mechanism may work. This could be checked by examining the ω dependence of T_1. Alternatively, we may also attribute this hump to the anomalous phonon spectrum.

3.3. Comparison of NaY and NaX

Since the sites for Na$^+$ are separated into five groups with different values of e^2Qq, as shown in Table 2, and the transition probability is proportional to e^2Qq, the recovery curve should be represented by five exponential terms, weighted by the fractional number of the sites multiplied by the occupation probabilities. In spite of it we have fitted the curve with only two terms. Therefore T_{1s} and T_{1l} obtained in the present analysis are a kind of averages of the shorter and longer T_1's, respectively. This is the reason why the ratio of T_{1s}^{-1}/T_{1l}^{-1} ($\approx$ 10) in both zeolites does not reach the squared ratio of the largest coupling constants to the smallest one, $(4.7/0.4)^2 \approx 140$. This is supported by the fact that T_{1s} in NaY is comparable with T_{1l} in NaX. Therefore the large difference in the T_1's of the two zeolites can be explained by considering that at low concentration the probability of occupation of the site with high symmetry is high, while at high concentration that of the site with low symmetry becomes high.

At room temperature, T_2 in NaY was 3.4 msec, in contrast to 0.8 msec in NaX. This corresponds to a lower concentration of Na cations in NaY.

4. Conclusion

The temperature dependence of T_1 of ^{23}Na-NMR in NaY has been analyzed with a theory of the Raman process based on covalency and the BPP theory. The phonon spectrum has been predicted to be different from that in the bulk, and a motion of the cations has been suggested. The large difference of the T_1's between NaY and NaX can be attributed mainly to the difference of the occupancy of the Na$^+$ to the sites on the framework of zeolite.

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