FAST ION TRANSPORT IN THE NASICON ANALOG $Na_3Sc_2(PO_4)_3$: STRUCTURE AND CONDUCTIVITY*

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The room temperature modification of stoichiometric NASICON(Sc) is monoclinic Cc. At 64°C there is a first order transition to a normal-conducting rhombohedral form $R\bar{3}c$. Na(1) sites are fully occupied whereas Na(2) sites are partially occupied. At 167°C there is a transition to a superionic phase, but the structure remains rhombohedral $R\bar{3}c$. Vacancies are now shared equally by Na(1) and Na(2) sites. Fast Na-ion motion in stoichiometric $Na_3Sc_2(PO_4)_3$ arises from vacancy motion in a "dogleg" path between Na(1) and Na(2) sites.
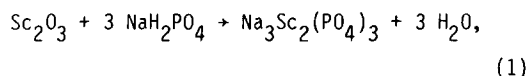
I. INTRODUCTION

The framework compound $Na_3Zr_2Si_2PO_{12}$ (named NASICON) is an excellent fast sodium ion conductor [1]. However, it cannot be grown as a single crystal; and in our laboratory and elsewhere [2] it has been shown that it cannot be prepared as a pure monophase. The presumed scandium analog $Na_3Sc_2(PO_4)_3$ [labelled here as NASICON(Sc)] can be prepared as a stoichiometric single crystal [3] and has come under considerable study. It is an excellent solid electrolyte in its own right. However, it has its own unique crystal chemistry which is not the same as the $Na_3Zr_2SiPO_{12}$ parent compound [4,5]. Efforts have been made to correlate its structural phase changes and its ionic conductivity [4,6,7,8]. However, considerable confusion exists in the literature as to the structure of the stable polymorphic modifications. At room temperature $Na_3Sc_2P_3O_{12}$ is variously described as monoclinic $C2/c$ [3], monoclinic Cc [5] and rhombohedral $R\bar{3}c$ [8,9]. The "intrinsic" structure has even been stated as being dependent on whether the sample is a sintered powder, a powdered crystal [8] or a single crystal [9]. There is general agreement that at least one high-temperature phase is rhombohedral [8, 9, 10, but not 3].

In this paper we shall present neutron and x-ray diffraction data that confirm the nature of the transition from an ordinary-conducting, high temperature phase to a still higher temperature, superionic-conducting phase [11]. 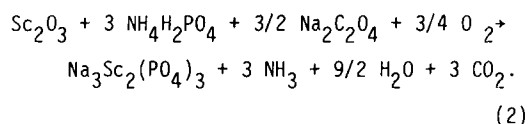We shall also discuss the unresolved discrepancies associated with the lower temperature conducting phases and present appropriate optical, X-ray and neutron diffraction data. These data will be correlated with ionic conductivity measurements as a function of temperature.

II. EXPERIMENTAL

Polycrystalline $Na_3Sc_2(PO_4)_3$ powder was prepared by the solid state reaction

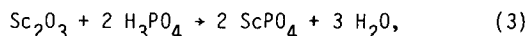$$Sc_2O_3 + 3\ NaH_2PO_4 \rightarrow Na_3Sc_2(PO_4)_3 + 3\ H_2O, \tag{1}$$

or by the solid state reaction

$$Sc_2O_3 + 3\ NH_4H_2PO_4 + 3/2\ Na_2C_2O_4 + 3/4\ O_2 \rightarrow$$
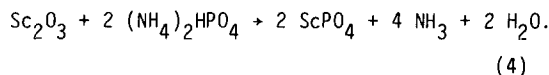$$Na_3Sc_2(PO_4)_3 + 3\ NH_3 + 9/2\ H_2O + 3\ CO_2. \tag{2}$$

The details of processing into polycrystalline ceramic pellets are given in Fig. 1.

