Sodium Ion Exchange in $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ as Studied by ^{23}Na Nutation NMR *

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^{23}Na two-dimensional nutation NMR was applied to $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ with $x = 0$, 1, and 2. The nutation spectrum in each compound consists of two clearly separated peaks corresponding to the two crystallographically inequivalent sodium sites. In the compound with $x = 2$ the nuclear quadrupole coupling constants (e^2Qq/h) and the asymmetry parameters (η) were by spectral simulation estimated to be 1.0 MHz and 0 for one site, and 1.5 MHz and 0.8 for the other site. The spectrum varies considerably on heating; the two peaks merge into a single peak at high temperatures due to fast ion exchange between the two different sites. For $x = 0$ and $x = 1$ the nutation spectra did not show any significant temperature dependence, suggesting that the rates of the sodium ion exchange are negligibly low.

Key words: Nutation NMR, Quadrupole effect, Superionic conductor, Chemical exchange.

Introduction

In solid electrolytes the knowledge of local site symmetry and local motion of the mobile ions is of central importance for the understanding of the conduction mechanism. Quadrupole interaction as a probe for the local structure and ionic motion has hitherto been applied to a variety of solid electrolytes and superionic conductors [1], however, the method has been limited to one-dimensional NMR technique, which in case of two or more crystallographically inequivalent ionic sites is often not applicable.

The two-dimensional nutation NMR, however, can distinguish crystallographically inequivalent sites and determine the quadrupole interaction parameters at the individual sites [2].

We proposed recently a new method to incorporate the chemical exchange effect into the 2D nutation NMR [3]. This method made it possible to derive quantitative information about the dynamic structure of the crystal through 2D nutation NMR experiments. We have just applied the method to ^{23}Na nutation NMR in the typical NASICON-type superionic con-

ductors $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, where $x = 0$, 1, and 2, and succeeded in distinguishing the two crystallographically inequivalent sodium sites. Moreover, we found evidence of fast ionic exchange between these inequivalent sites in the compound with $x = 2$. The present paper describes the results of the experiments and of the analysis of the data by spectral simulation, which sheds light on the dynamical characteristics of the mobile sodium ions and the mechanism of the ionic conduction in these materials.

Experimental

The powdered samples were synthesized according to [4]. The stoichiometric mixtures of Na_2CO_3, ZrO_2, SiO_2, and $NH_4H_2PO_4$ were at first heated to 900 °C for several hours to decompose Na_2CO_3 and $NH_4H_2PO_4$ completely, and then they were heated up to 1200 °C for 10 to 20 hours in a platinum crucible. The white fine powdered samples thus obtained were identified by X-ray powder diffraction.

The ^{23}Na 2D nutation NMR spectra were measured with a Bruker MSL-200 NMR system at a Larmor frequency of 52.938 MHz. The pulse length was increased from 2 to 25 μs every 2 μs. The free induction signal was sampled every 0.8 μs, usually up to 1 k words. The temperature of the sample was controlled within ±1 K using the VT-1000 temperature control system in the MSL-200 system. The data acquired

were 2D Fourier transformed by a Bruker ASPECT-3000 computer after zero-filling up to 1 or 2 k words in the F_1 dimension in order to increase the spectral resolution.

Results and Discussion

The compounds with $x = 0$ and $x = 1$ crystallize in a rhombohedral unit cell of the space group $R\bar{3}c$, which can also be indexed as a monoclinic system, $C2/c$ [5, 6]. The crystal with $x = 2$ is monoclinic $C2/c$, which is regarded to have a slightly distorted hexagonal structure [5]. There are three inequivalent sodium sites; one (site 1) is an octahedral site surrounded by six oxygen atoms of ZrO_6, and the others (sites 2 and 3) are asymmetric polyhedral sites, the former being energetically more favorable than the latter. In the case of $x = 0$, the sodium ions occupy the site 1, and for $x > 0$ the excess cations are randomly distributed over the sites 2 and 3. The ionic conduction is thought to be due to sodium transport through channels connecting site 1 and other sites. It was found that the activation energy depends only slightly on x in the range $0 \leq x \leq 3$, and the conductivity assumes a maximum value for $x = 2$ [4].

The 2D nutation NMR spectra of ^{23}Na in the compounds with $x = 0$ and $x = 1$ consist of two clearly separated peaks, indicating that a considerable amount of sodium ions is excited at the sites 2 and 3. The spectra of these materials did not show any significant temperature dependence.

