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Mutsuo Igarashi [a]

[a] Department of Applied Physics, Gunma College of Technology, Toribamachi 580, Maebashi, 371-8530, Japan

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Spin-Spin Relaxation Process of ^{23}Na-NMR in Na-Loaded NaY

MUTSUO IGARASHI

Department of Applied Physics, Gunma College of Technology, Toribamachi 580, Maebashi 371–8530, Japan

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Spin-spin relaxation of ^{23}Na-NMR is observed by the spin echo method at room temperature for Y-type zeolite loaded with Na metal without hydration. For saturated and no levels of loading, the echo decay is well fitted by single exponential function. T_2 decreases to be 0.25 times smaller by loading. This decrease of T_2 is explained semiquantitatively with assuming nuclear dipole-dipole interaction between neighboring Na.

Keywords: Zeolite; NaY; ^{23}Na-NMR; spin-spin relaxation; T_2; reduction of the distance between cations

INTRODUCTION

It is known that paramagnetic cluster of Na_4^{3+} is formed in zeolite NaY when Na is dilutely loaded.[1] As loading level of Na increases, the 13-split ESR lines corresponding to this cluster disappear and another single line appears with narrow width.[2] This narrowing had been said to come from conducting state of electron. However, NMR relaxation studies failed to show an existence of conduction electron.[3][4] Then the electronic state in Na-loaded NaY is still in question.

In order to explain the electronic state of Na-loaded NaY, the configuration of Na ion is to be understood. For this purpose the NMR technique may be useful since the spin-spin relaxation process is often determined by the dipole-dipole interaction between neighboring atoms in crystal. We report our observation on the spin-spin relaxation time T_2 of ^{23}Na-NMR.

EXPERIMENTAL

The chemical formula is $Na_{104}[(AlO_2)_{104}(SiO_2)_{280}]\ xH_2O$ ($x \sim 250$) for original NaY used in this study. There are three sites (sites I, II, and III) for Na.[5] Almost every Na exists at site I or II.[6] Both of the sites belong to β cage,[7] which is the unit structure of NaY.

Dehydrated NaY was packed in glass tube simultaneously with Na, and the whole material was heated in furnace at 433 K for several days. The sample color changed gradually from white, through variety of red, to black. During this heating process the glass tube was often shuffled to make homogeneous distribution of the loading level. After cooling down, Na-loaded zeolite was transferred to quartz ampoule without exposure to the air.

The measurement of ^{23}Na-NMR was done within the 7 T superconducting magnet. The spin echo method with a pulse sequence $\pi/2$-τ-π,[8] where τ is a variable time, was used to measure the spin-spin relaxation time T_2.

RESULTS AND DISCUSSION

Amplitude of the spin echo versus 2τ is shown in Fig. 1 with semi-logarithmic scale. In the figure, for NaY without loading of Na (open circle) and for Na-loaded NaY with saturating level of loading (closed circle), sequences of

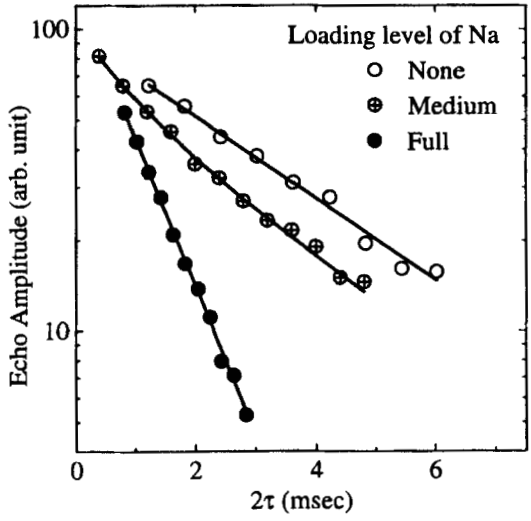

Fig. 1 Echo Amplitude of ^{23}Na-NMR in Na-loaded NaY versus 2τ.