Single crystals were grown by first synthesizing $ScPO_4$ according to

$$Sc_2O_3 + 2\ H_3PO_4 \rightarrow 2\ ScPO_4 + 3\ H_2O, \tag{3}$$

or

$$Sc_2O_3 + 2\ (NH_4)_2HPO_4 \rightarrow 2\ ScPO_4 + 4\ NH_3 + 2\ H_2O. \tag{4}$$
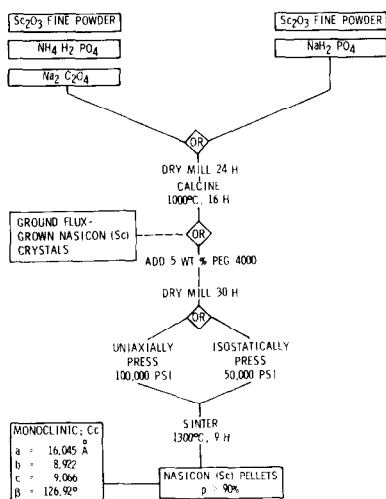
Fig. 1. Preparation of ceramic pellets of stoichiometric NASICON(Sc), $Na_3Sc_2(PO_4)_3$.

Then, fluxed melts with $Na_4P_2O_7$ were prepared for unseeded [4] or seeded crystal growth by the classic Kyropolous method:

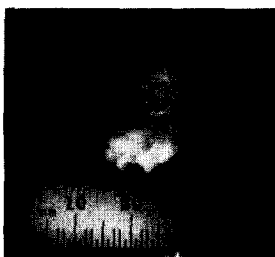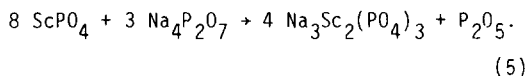$$8 ScPO_4 + 3 Na_4P_2O_7 \rightarrow 4 Na_3Sc_2(PO_4)_3 + P_2O_5.$$

$$(5)$$

Fig. 2. A rosette of NASICON(Sc) crystals grown from a $ScPo_4:4Na_4P_2O_7$ molten flux by the Kyropolous method.

A cluster of Kyropolous-grown crystals is shown in Fig. 2. Extensive primary and secondary twinning is observed [4] in the virgin crystals, or is readily introduced upon handling the crystals or cycling through the 64°C transition. This prevalent domain structure is responsible for several inconsistencies among the single-crystal results reported in the literature and is the reason why all the present data are obtained using powder diffraction procedures. Figure 3 is a photomacrograph of a 0.2-mm diameter

crystal viewed along the unique $\vec{b}$ monoclinic axis. The virgin, untwinned crystal was mounted on a glass fiber for x-ray analysis and subsequently developed additional (spurious) reflections upon cycling to 100°C and back to room temperature. The twin banding is evident and was introduced during the phase transformation from the monoclinic polymorph.
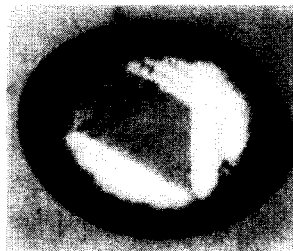

Fig. 3. Polarized-light photomacrograph of transformation-induced twinning in a single crystal of $Na_3Sc_2(PO_4)_3$. The β-angle is seen in this view along the $\vec{b}$ axis of the monoclinic, room temperature modification.

X-ray diffraction data were obtained as a function of temperature on a General Electric Corp. XRD diffractometer from 20°C to 200°C. Phase changes were conveniently monitored by following the intensity changes of single Bragg reflections as a function of slowly varying temperature.

Neutron powder diffraction patterns were collected at 20°C, 55°C, 100°C and 225°C on the five detector, high-resolution, powder diffractometer at the National Bureau of Standards research reactor. The patterns covered a 2θ range from 10° to 122° in five overlapping segments, with a step size of 0.05° and a wavelength of 1.5423 Å. The data were analyzed by the Rietveld [12] method modified to include the background intensity in the model and to simplify the application of constraints.

Optical microscopy was carried out on a Zeiss Universal microscope equipped with an ultra-precision (±0.01°C) warm stage. Above 70°C, the standard Kofler hot stage was used. Observations were made in transmitted and reflected polarized light and by Nomarski differential interference contrast.