The ^{23}Na one-dimensional spectrum of the compound with $x = 2$, $Na_3Zr_2Si_2PO_{12}$, shows a remarkable temperature dependence (Figure 1). This figure suggests strongly that ionic exchange between different sodium sites or self-diffusion is excited at high temperatures. However, one can neither distinguish the different sites nor assign the nature of the ionic motion which is responsible for the variation of the lineshape.

Figure 2 shows the contour plot of the ^{23}Na 2D nutation spectrum at 116 K. The spectra in the directions F_1 and F_2 correspond to the nutation spectrum and the normal 1D spectrum, respectively. It consists of two clearly distinguishable peaks with the approximate intensity ratio of 1:2. Referring to the structural data [5], the peak at the low-field side (left side) is assigned to the sodium ions at the site 1, and the high-field one to the other sites (sites 2 and 3). The
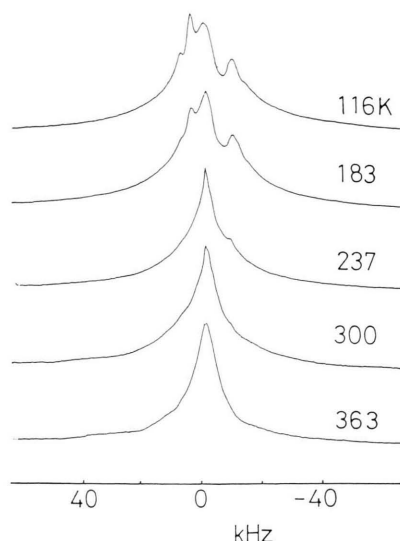

Fig. 1. Temperature dependence of the ^{23}Na 1D spectrum in $Na_3Zr_2Si_2PO_{12}$.

Site	e^2Qq/h/MHz	η
1	1.0 ± 0.1	0.0 ± 0.1
2	1.5 ± 0.1	0.8 ± 0.2

Table 1. ^{23}Na quadrupole interaction parameters in $Na_3Zr_2Si_2PO_{12}$.

sodium ions at sites 2 and 3 could not be distinguished. The difference between the chemical shifts in these different sites was determined to be 16 kHz; it seems that the rate of ionic motion is negligibly low at 116 K.

We compared the spectral patterns sliced at the positions marked by arrows a and b along the F_1 axis with simulated spectral patterns and estimated the quadrupole interaction parameters as listed in Table 1. The small value of e^2Qq/h and nearly zero asymmetry parameter η at the site 1 are consistent with the structural data. The large η at the sites 2 and 3 reflects the low point symmetries at these sites.

The two peaks began to merge at 186 K, as shown in Fig. 3, and merged completely to give a single peak above 300 K (Figure 4). This phenomenon indicates that a rapid ionic exchange between the different sites takes place above 300 K. The apparent e^2Qq/h and η were estimated to be 1.1 MHz and 1.0, respectively, at 363 K from the spectral simulation.

