

Phase Equilibrium Study of the System $\text{NaV}_2\text{O}_5\text{--V}_2\text{O}_3\text{--V}_2\text{O}_5$ at 923 KY. KANKE,¹ E. TAKAYAMA-MUROMACHI, K. KATO,
AND Y. MATSUI*National Institute for Research in Inorganic Materials, 1-1 Namiki,
Tsukuba, Ibaraki, 305 Japan*

Received April 23, 1990; in revised form June 28, 1990

The phase diagram of the system $\text{NaV}_2\text{O}_5\text{--V}_2\text{O}_3\text{--V}_2\text{O}_5$ at 923 K was established. Two new phases, $\delta\text{-Na}_x\text{V}_2\text{O}_5$ ($0.55 \leq x \leq 0.57$) and $\text{Na}_x\text{V}_{12}\text{O}_{29}$ ($0.55 \leq x \leq 0.65$), were found. The $\delta\text{-Na}_x\text{V}_2\text{O}_5$ is hygroscopic and isostructural with $\delta\text{-Ag}_x\text{V}_2\text{O}_5$. The $\text{Na}_x\text{V}_{12}\text{O}_{29}$ is a member of a homologous series of compounds $M_x\text{V}_{6n}\text{O}_{15n-m}$ found also for $M = \text{Li}$ or Cu . The dc conductivity of a single crystal of $\text{NaV}_6\text{O}_{11}$ was measured at 5–298 K. © 1990 Academic Press, Inc.

Introduction

Various types of bronze phases have been found in $M_x\text{V}_2\text{O}_5$ (M : alkaline metals) systems. When $M = \text{Na}$, five bronze phases have been reported, α ($0 < x \leq 0.02$), β ($0.22 \leq x \leq 0.40$), α' ($0.70 \leq x \leq 1.00$), η ($1.28 \leq x \leq 1.45$), and χ ($1.68 \leq x \leq 1.82$) (1). The α - and α' -phases have nearly the same V–O frameworks as in the vanadium pentoxide V_2O_5 but have different space groups (α -phase: $Pm\bar{m}n$, α' -phase: $P2_1mn$) caused by framework distortion and slightly different Na positions (2, 3). In the β -phase (4), a major structural rearrangement of the V–O framework occurs; V–O layers, having a composition of V_2O_5 , are linked with each other by sharing O atoms and Na atoms are located in a tunnel between the layers. The structures on the η - and χ -phases are still unknown.

In the previous studies (5, 6), we investi-

gated the systems $M\text{V}_2\text{O}_5\text{--V}_2\text{O}_4\text{--V}_2\text{O}_5$ ($M = \text{Li}, \text{Cu}$) and found a new homologous series of bronze phases, $M_x\text{V}_{6n}\text{O}_{15n-m}$ (7), in which the case of $n = 1, m = 0$ corresponds to the $\beta\text{-}M_x\text{V}_2\text{O}_5$ phase described above. Besides it, the compounds with $n = 3, m = 1$ ($M_x\text{V}_9\text{O}_{22}$) and those with $n = 2, m = 1$ ($M_x\text{V}_{12}\text{O}_{29}$) have been obtained for both $M = \text{Li}$ and $M = \text{Cu}$. When $M = \text{Li}$, however, two different phases are present in each $\text{Li}_x\text{V}_{6n}\text{O}_{15n-m}$ system: the phase with lower Li content is called the β -phase ($\beta\text{-Li}_x\text{V}_{6n}\text{O}_{15n-m}$) and that with higher Li content is termed β' -phase. The β - and β' -phases have essentially the same structure with slightly different lattice constants and the phase separation is believed to be caused by the different Li positions (5). The overall phase diagram of the Li-containing system resembles very closely that of the Cu-containing system, probably due to the similar ionic radii of Li^+ and Cu^+ . Since the ionic radius of Na^+ is much larger, different phase relationships are expected for the Na–V–O system.

¹ To whom correspondence should be addressed.

In particular, it seems interesting to elucidate whether the $M_x\text{V}_9\text{O}_{22}$ - or $M_x\text{V}_{12}\text{O}_{29}$ -type phases are stable for a larger M ion.

Pouchard *et al.* investigated the $\text{Na}_2\text{V}_2\text{O}_5$ - V_2O_4 system (i.e., $\text{Na}_{2y}\text{V}_2\text{O}_{4+y}$; $0 \leq y \leq 1.0$) at 873 K (8) and reported three phases, A ($0.17 \leq y \leq 0.25$), B ($0.42 \leq y \leq 0.44$) and C ($0.67 \leq y \leq 0.71$). They also prepared several samples between the α' - NaV_2O_5 and the phase A and concluded that there was a continuous solid solution in which the α' and A phases were end members. They claimed similar solid solutions existed between the η - $\text{Na}_x\text{V}_2\text{O}_5$ and the phase B and between the χ - $\text{Na}_x\text{V}_2\text{O}_5$ and phase C.