Heat capacities were measured [6] on a Perkin Elmer DSC-2. Differential thermal analyses were carried out [7] on a Perkin Elmer DTA 1700. Procedures for measuring dielectric properties [6] and ionic conductivity [7] have been described elsewhere.

Chemical analyses for sodium and scandium were by atomic absorption spectrophotometry.

Phosphorus was determined colorimetrically by developing the hetero poly-blue complex with molybdate.

III. RESULTS AND CONCLUSIONS

A. The Room-Temperature Crystal System of Stoichiometric NASICON(Sc).

Detailed structure determinations are not necessary to resolve one aspect of the confusion surrounding the room-temperature polymorphic modification of $Na_3Sc_2(PO_4)_3$. Polarized-light microscopy of NASICON(Sc) mounts in Arachlor immediately reveals that the material is biaxial at 20°C. Upon careful warming of the sample, it transforms at 64°C with a colorful and delightful twinkling under crossed polars. With a suitably oriented grain, a uniaxial interference figure is observed conoscopically above 64°C. There is a hysteresis in the transform that varies from 1°C to 2°C. Therefore, we conclude that stoichiometric $Na_3Sc_2(PO_4)_3$ undergoes a first-order phase change from biaxial to uniaxial at 64°C. This transformation is observed in virgin single crystals (eqn. (5)), in crushed crystals, and in powders synthesized by the solid state reactions eqns. (1) or (2).

Between 15°C and 64°C, there is no observable optical change, and between 64°C and 225°C, the system remains uniaxial.

B. Single Crystal Data vs. Powder Data for Stoichiometric NASICON(Sc).

Crystals grown from a molten pyrophosphate flux, powders synthesized by solid-state reactions and sintered ceramic pellets of $Na_3Sc_2(PO_4)_3$ are routinely scanned with the petrographic microscope before making any experimental measurements. For pure, stoichiometric NASICON(Sc), the biaxial → uniaxial transformation at 64°C is always observed. Chemical analyses for the flux-grown crystals typical of the data shown in Fig. 4 are Na: calc. 15.5 wt. %, anal. 15.1; Sc: calc. 20.3 wt. %, anal. 20.0; P: 20.9 wt. %, anal. 20.8. The estimated errors are approximately ± 0.3 wt. %.

We have made measurements of the loss tangent on virgin crystals, crystals ground into powder, and ceramic pellets derived from powdered crystals [4,6]. The essential features, including the dielectric anomaly at 64°C, are sample independent. Heat capacity measurements [6] on these same specimens reveal that they all have thermal anomalies at 64°C (with hysteresis) and at 167°C (without hysteresis). Differential thermal analyses and complex admittance measurements have been made on these crystalline materials and on ceramic pellets derived either from solid-state-synthesized powders [7] or from ground and pelletized crystals. Ceramic bodies have

been formed either by uniaxial pressing, isostatic pressing, or hot pressing (see Fig. 1) followed by sintering. The DTA data and the ionic conductivity data show the same essential features with singularities at 64°C and 167°C.
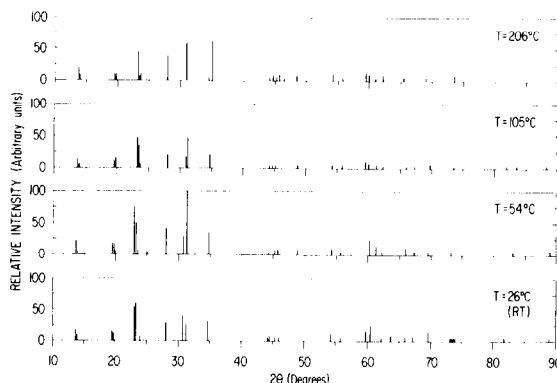

Fig. 4. X-ray diffraction of flux-grown powdered crystals of NASICON(Sc), $Na_3Sc_2(PO_4)_3$. Overlapping reflections with Al, Be, or the Si internal standard are omitted. Cu Kα.

