Nuclear Quadrupole Interaction and Ionic Dynamics in Sodium Superionic Conductors*

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Recent work on the $^{23}$Na quadrupole interaction in the NASICON family is reviewed. The applicability and the limitation of the two-dimensional nutation NMR to complex systems with more than one quadrupolar nuclear sites is discussed and the possibility of sodium ion exchange in some of the NASICON-type compounds is pointed out. The microscopic mechanism of the site exchange is examined by molecular dynamics simulation. A model potential energy function for the site exchange and/or hopping transport of the sodium ions is proposed. It interprets qualitatively the difference between the activation energies deduced by NMR and by conductivity measurement.

Key words: Nutation NMR; Quadrupole effect; Superionic conductor; NASICON; Chemical exchange; Molecular dynamics.

Introduction

Usual superionic conductors contain small mobile ions such as Li$^+$, Ag$^+$, and Cu$^+$, which transport the electric charge. The activation energy for the diffusion or hopping of these ions in the crystalline lattices or amorphous materials is generally low (0.1 eV) and the conductivity amounts to $0.1 \text{ S cm}^{-1}$ [1]. On the other hand, NASICON compounds, the typical sodium ion conductors, have relatively high activation energy and show low conductivity as summarized in Table 1 [2–7]. NMR and NQR are superior methods to examine the local structure and the mechanism of the ionic conduction in superionic conductors and have widely been applied to a variety of materials, especially to small ion conductors [8, 9]. However, few of these techniques have been applied to NASICON so far. We have been engaged in studies of the local structure and the dynamical properties of the NASICON family by probing the $^{23}$Na nuclear quadrupole interaction in these materials for the last few years. This article reviews the results of our NMR experiments on some NASICONS together with a molecular dynamics simulation on one of the NASICON compounds.

Methods

The NASICON samples were synthesized according to [2–4, 6, 7, 10] and characterized by powder X-ray diffraction. The existence of the phase transitions was examined by differential thermal analysis. We carried out normal one-dimensional $^{23}$Na NMR and two-dimensional nutation NMR [11, 21] in order to determine the individual quadrupole coupling parameters, $e^2Qq/h$ and $\eta$, separately at two or more crystallographically inequivalent sodium sites. All the NMR experiments were performed by the use of a Bruker MSL-200 NMR system. The temperature of the samples was measured by chromel-P-constantan thermocouples inserted into the NMR probe head. The details of the nutation NMR have been described in [13, 14].

Results and Discussion

1. $\text{Na}_{1+x}\text{Zr}_2\text{Si}_3\text{P}_{3-x}\text{O}_{12}$

These ceramic materials are called “NASICON”. They have a high conductivity via transport of sodium ions [2, 3], the conductivity reaching the highest value for $x = 2$ (see Table 1). The structure is rhombohedral $\text{R}3\text{c}$ except for the range $1.8 \leq x \leq 2.2$, where it is monoclinic $\text{C}2/\text{c}$ with the monoclinic angle $\beta$ close to 120°, so that the crystal symmetry can be regarded as pseudo-trigonal [2].