We proposed previously a theoretical method to incorporate the chemical exchange effect into the 2D nutation NMR [3]. The essence of the theory is to use
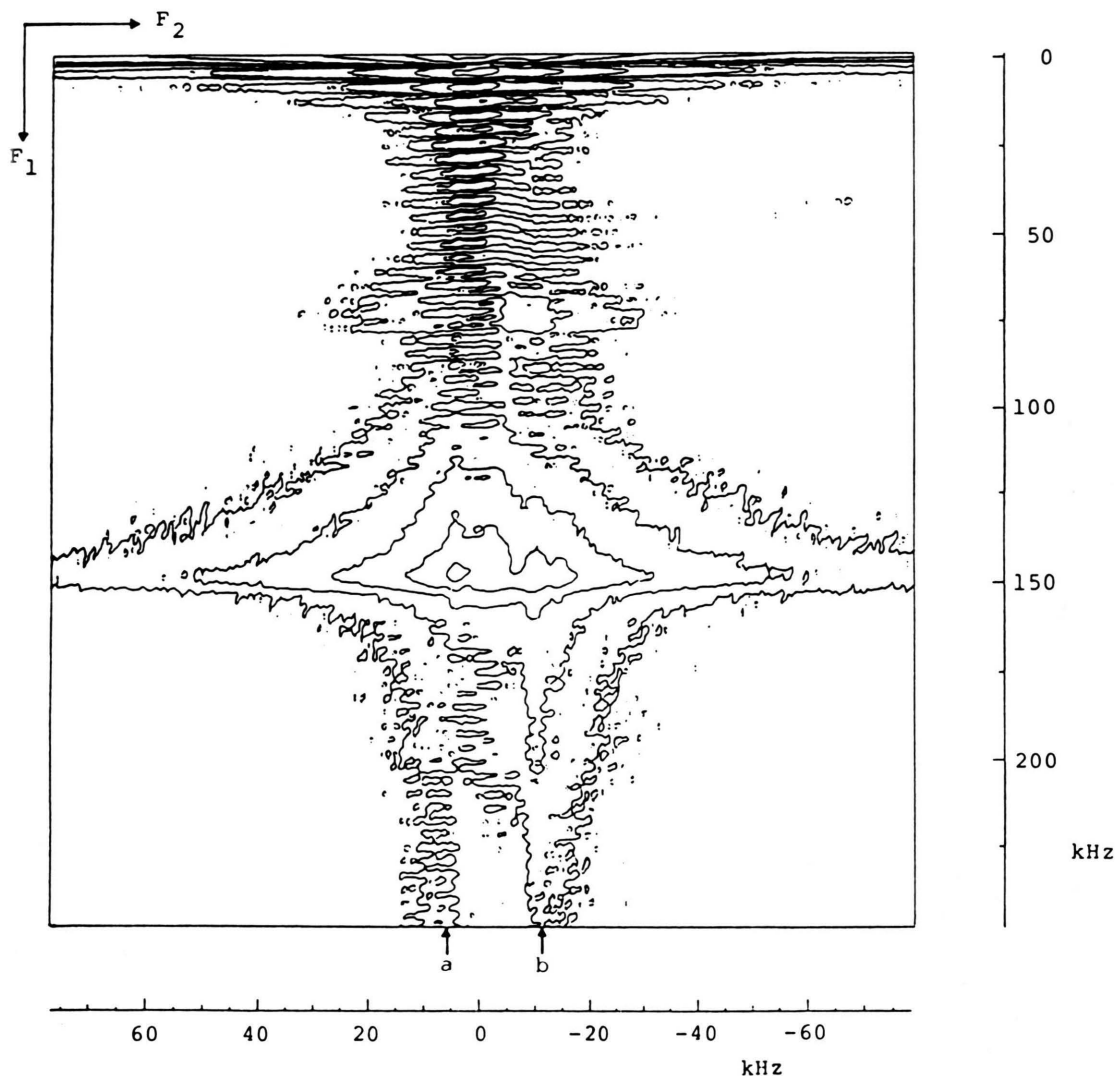
Fig. 2. Contour plot of ^{23}Na 2D nutation spectrum in $Na_3Zr_2Si_2PO_{12}$ at 116 K. The meaning of two arrows marked by a and b is explained in the text.

the Liouville space formalism to describe the time evolution of the spin system instead of using the usual Schroedinger representation.

We consider the exchange of the cations between two different sites, 1 and 2. We assume that the interaction between the spins at these sites can be ignored and that the jump mechanism applies to the exchange process. Then in the Liouville space representation the time evolution of the density matrix kets $|\varrho\rangle$ can be represented by

$$d|\varrho\rangle = [-iL+K]|\varrho\rangle, \qquad (1)$$

where L represents the Liouville operator which comprises the quadrupole interaction and the interaction between the spin and the strong radio-frequency field and K is the exchange operator.