In several instances, crystals grown onto a platinum cold finger from a seeded molten flux (Fig. 2) exhibit none of the anomalies described above and display uniaxial interference figures at room temperature. These non-equilibrium growth conditions can lead to departures from the stoichiometric composition $Na_3Sc_2P_3O_{12}$. However, we have not done enough chemical analyses on these few specimens to verify this supposition. The possible stabilization of a hexagonal polymorph at room temperature will be discussed below.

C. The Room-Temperature Structure of Stoichiometric NASICON(Sc), $Na_3Sc_2(PO_4)_3$.

At 20°C, the neutron diffraction data were refined according to the monoclinic lattice parameters first reported by Efremov and Kalinin [5] and later by Hong [3]. Refining only the scale factor, the cell constants, and the background in a model based upon space group Cc, we obtain the parameters listed in Table I, column 1. These values compare well with those of Efremov and Kalinin, predict the observed peak positions exactly, and may be considered to be quite accurate. They differ markedly from the values reported by Hong listed in column 3. A possible explanation follows.

It has been observed [13] that C-face-centered monoclinic lattices are very easily confused with rhombohedral lattices. Analysis of our room temperature patterns, derived from either X-ray or neutron diffraction, indicates that

stoichiometric $Na_3Sc_2(PO_4)_3$ is indeed mono-
clinic. For example, a peak at a 2θ of about
27.5°, which would be a well-resolved, 024
single peak as referred to hexagonal axes,
splits into a doublet, 400 and $\overline{2}22$, for the
monoclinic lattice. This reflection is
observed to be both broadened and skewed, in
good agreement with the predicted separation
of 0.23°. This is consistent with [5] and the
space group assignment Cc.

TABLE I. ROOM TEMPERATURE STRUCTURE OF NASICON(Sc), $Na_3Sc_2(PO_4)_3$.

Space Group Monoclinic Parameters	Cc at 20°C (Experimental)	Cc at 20°C (Efremov & Kalinin)	C2/c at 20°C (Hong)	$R\bar{3}c^{\dagger}$ at 20°C (Extrapolated)	$R\bar{3}c^{*}$ at 100°C (Experimental)
a_m (Å)	16.045	16.100	15.461	15.462	15.462
b_m (Å)	8.922	8.928	8.913	8.927	8.927
c_m (Å)	9.066	9.109	9.016	9.032	9.064
β (°)	126.92	127.15	124.80	124.80	124.66

*For R3c at 100°C: a_h = 8.9273(2) Å, c_h = 22.3668(6) Å.

$†c_h$ = 22.251 Å at 20°C (linear extrapolation).

$a_m = \sqrt{3}\, a_h$. $b_m = a_h$. $c_m = 1/3(3a_h^2 + c_h^2)^{1/2}$.

$\beta = 180° - \arctan(c_h/\sqrt{3}\, a_h)$.

Above 64°C, we observe a rhombohedral modifi-
cation of NASICON(Sc), as will be discussed in
section III-D of this paper. The actual $R\bar{3}c$
parameters are given in the footnote to
Table I. Equivalent monoclinic parameters can
be calculated and are listed in column 5. The
relation between the rhombohedral and the
equivalent monoclinic unit cell is given in
the footnote (also, see Ref. [14]). If we
assume that this rhombohedral form is somehow
stabilized at room temperature, we obtain at
20°C the equivalent monoclinic parameters
listed in column 4. These compare well with
those of Hong [3]. It is reasonable to infer
that Hong's specimens were rhombohedral at
room temperature. A $R\bar{3}c$ space group at 20°C
has been reported by others [8,9] and associ-
ated with deviations from the stoichiometric
composition $Na_3Sc_2P_3O_{12}$. Non-stoichiometric
NASICON(Sc) may be rhombohedral at room tem-
perature or there may be an impurity-induced
stabilization of a C2/c space group as sug-
gested elsewhere [15].