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Table 1. Structure and conductivity data for NASICONs.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$T$ [K]</th>
<th>Structure</th>
<th>$\sigma$ [S cm$^{-1}$]</th>
<th>$E^*$ [eV]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NaZr}_2\text{P}<em>3\text{O}</em>{12}$</td>
<td>300</td>
<td>R3c</td>
<td>-</td>
<td>-</td>
<td>[3]</td>
</tr>
<tr>
<td>$\text{Na}<em>{1.4}\text{Zr}</em>{2}\text{Si}<em>{0.4}\text{P}</em>{2.6}\text{O}_{12}$</td>
<td>300</td>
<td>R3c</td>
<td>$5.4 \times 10^{-4}$</td>
<td>0.26</td>
<td>[3]</td>
</tr>
<tr>
<td>$\text{Na}_2\text{Zr}<em>2\text{PO}</em>{4}$</td>
<td>300</td>
<td>C2/c</td>
<td>0.2</td>
<td>0.29 [3]</td>
<td></td>
</tr>
<tr>
<td>$\text{Na}_3\text{Zr}_2\text{Si}_2\text{P}<em>0\text{O}</em>{12}$</td>
<td>300</td>
<td>R3c</td>
<td>$1.8 \times 10^{-2}$</td>
<td>0.24</td>
<td>[3]</td>
</tr>
<tr>
<td>$\text{Na}_3\text{In}_2\text{P}<em>3\text{O}</em>{12}$</td>
<td>298</td>
<td>C2/c</td>
<td>$2.3 \times 10^{-3}$</td>
<td>0.36</td>
<td>[4]</td>
</tr>
<tr>
<td>$\text{Na}_3\text{Sc}_2\text{P}<em>3\text{O}</em>{12}$</td>
<td>300</td>
<td>Cc</td>
<td>$1.1 \times 10^{-6}$</td>
<td>0.41</td>
<td>[6]</td>
</tr>
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Table 2. Quadrupole coupling constants and asymmetry parameters in NASICONs.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$T$ [K]</th>
<th>Nucleus</th>
<th>$e^2Qq/\hbar$ [MHz]</th>
<th>$\eta$</th>
<th>$k$ [kHz]$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NaZr}_2\text{P}<em>3\text{O}</em>{12}$</td>
<td>300</td>
<td>$^{23}\text{Na}$</td>
<td>$1.2 \pm 0.04$</td>
<td>$0.1^b$</td>
<td>$0.04^b$</td>
</tr>
<tr>
<td>$\text{Na}_3\text{Zr}_2\text{Si}_2\text{P}<em>0\text{O}</em>{12}$</td>
<td>116</td>
<td>$^{23}\text{Na}$</td>
<td>$1.0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{23}\text{Na}$</td>
<td>$1.5$</td>
<td>$0.1$</td>
<td>$0.8$</td>
</tr>
<tr>
<td></td>
<td>237</td>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>363</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>$\text{Na}_3\text{In}_2\text{P}<em>3\text{O}</em>{12}$</td>
<td>300</td>
<td>$^{23}\text{Na}$</td>
<td>$1.04 \pm 0.04$</td>
<td>$0.2^b$</td>
<td>$0.04^b$</td>
</tr>
<tr>
<td></td>
<td>237</td>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>330</td>
<td></td>
<td></td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>$\text{Na}_3\text{Sc}_2\text{P}<em>3\text{O}</em>{12}$</td>
<td>300</td>
<td>$^{23}\text{Na}$</td>
<td>$&lt;0.01$</td>
<td>$&lt;0.01$</td>
<td>$&gt; \Delta v$</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td></td>
<td></td>
<td></td>
<td>$&gt; \Delta v$</td>
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<td>250</td>
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<td></td>
<td></td>
<td>$&gt; \Delta v$</td>
</tr>
<tr>
<td>$\text{Na}_3\text{Hf}_2\text{Si}_2\text{P}<em>0\text{O}</em>{12}$</td>
<td>298</td>
<td>$^{23}\text{Na}$</td>
<td>$0.5$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$\text{Na}_3\text{In}_2\text{P}<em>3\text{O}</em>{12}$</td>
<td>300</td>
<td>$^{23}\text{Na}$</td>
<td>$0.8$</td>
<td>$&lt;0.01$</td>
<td>$&gt; \Delta v$</td>
</tr>
<tr>
<td>$\text{Na}_3\text{Sc}_2\text{P}<em>3\text{O}</em>{12}$</td>
<td>300</td>
<td>$^{24}\text{Na}$</td>
<td>$0.4$</td>
<td>$&lt;0.01$</td>
<td>$&gt; \Delta v$</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>$^{45}\text{Sc}$</td>
<td>$3.0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>$^{45}\text{Sc}$</td>
<td>$2.0$</td>
<td>$&lt;0.01$</td>
<td>$&gt; \Delta v$</td>
</tr>
</tbody>
</table>

$^a$ Exchange rate [13] and [14]; $^b$ [15].