the data points appear to be on straight lines on semi-logarithmic scale. Then an exponential decay function $S_0 e^{-t/T_2}$ is fitted to these two sequences of data. Obtained value of T_2 is 3.2 msec for no-loading case and is 0.8 msec for saturated case. In this study the measurement of T_2 was done by spin echo method. T_2 is determined by the dipole-dipole interaction between like spins ^{23}Na, except for the case that the electronic interaction concerns to the spin flop. Then, for this study, the second moment, which corresponds to T_2^{-2}, is calculated by the following equation:[8]

$$< \Delta\omega^2 >_{II} = \frac{3}{4}\gamma_I^4 \hbar^2 I(I+1) \sum_k \frac{(1 - 3\cos^2\theta_k)^2}{r_k^6}, \qquad (1)$$

where γ_I is the gyromagnetic ratio of ^{23}Na nuclei, and $\hbar$ the planck constant divided by 2π. r_k corresponds to the distance between neighboring Na nuclei, and θ_k the angle between the direction of external magnetic field and the vector from observed Na to neighboring one.

By taking the chemical formula into account, the average number of Na nuclei per β cage is estimated approximately as 3 for the original compound. And the set of 13-split ESR lines in the loaded sample[1] reveals us that 4 site configuration of Na in β cage is one of the probable configurations with loading of Na. Then, to estimate the order of magnitude of T_2, we suppose a trigonal configuration in β cage for no-loading case and a tetragonal configuration for loaded case. Since the inner diameter of β cage is 6.5 Å, the distance between ^{23}Na is evaluated as 5.6 Å for the trigonal case and as 4.6 Å for the tetragonal case. Using these values and eq. (1), we get, by averaging of θ_k in space, T_2 = 6.5 msec for the trigonal case and T_2 = 3.1 msec for the tetragonal case. Reduction factor $(T_2)_{[\text{tetragonal}]}/(T_2)_{[\text{trigonal}]}$ is 0.48, while the experimental one $(T_2)_{[\text{saturate}]}/(T_2)_{[\text{no load}]}$ takes smaller value, 0.8/3.2 = 0.25.

The actual value of T_2 can be smaller than these estimations since the actual location of the ^{23}Na nucleus is not just on the wall of β cage. Moreover, for dense state of Na or loaded condition, the neighboring β cages are also occupied with loaded external Na. Then the location of ^{23}Na nucleus is to be push more into β cage by repulsive force from neighbors. These adjacent Na also give some contribution to $< \Delta\omega^2 >_{II}$. For example, 1 Å reduction gives approximately 0.5 times smaller T_2. There is another possibility for increase of the number of Na (5 or 6 atoms in β cage). This also gives shorter T_2. Therefore, the reduction of T_2 can possibly be explained by the dipole-dipole interaction. We do not deny a possible contribution from the

electronic interaction to the spin-spin relaxation process, but may say that it is not dominant process.

For a sample with medium loading level (daggered circle in Fig. 1), whose color is light brown, the decay of the echo amplitude versus 2τ is approximated by linear combination of two exponential functions much better than by single exponential function. When we define the fitting function as,

$$D(2\tau) = S_L\, e^{-\frac{2\tau}{T_{2L}}} + S_S\, e^{-\frac{2\tau}{T_{2S}}} \quad (T_{2L} > T_{2S}), \tag{2}$$

the time constants T_{2L} and T_{2S} are similar to T_2 of the sample with no-loading and to that of the one with saturation, respectively. The ratio $S_S/(S_S + S_L)$ increases with the loading level of Na, and does not change from saturated value 1 any more after certain loading level, where sample color is dark brown. For every loading level, intermediate value was hardly applicable for T_2 in the fitting of eq. (2) to obtain a good fitting. This may correspond to seldom existence of the intermediate configuration of Na atoms in NaY.

As a conclusion, we observed strong reduction of T_2 in NaY by loading of external Na. Relative reduction factor of T_2 can roughly be explained by assuming a reconfiguration of Na atoms by loading. The dipole-dipole interaction between ^{23}Na nuclei determines the spin-spin relaxation process of ^{23}Na-NMR in Na-loaded NaY.

Acknowledgments

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