D.   The Polymorphic Modifications of
     Stoichiometric NASICON(Sc), $Na_3Sc_2(PO_4)_3$.

There are at least three or, possibly, four
polymorphic modifications of pure, stoichio-
metric $Na_3Sc_2(PO_4)_3$ [11]. Figure 4 presents
X-ray data for powdered crystals well away
from the observed transition temperatures.

At room temperature, the refined neutron
diffraction data confirm the Cc space group
reported by Efremov and Kalinin [5] but with
a = 16.0449(24), b = 8.9225(15),
c = 9.0656(13)Å, β = 126.918°(21),
$R_{weighted\ pattern}$ = 17.5%, and

$R_{expected}$ = 7%. We shall call this polymorph
A.

Between 25°C and 64°C, a second polymorph B
appears as indicated in Fig. 1. The structure
is monoclinic but has not yet been refined.
The A ↔ B transition is clearly dependent on
sample stoichiometry and purity [4,11].

At 64°C, a third polymorph C appears. It is
rhombohedral $R\bar{3}c$. Using hexagonal axes,
a = 8.9273(2), c = 22.3668 Å, R_{wp} = 6.28%, and
R_e = 3.83% at 100°C. B ↔ C is accompanied by
a tenfold increase in ionic conductivity but
only a small decrease in activation energy
from 0.56 eV to 0.45 eV. A, B and C are
ordinary ionic conductors.

At 166°C, the high temperature polymorph D
appears. It is the superionic phase of
NASICON(Sc). It, too, is rhombohedral $R\bar{3}c$
with a = 8.9274(1), c = 22.5493(6)Å,
R_{wp} = 5.81% and R_e = 3.87% at 225°C. The
activation energy for Na-ion motion in phase D
is only 0.15 to 0.20 eV.

From room temperature to 100°C, our structural
results are in general agreement with the
Russian crystallographers [5, 15, 10]. The
anomalies in our Cp, DTA, tan δ and ionic
conductivity data at 64°C and 167°C are in
agreement with the refined polymorphic
modifications A, C and D.

E.   The Relation Between Structure and Fast
     Ionic Transport in Stoichiometric
     NASICON(Sc).

Figure 5 presents recent, detailed
measurements of the temperature dependence of
the conductivity of stoichiometric
NASICON(Sc). Polymorph A (and possibly
polymorph B) is stable from room temperature
to 64°C. The activation energy associated
with Na-ion motion in this monoclinic struc-
ture is 0.57 eV as given by the Arrhenius
plot.

At 64°C, the monoclinic distortion is removed,
the ionic conductivity increases by an order
of magnitude, but the activation energy
remains relatively high. The hysteresis in
the conductivity associated with this first-
order, monoclinic ↔ rhombohedral phase
transition is clearly indicated. The same
hystersis has been observed while monitoring
the (400, $\overline{2}22$) ↔ 024 reflections by X-ray
diffraction.

At 167°C, there is a slight increase in the
ionic conductivity on going from the normal-
conducting phase C to the high-temperature
superionic phase D. The salient feature at
167°C is the decrease in activation energy
from 0.45 eV to 0.20 eV. Careful measurements
reveal no hysteresis in the conductivity
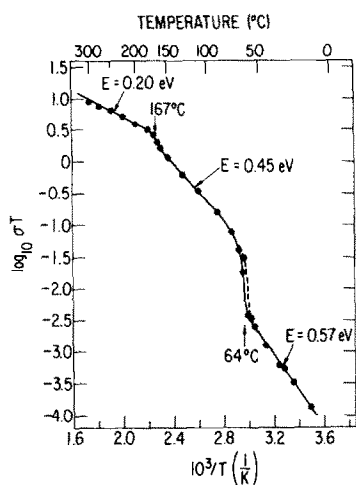within experimental error.

Fig. 5. Temperature dependence of the conductivity of stoichiometric NASICON(Sc). Solid line for rising or falling temperature except in the region of the dashed curve which is for falling temperature only.