By measuring one dimensional $^{23}\text{Na}$ NMR spectra as well as $^{23}\text{Na}$ cross-polarization magic angle spinning (CP/MAS) spectra for the central transitions between $m = + 1/2$ and $-1/2$ the nuclear quadrupole parameters were determined for the materials with $x = 0, 1, 2,$ and 3 as given in Table 2 [15]. All Na$^+$ ions were found to be crystallographically equivalent for $x = 0$, which is consistent with the result of X-ray diffraction studies [2, 16]. For $x = 3$ there are two crystallographically inequivalent sodium sites in the unit cell with different quadrupole parameters, the occupation ratio being about 1:3. It is interesting to see that the $x = 2$ compound contains only one sodium site, although previous X-ray diffraction studies [2, 17] reported that the sodium ions are distributed over two or more inequivalent sites.

We carried out one-dimensional $^{23}\text{Na}$ line shape measurements for $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (i.e., $x = 2$) and found that the line shape varies significantly with temperature. We then measured the two-dimensional $^{23}\text{Na}$ nutation spectrum as a function of temperature. It was found that there are at least two crystallographically inequivalent sodium sites below about 120 K, and that the exchange of sodium ions between these inequivalent sites takes place at higher temperatures [13, 14]. By a theory, on the basis of the Liouville representation, for the quadrupolar nutation spectrum in the presence of chemical exchange it was possible to interpret the temperature dependence of the $^{23}\text{Na}$ nutation spectrum for this compound. The analysis of the 2D spectra with the theory led to the quadrupolar parameters at 116 K and to the exchange rate of Na$^+$ at several temperatures as listed in Table 2, yielding an estimated activation energy for the site exchange of $13$ kJ mol$^{-1}$. This value is about half that determined by a previous conductivity measurement [3]. We will discuss this point in a subsequent section.

2. $\text{Na}_1+x\text{Hf}_2\text{Si}_2\text{P}_3-x\text{O}_{12}$

This series of materials is called hafnium NASICON. The conductivity reaches a maximum for $x \approx 2.2$ [4]. We measured the two-dimensional $^{23}\text{Na}$ nutation spectrum of $\text{Na}_3\text{Hf}_2\text{Si}_2\text{P}_{0.8}\text{O}_{12}$ [18]. The quadrupole $F_1$ spectrum of the 2D nutation spectrum at 120 K has one main component only at $\omega_1$, where $\omega_1 = \gamma H_1$ represents the strength of the rf-field, indicating that $e^2Qq/\hbar$ is smaller than 0.01 MHz and the asymmetry parameter $\eta$ is nearly 1 at 298 K, as listed in Table 2. It is difficult to consider that a single, very small $^{23}\text{Na}$ quadrupole coupling constant is intrinsic because, by analogy to other NASICON structures, the site symmetry of the sodium ions is not expected to be nearly spherical. Therefore our NMR result suggests that a fast site-exchange of sodium ions occurs at low temperatures. However, it is also questionable whether the site exchange brings about such a small $e^2Qq/\hbar$ or not. The crystal structure determination of this compound is needed for the critical examination of the extremely small $e^2Qq/\hbar$. 
3. \(Na_3In_2P_3O_{12}\)

This compound and \(Na_3Sc_2P_3O_{12}\), which will be considered in the next section, have also been classified as members of the NASICON family. Their conductivity is low compared with the other NASICONS. They undergo phase transitions just above room temperature, but their conductivities do not change appreciably at the transition point [5–7].

At room temperature, \(Na_3In_2P_3O_{12}\) belongs to the monoclinic space group \(Cc\). The phase behavior of this material is complex [6]. Specimens cooled slowly or quenched from 1300 K undergo phase transitions in the temperature ranges 325–335 K and 500–505 K, but a specimen quenched from 1550 K shows only one phase transition at about 505 K. By differential thermal analysis we confirmed for our specimen that the lower phase transition occurs at around 330 K and is of first order. Although the atomic positions have not been determined, it is probable that the unit cell contains two or more crystallographically inequivalent sodium sites.