We applied (1) to simulate the spectrum at each temperature using the quadrupole interaction parameters listed in Table 1 and estimated the rate of the ionic exchange as listed in Table 2. Because the spectral simulation is very time-consuming, we could determine only the order of magnitude of the exchange rate at each temperature. The activation energy was also estimated from the exchange rates in Table 2; it
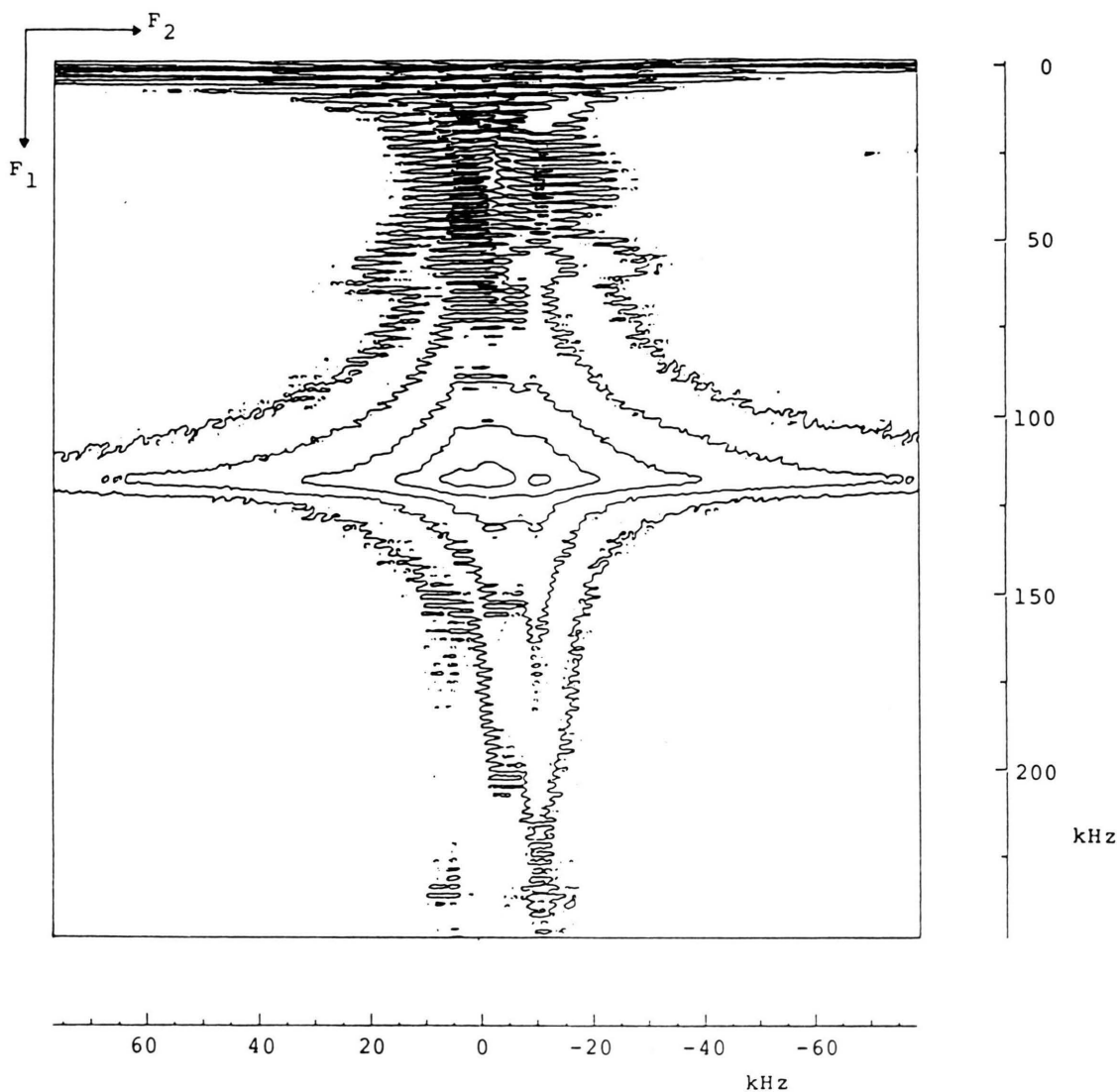
F$_2$

F$_1$

0

50

100

150

200

kHz

60   40   20   0   -20   -40   -60

kHz

Fig. 3. Contour plot of ^{23}Na 2D nutation spectrum in $Na_3Zr_2Si_2PO_{12}$ at 186 K.

Table 2. The ionic exchange rate in $Na_3Zr_2Si_2PO_{12}$.

Temperature K	Exchange rate kHz
116	> 0.001
186	0.01
237	0.1
300	1.0
363	10

lies between 11 and 20 kJ/mol, the probable value being 13 kJ/mol.