At 100°C (phase C) and at 225°C (phase D) the neutron diffraction patterns were refined in space group R$\bar{3}$c. The cell constants and refined parameters are presented in Table II. Thermal expansion between 100°C and 225°C is entirely along the $\vec{c}$ axis. At both temperatures the Na-ions are distributed among sites 6b Na(1) and 18e Na(2) giving 24 sites to accommodate only 18 atoms. As indicated in Table III, full occupancy of the Na(1) site corresponds to 1/6, and full occupancy of the

Na(2) site corresponds to 1/2. Thus, all of the vacancies are on the Na(2) sites below 167°C, but both sites contain 0.25 vacancies above 167°C.

In addition to the crucial change in Na-site occupation associated with the C ↔ D transition to the superionic state, Table II demonstrates the highly anisotropic character of the thermal ellipsoids associated with the Na sites. At both temperatures, the ellipsoid for the Na(1) site is flattened, with large amplitudes perpendicular to the $\vec{c}$ axis and a small amplitude parallel to it. Conversely, the Na(2) site has a large amplitude parallel to the $\vec{c}$ axis and small amplitudes perpendicular to it. Figure 6 is a picture of the rhombohedral, high-temperature structure.

All of these observations are consistent with a model for the ionic conduction that involves Na-ion motion parallel to the $\vec{c}$ axis through channels passing through the Na(2)sites--and perpendicular to the $\vec{c}$ axis through channels passing through the Na(1) site. Sites of the same type do not communicate with each other, but each site of one type communicates with two or more sites of the other type. The ions can, therefore, move in any direction in a dogleg fashion along paths that involve both types of channels. The activation energy is high below 167°C because of the need to create vacancies on the Na(1) sites for conduction to occur. Above 167°C there are sufficient vacancies on both sites for there to be relatively free movement from one to another. The resistivity dependence on temperature at the C ↔ D transition has features of an order-disorder transition. A future publication will analyze the transition to the superionic state on that basis.

TABLE II. Refined Atomic Parameters for NASICON(Sc), Na$_3$Sc$_2$(PO$_4$)$_3$, at 100°C and 225°C. Space group = R$\bar{3}$c .
At 100°C a = 8.9273(2), c = 22.3668(6)Å
At 225°C a = 8.9274(1), c = 22.5493(6)Å

Atom	Coordinates			Occupation	Anisotropic Thermal Parameters (Å²)					
	x/a	y/b	z/c		B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
100°C. Phase C. Ordinary Na⁺ conductor.										
Na(1)	0.0000	0.0000	0.0000	0.1647(49)	26.2(1.2)	26.2(1.2)	1.9(1.0)	13.1(6)	0.00	0.00
Na(2)	0.6399(9)	0.0000	0.2500	0.3353(49)	1.0(3)	1.3(4)	12.5(1.0)	0.7(2)	1.4(2)	2.8(5)
Sc	0.0000	0.0000	0.1490(1)		0.73(4)	0.73(4)	1.49(8)	0.36(2)	0.00	0.00
P	0.2929(3)	0.0000	0.2500		0.82(12)	0.52(14)	1.51(16)	-0.2(2)	-0.1(1)	0.63(10)
O(1)	0.1857(3)	-0.0250(3)	0.1948(1)		1.96(12)	2.06(12)	3.78(14)	1.28(11)	-1.55(11)	0.63(10)
O(2)	0.3138(3)	-0.1595(2)	0.2561(1)		1.37(12)	0.45(9)	2.41(12)	0.59(9)	-0.39(10)	0.40(9)
225°C. Phase D. Superionic Na⁺ conductor.										
Na(1)	0.0000	0.0000	0.0000	0.1332(42)	40.7(2.0)	40.7(2.0)	-0.11(83)	20.4(1.0)	0.00	0.00
Na(2)	0.6356(8)	0.0000	0.2500	0.3668(42)	0.89(27)	1.07(36)	20.6(1)	0.53(18)	3.09(21)	6.18(43)
Sc	0.0000	0.0000	0.1494(1)		1.12(4)	1.12(4)	1.50(7)	0.56(2)	0.00	0.00
P	0.2919(3)	0.0000	0.2500		0.47(10)	1.22(12)	1.26(15)	0.61(6)	-0.11(5)	-0.22(10)
O(1)	0.1827(3)	-0.0306(3)	0.1955(1)		2.55(12)	1.90(11)	3.14(15)	1.51(6)	-1.49(11)	-0.19(9)
O(2)	0.3118(3)	-0.1594(2)	0.2575(1)		1.58(10)	0.48(5)	2.49(11)	0.43(8)	-0.59(9)	0.34(8)