We measured the one-dimensional \(^{23}\text{Na}\) spectrum at three temperatures as shown in Figure 1. The spectrum at 250 K indicates the existence of at least two inequivalent sodium sites, but it is quite difficult to evaluate the quadrupole interactions in the individual sites. The line shape varies to some extent on heating the specimen up to room temperature, and a remarkable narrowing occurs on passing through the transition point, 330 K. In order to determine the \(^{23}\text{Na}\) quadrupole parameters we applied 2D nutation NMR [18, 19]. The spectrum at 330 K is shown in Fig. 2 as an example. From this spectrum and those at other temperatures we estimated the \(e^2Qq/h\) and \(\eta\) as listed in Table 2. The uncertainty in the values of the quadrupole parameters are large because of the disadvantageous superposition of the lines. Since the values of \(e^2Qq/h\) do not change appreciably on heating, the line narrowing may be caused by the decrease in the chemical shift difference at these sites due to an exchange of the sodium ions between the inequivalent sites.

4. \(Na_3Sc_2P_3O_{12}\)

Early structural studies on powdered samples of this material indicated that its crystal structure is monoclinic at room temperature and undergoes a phase transition at 65 °C to a rhombohedral structure [7, 20–24]. However, it was recently pointed out that the structure of this material depends sensitively on the conditions of the sample preparation [10, 25]; the specimen prepared by fusion is monoclinic but those obtained by crystallization of powder at 1470 °C and by the flux method are rhombohedral. There are three crystallographically inequivalent sodium atoms in the monoclinic structure, and a quarter of their sites is vacant. In the trigonal unit cell there are two kinds of independent sodium ions, one is at a high symmetry special position on the trigonal axis (Na(1)) and the other at a lower symmetry position (Na(2)); the Na(1) sites are almost fully occupied, but about one-third of the Na(2) sites is vacant [10].
Fig. 2. Two dimensional $^{23}$Na nutation spectrum of Na$_3$In$_2$P$_3$O$_{12}$ at 52.9 MHz at 330 K. Arrows indicate the frequencies which give the chemical shifts. The chemical shift difference between two sodium sites is 8.2 ppm.
We confirmed by powder X-ray diffraction that our powdered specimen is monoclinic, and DTA-shows that it undergoes a first order phase transition at 336 K. We then measured the two-dimensional nutation spectra of $^{23}\text{Na}$ and $^{45}\text{Sc}$ [18, 19]. The 2D nutation spectrum of $^{45}\text{Sc}$ at room temperature is shown in Fig. 3, and the results of the spectral analysis are summarized in Table 2. The data analysis indicated two crystallographically inequivalent scandium sites, being consistent with a previous structure analysis [10]. As to $^{23}\text{Na}$, there should be three and two inequivalent sites in the low- and the high-temperature phases, respectively, but 2D nutation NMR revealed only one site in both phases (see Figure 3). This may be caused by a rapid exchange of the sodium ions between the Na(1) and Na(2) sites at and above room temperature. The site exchange of the sodium ions is also indicated by relatively large isotropic temperature factors in the X-ray structure analysis [10].

5. Molecular Dynamics Simulation

We found by $^{23}\text{Na}$ NMR that probably site exchange of sodium ions takes place in some of the NASICON-type compounds, but in some cases this is difficult to establish. This difficulty comes from two facts: i) the one-dimensional quadrupolar spectra become too complex if there is more than one sodium site per unit cell; ii) for the two-dimensional nutation spectra it is too time-consuming to examine the details of the change in the spectra with temperature by using spectral simulation. Therefore it is almost impossible at the present stage to shed more light on the mechanism of the site exchange as well as possible long range hopping of the ions.

However, it is true that the activation energy for site exchange observed by NMR differs appreciably from that for ionic conduction in the case of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_12$ as described in Section 1. Such a discrepancy in the...
activation energies has also been recognized in some
other superionic conductive materials [8, 26–28]. Al­
though several theoretical attempts have been made
to interpret the above discrepancy by assuming differ­
ent relaxation mechanisms for NMR and electrical
conduction [29–32], these models are still not com­
prehensive.

In order to examine what kind of motion of the
sodium ions takes place in the NASICON we carried
out molecular dynamics simulation on NaZr2P2O12,
Na2Zr2Si2P2O12, and the rhombohedral structure of
Na2Sc2P3O12.