The activation energy for the ionic conduction in the above material was determined to be 28 kJ/mol by a conductivity measurement [4]. It corresponds to the average potential barrier for the net sodium ion transport. The activation energy for the ion exchange deduced by our NMR method is about half of that for the net sodium transport. The discrepancy between the activation energies by two different methods may be interpreted by a correlated hopping model proposed by Richards [1]. This model states that a local exchange between two energetically different sites does not depend on the population of other sites and can be stochastically realized. Such a local motion governs the lineshape and the relaxation of the
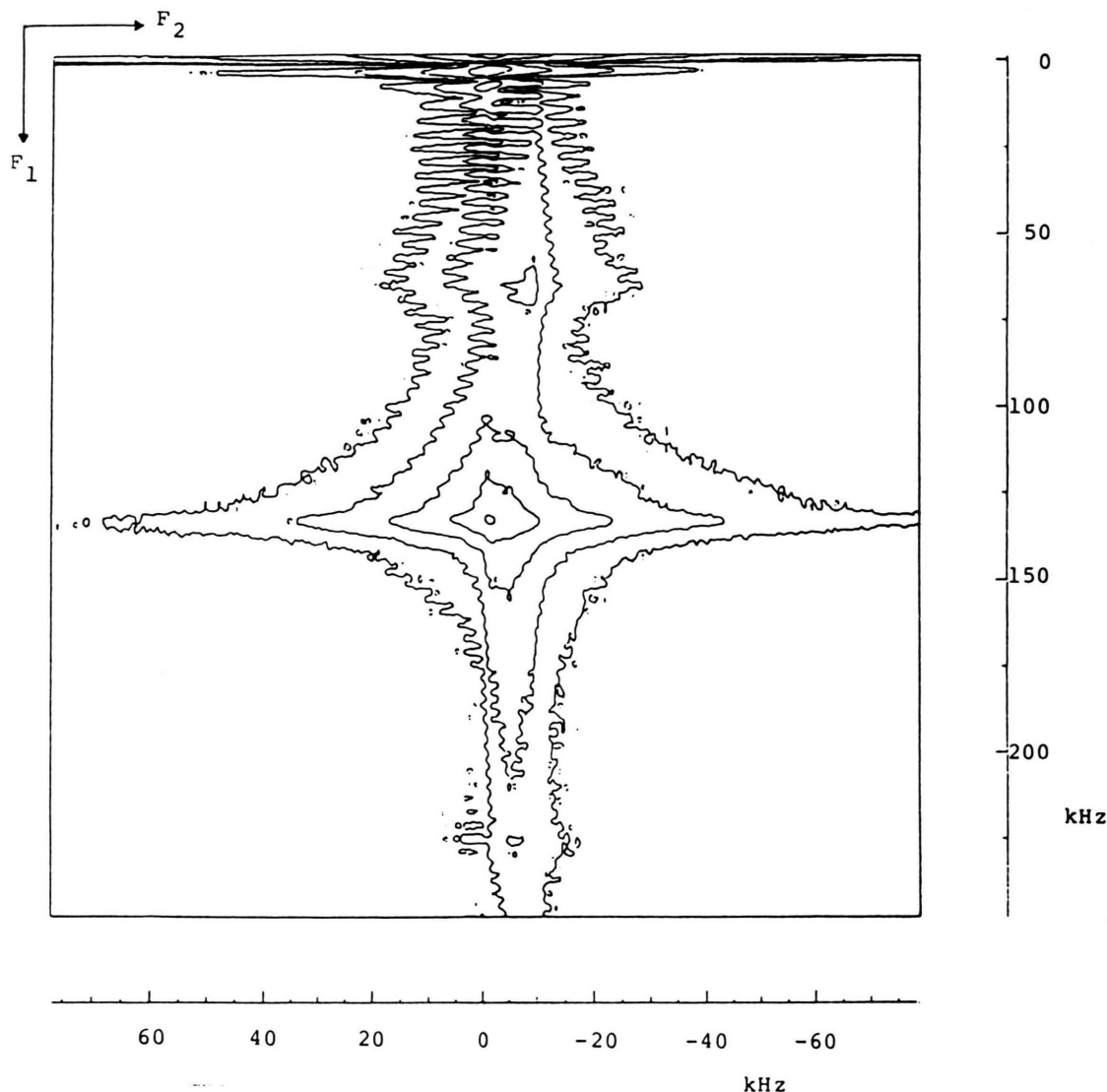
Fig. 4. Contour plot of ^{23}Na 2D nutation spectrum in $Na_3Zr_2Si_2PO_{12}$ at 300 K.

quadrupolar nucleus. However, in order for one sodium ion to undergo a long-range transport, the site next to the ion should be vacant. And so the translational motion of the individual ions can not be independent from each other and must be closely correlated. Since some amount of energy is necessary to form a new vacancy, the effective activation energy for the sodium ion transport is higher than that for the local ion exchange.

In the case of $Na_3Zr_2Si_2PO_{12}$, however, one-forth of the sites 2 and 3 are always unoccupied so that the net sodium ion transport can be realized without any excess activation energy. Hence the activation energy for the local exchange should coincide with that for the ionic conduction in the material. We attempted to measure the spin-lattice relaxation time T_1 of ^{23}Na as a function of temperature in order to obtain a reliable value of the activation energy. But the recovery of the magnetization after two 90° pulses was strongly non-exponential and we could not determine the activation energy by the relaxation measurement. Some other experimental method will be necessary to clarify the above discrepancy in the activation process.

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