Anisotropic thermal parameters are the coefficients of the temperature factor expression

exp [-(1/4)(h²a*²B$_{11}$ + k²b*²B$_{22}$ + l²c*²B$_{33}$ + 2hka*b*B$_{12}$ + 2hla*c*B$_{13}$ + 2klb*c*B$_{23}$)]

The estimated standard deviations of the least significant digits of refined parameters are given in parentheses.

TABLE III. VACANCY DISTRIBUTION IN NASICON(Sc), Na$_3$Sc$_2$(PO$_4$)$_3$.

	Sites	Atom	Number of Atoms/ Unit Cell	Observed Occupation	Full Occupation	Total Vacancies	Vacancies Per Site	Activation Energy for Na$^+$ Motion (eV)
Normal Phase C (100°C)*	6b	Na(1)	18	0.16	0.17	0	0.00	0.45
	18e	Na(2)	•	0.34	0.50	6	0.33	
Superionic Phase D (225°C)**	6b	Na(1)	18	0.13	0.17	1.5	0.25	0.20
	18e	Na(2)		0.37	0.50	4.5	0.25	

*a = 8.9273 Å, c = 22.3668 Å
**a = 8.9273 Å, c = 22.5483 Å

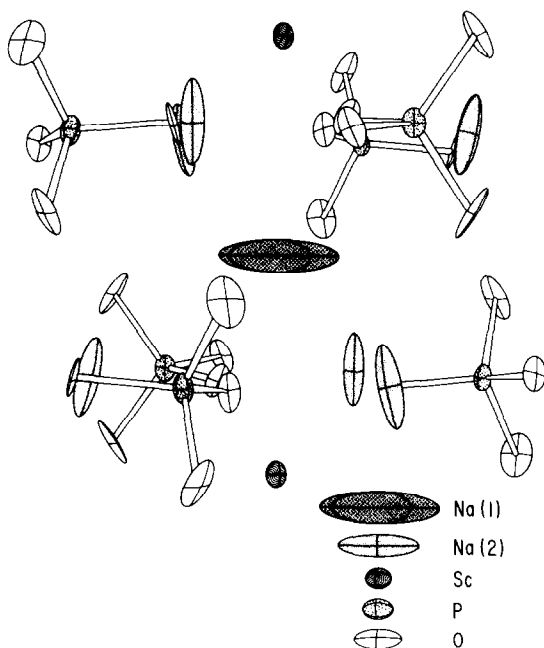These conclusions are in agreement with the optical, thermal and conductivity data.

Na(1)
Na(2)
Sc
P
O

Fig. 6   Structure of NASICON(Sc), Na$_3$Sc$_2$(PO$_4$)$_3$, in both high temperature R$\bar{3}$c phases C and D. Ordinary phase C is stable from 64 to 167°C. Superionic phase D is stable above 167°C. Viewed perpendicular to the c axis.

IV.   SUMMARY

The room temperature modification of stoichiometric NASICON(Sc) is monoclinic Cc.

At 64°C there is a first order transition to a normal-conducting rhombohedral form R$\bar{3}$c. Na(1) sites are fully occupied, whereas Na(2) sites are partially occupied.

At 167°C there is a transition to a superionic phase, but the structure remains rhombohedral R$\bar{3}$c. Vacancies are now shared equally by Na(1) and Na(2) sites.

Fast Na-ion motion in stoichiometric Na$_3$Sc$_2$(PO$_4$)$_3$ arises from vacancy motion in a dogleg path between Na(1) and Na(2) sites.

V.   REFERENCES

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