We investigated the NaV_2O_5 - V_2O_3 - V_2O_5 system at 923 K and found two new phases, δ - $\text{Na}_x\text{V}_2\text{O}_5$ ($0.55 \leq x \leq 0.57$) and $\text{Na}_x\text{V}_{12}\text{O}_{29}$ ($0.55 \leq x \leq 0.65$). The solid solutions reported by Pouchard *et al.* (8) were not found.

$\text{NaV}_6\text{O}_{11}$ synthesized originally by electrolytic reduction (9) was found to exist stably at 923 K in the present work. It showed metallic conductivities at 5 ~ 80 K.

Experimental

V_2O_4 was prepared by heating an equimolar mixture of V_2O_5 (99.9%) and V_2O_3 in a sealed silica tube at 1273 K for 3 days. The V_2O_3 had been obtained by reducing the V_2O_5 in hydrogen at 1073 K. NaVO_3 was prepared by heating an equimolar mixture of Na_2CO_3 (99.9%) and V_2O_5 at 823 K for 7 days with several intermediate grindings.

We divided the NaV_2O_5 - V_2O_3 - V_2O_5 system into two subsystems, NaV_2O_5 - V_2O_4 - V_2O_5 and NaV_2O_5 - V_2O_3 - V_2O_4 . V_2O_5 , V_2O_4 , and NaVO_3 were used as starting reagents for the former region, while for the latter V_2O_3 was used instead of V_2O_4 . The starting reagents were mixed in an agate mortar with ethanol (or acetone) but the samples including V_2O_3 were mixed without using ethanol (or acetone), because it

seemed rather difficult to dry V_2O_3 completely after being soaked with ethanol (or acetone). About 1.5 g of the mixture was placed into a silica tube and dried in nitrogen gas at 423 K for 30 min and sealed after evacuation. Because the tube was attacked by the $\text{NaV}_6\text{O}_{11}$ -containing product, such a sample was placed in a gold capsule and the capsule was sealed in a silica tube. The mixtures were heated at 823 ± 2 K for 12 hr, then 923 ± 2 K for 48–72 hr, and cooled to room temperature.

The product was ground and examined by powder X-ray diffraction using $\text{CuK}\alpha$ radiation. This procedure was repeated until the powder X-ray pattern changed no further. Usually, one heating cycle was sufficient to reach equilibrium, but the formation of the $\text{NaV}_6\text{O}_{11}$ phase was so sluggish that three cycles with prolonged heating (168–240 hr, respectively) were required for the $\text{NaV}_6\text{O}_{11}$ -containing region. The $\text{NaV}_6\text{O}_{11}$ phase could be prepared more readily at 973 K, but decomposed above 1023 K. The δ - $\text{Na}_x\text{V}_2\text{O}_5$ was hygroscopic so that products containing it were treated using the dry-box technique in a N_2 atmosphere. Their powder X-ray patterns were taken in a specially designed sample holder wherein the sample surface was covered by a mylar film. Cell parameters of new compounds were determined by the powder X-ray method using Si as an internal standard.

Single crystals of the $\text{NaV}_6\text{O}_{11}$ were prepared by the following procedure. A mixture of NaVO_3 and V_2O_3 (4:1 mole ratio) was placed in a gold capsule and sealed in a silica tube, then heated at 923 K for 2 days. The product was reground, dried, and fired again at 973 K for 4 days. The final product was a mixture of $\text{NaV}_6\text{O}_{11}$, α' - $\text{Na}_x\text{V}_2\text{O}_5$ and an unknown colorless hygroscopic substance. Crystals of $\text{NaV}_6\text{O}_{11}$ were hexagonal plate-shaped and a typical size was 1.5 mm in diameter and 0.4 mm in thickness. The dc conductivity was obtained using the standard four-probe method.

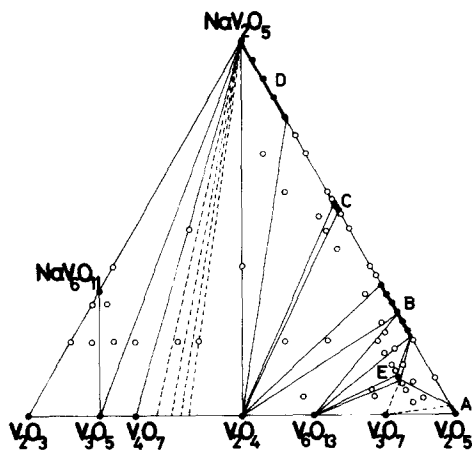


FIG. 1. Phase diagram of the NaV_3O_5 - V_2O_5 - V_2O_5 system at 923 K (A) α - $\text{Na}_x\text{V}_2\text{O}_5$, (B) β - $\text{Na}_x\text{V}_2\text{O}_5$, (C) δ - $\text{Na}_x\text{V}_2\text{O}_5$, (D) α' - $\text{Na}_x\text{V}_2\text{O}_5$, (E) $\text{Na}_7\text{V}_{12}\text{O}_{29}$. Circles indicate experimental points. Solid circles show compositions where a single phase was obtained. Open circles show the multiphase compositions.