The MD simulation was performed at constant
temperature and constant pressure using a program
code based on the usual Verlet algorithm [33]. The
electrostatic interaction between ions with the formal
charges (+1, +4, +3, +4, +5, and —2 for Na, Zr, Sc,
Si, P, and O, respectively) was calculated by the Ewald
method. The repulsive interaction between two
atomic species i and j was represented by a modified
Born-Mayer type atomic pair potential function [34]

\[ u_{ij} = f_0 (b_i + b_j) \exp \left\{ \frac{(a_i + a_j - r_{ij})}{(b_i + b_j)} \right\}, \]

where \( r_{ij} \) is the interatomic distance and \( a_i, b_i \) and so
on are the potential parameters defined for the atom i.
The constant \( f_0 \) denotes a standard force with units of
kcal mol
\(^{-1}\) \( \text{Å}^{-1}\). The potential parameters \( a \) and \( b \) for
Na
\(^{+}\), Si
\(^{4+}\), P
\(^{5+}\), and O
\(^{2-}\) were taken from [35], and
those for Zr
\(^{4+}\) and Sc
\(^{3+}\) were optimized so as to
reproduce and to stabilize the actual crystal structure
at room temperature (see Table 3). The calculation
started from the crystal structure at room temperature
and was carried out with a time step of 2.5 fs.

It was confirmed for NaZr2P2O12 that its actual
structure [2] is stable, the motion of the ions is local­
ized, and there is nearly no chance for sodium ions to
exchange their positions. These results of the simu­
lation are consistent with the fact that this compound
is a poor conductor. Next, we simulated the structure of
Na2Zr2Si2PO12 [2] with a unit cell in which one-third
of the general, interstitial sodium positions is vacant.
We found, however, that the crystal lattice is unstable
and decomposes at early stages of the simulation.

We conducted a rigorous molecular dynamics simu­
lation on the trigonal phase [10] of Na2Sc2P3O12 at
300 and 1500 K. It was then confirmed that the set of
potential parameters listed in Table 3 reproduces well
the crystal structure of the material at room tempera­
ture: All kinds of ions undergo local vibrations around their equilibrium positions at 300 K. Neither

<table>
<thead>
<tr>
<th>Atom</th>
<th>Charge</th>
<th>( a [\text{Å}] )</th>
<th>( b [\text{Å}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>+1</td>
<td>1.432</td>
<td>0.082</td>
</tr>
<tr>
<td>Si</td>
<td>+4</td>
<td>1.002</td>
<td>0.031</td>
</tr>
<tr>
<td>P</td>
<td>+5</td>
<td>0.887</td>
<td>0.019</td>
</tr>
<tr>
<td>Zr</td>
<td>+4</td>
<td>1.557</td>
<td>0.132</td>
</tr>
<tr>
<td>Sc</td>
<td>+3</td>
<td>1.430</td>
<td>0.086</td>
</tr>
<tr>
<td>O</td>
<td>—2</td>
<td>1.853</td>
<td>0.168</td>
</tr>
</tbody>
</table>

site exchange nor hopping transport of Na
\(^{+}\) was

detected at this temperature, and no tendency of the
triclinic phase to transform into the more stable mon­
oclinic structure was observed.

In Fig. 4 the gross feature of the ionic dynamics at
1500 K is shown by atomic trajectories viewed along
the trigonal c-axis. The cell in this figure corresponds
to one-fourth of the rectangular unit cell generated
from the original trigonal unit cell by the coordinate
transformation. The atomic trajectories were obtained
by tracing the ionic movement for 3 ps after a waiting
time of 75 ps. It can be seen that the positional fluctu­
ation of the ions is very large at 1500 K and that site
exchange of the Na
\(^{+}\) between the Na(1) and the Na(2)
sites occurs.

The exchange process proceeds as follows. The Na
\(^{+}\) at the Na(1) site on the trigonal axis attempts to move
into one of the unoccupied Na(2) sites. In this figure
three successful attempts are indicated by arrows.
However, close examination of the whole result of the
simulation over 50 ps indicates that several attempts
for a particular Na(1) to reach a stable vacant Na(2)
site are unsuccessful; the Na
\(^{+}\) stays for a moment in
an intermediate area and then moves back to the origi­
nal Na(1) site. It takes about 0.2 ps for this unsuc­
sessful process. The successful jump from a particu­
lar Na(1) to an Na(2) site occurs only once or twice in
50 ps period. It takes about 0.15 ps for this process.
In less than 1 ps after a successful jump from a Na(1) site
to a Na(2) site, the Na
\(^{+}\) at the Na(2) site moves to the
vacant Na(1) site. It takes about 0.1 ps for this jump.
Any other type of exchange of Na
\(^{+}\), e.g., site exchange
between two Na(2) sites never occurs, as was already
suggested from the point of view of structural charac­
teristics [2, 3].

The results of the simulation suggest that there is a
metastable region on the exchange path from Na(1) to
Na(2) sites, and this region traps the ion for a short
time. This situation may schematically be represented
Fig. 4. Trajectories of the atoms in trigonal Na$_3$Sc$_2$P$_3$O$_{12}$ at 1500 K viewed along the trigonal c-axis. The vertical and the horizontal axes correspond to the a- and the $b^*$-axis, respectively. Ions contained in the region, $a \times (b^*/2) \times (c/2)$, are shown. The trajectories are traced for 3 ps after a waiting time of 75 ps.

by the potential energy curve shown in Figure 5. A sodium ion reaches a potential minimum in an intermediate region by overcoming a low potential barrier, but it has to overcome another higher barrier in order to achieve a jump into the Na(2) site.

The line shape and the longitudinal relaxation time of the $^{23}$Na resonance may be affected significantly by the local jump between Na(1) site and the metastable site by overcoming the lower barrier. On the other hand, the sodium ion has to overcome the higher potential barrier in order to realize the long-range transport and to contribute to the electric conductivity. This model may therefore interpret the appreciable difference between the activation energies measured by NMR and the conductometric method.

Conclusion and Prospect

The $^{23}$Na and $^{45}$Sc nuclear quadrupole coupling constants and the asymmetry parameters in several NASICON-type compounds were determined by 2D nutation NMR. This technique was found to be effective for examining the quadrupole interaction in these complex materials. Especially, in Na$_3$Zr$_2$Si$_2$PO$_{12}$, the local site exchange of sodium ions was evidenced and the exchange rate and the activation energy for this process were estimated.

Molecular dynamics simulation was applied to Na$_3$Sc$_2$P$_3$O$_{12}$. It suggests that there is a potential minimum for Na$^+$ on the pathway from the Na(1) site to Na(2) site. Existence of such a metastable region
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Fig. 5. Probable potential function for jumps of the sodium ions in Na$_3$Sc$_2$P$_3$O$_{12}$, elucidated by molecular dynamics simulation, suggesting that there is a metastable region on the pathway from the Na(1) site to the Na(2) site.

can explain the discrepancy in the activation energies deduced by NMR and conductivity measurements.

Many problems arose in the course of our works; 2D nutation spectra can hardly provide reliable quadrupole parameters when two or more crystallographically inequivalent sites for the probing nucleus exist. It is difficult to give a reasonable interpretation of the very small quadrupole coupling constants in the hafnium NASICON and to interpret the rather drastic change in the total line width at the phase transition in the indium NASICON; the conductivity does not vary appreciably at the phase change.

For other NASICONS, the evaluation of the NMR data in connection with the structural characteristics and superionic properties has not been done. In order to clarify this point we attempted to calculate the electric field gradients (EFG) in Zr- and Sc-NASICONs by the use of a computer program which has been recognized to be suitable for some ionic materials [36–38], but the calculation with the formal charges given in Table 3 led to EFGs about ten times larger than observed values. A close examination of this point is necessary. It has frequently been reported that the structure and physical properties of the NASICON family are strongly dependent on the condition of the preparation of the samples. We have often experienced such situations; very careful and thorough characterization of the samples is necessary to treat the NASICON-type materials.