Single crystals of the δ - $\text{Na}_{0.56}\text{V}_2\text{O}_5$ were prepared by the chemical transport method using HCl gas as transport medium. About 5 g of δ - $\text{Na}_{0.56}\text{V}_2\text{O}_5$ was prepared in advance and sealed into a silica tube with HCl gas. Initial HCl pressure was controlled so that the pressure became ca. 1 atm at 923 K. The sample was heated at 923 ± 2 K for 14 days and cooled to room temperature. Because the compound was hygroscopic, the crystal was sealed in a thin-walled glass capillary to take Weissenberg photographs.

Results and Discussion

$\text{Na}_x\text{V}_2\text{O}_5$ System

The phase diagram determined in the present study is shown in Fig. 1. We found a new phase, δ - $\text{Na}_x\text{V}_2\text{O}_5$ ($0.55 \leq x \leq 0.57$) (monoclinic with space group $C2/m$). Its powder X-ray pattern, indexed by means of Weissenberg photographs, is presented in Table I and unit cell parameters are given in Table IV. Of the five experimental points ($x = 0.54, 0.55, 0.56, 0.57$, and 0.58) covering

the δ - $\text{Na}_x\text{V}_2\text{O}_5$ region, the samples with $x = 0.55, 0.56$, and 0.57 were single-phase, whereas the sample with $x = 0.54$ was a mixture of β - and δ -phases, and that with $x = 0.58$ was a mixture of δ - and α' -phases. Thus the range of the δ -phase is $0.55 \leq x \leq 0.57$. The δ -phase does not appear in the phase diagram of the $\text{Na}_x\text{V}_2\text{O}_5$ system at 873 K reported by Pouchard *et al.* (1), though it is stable at this temperature. The δ -phase is hygroscopic and if it is exposed to air without precautions against moisture, its powder X-ray pattern will change drastically. In particular, an additional strong peak will appear at $d \approx 10.7$ Å. Pouchard *et al.* may have missed the δ -phase due to its instability in air.

The δ - $\text{Na}_x\text{V}_2\text{O}_5$ is isostructural to δ - $\text{Ag}_x\text{V}_2\text{O}_5$ (10). It consists of V_2O_5 layers stacked along (001) and Na atoms are placed between the layers (11).

The compositional range of the α -phase was very narrow and that in Fig. 1 ($0 < x \leq 0.02$) was taken from a previous report (1). The compositions of end members of the β - and α' -phases were determined by examining the variation of lattice constants (parameter a for β -phase, parameter c for α' -phase) with Na content x (see Figs. 2a, and 2b). The range of the β -phase ($0.21 \leq x \leq 0.35$) agrees reasonably with that reported earlier ($0.22 \leq x \leq 0.40$) (1). The range of the α' -phase ($0.79 \leq x \leq 1.00$) is slightly narrower than previously reported ($0.70 \leq x \leq 1.00$). We could not obtain the single-phased sample of the α' -phase, where $x = 0.75$.

Figures 2a, and 2b show lattice parameters of the β -phase (monoclinic with space group $C2/m$) and the α' -phase (orthorhombic with space group $P2_1mn$), respectively. In the β -phase, lattice parameters a and b change smoothly with x . However, the parameters c and β increase steeply between $x = 0.325$ and $x = 0.35$. In the structure of the β -phase, the number of Na sites is 2 per unit cell, i.e., the maximum x value is $1/3$ (6). The sample with $x = 0.35$ contains ex-

TABLE I
POWDER X-RAY PATTERN OF δ-Na_{0.56}V₂O₅

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs} /Å	<i>d</i> _{calc} /Å	<i>I</i> / <i>I</i> ₀ ^a	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs} /Å	<i>d</i> _{calc} /Å	<i>I</i> / <i>I</i> ₀ ^a
0	0	1	8.871	8.900	5	4	0	4	1.7531	1.7535	1
0	0	2	4.441	4.450	49	3	1	-4	1.7179	1.7178	1
2	0	2	3.5099	3.5071	5	2	0	5	1.6935	1.6940	2
1	1	0	3.4876	3.4871	6	1	1	5	1.5818	1.5820	1
1	1	-1	3.2530	3.2528	4	0	2	3	1.5557	1.5558	1
0	0	3	2.9670	2.9668	100	4	0	-5	1.5319	1.5316	1
4	0	0	2.9148	2.9152	2	2	2	-3	1.5067	1.5068	1
4	0	-1	2.7861	2.7853	1	2	2	3	1.4993	1.4997	<1
4	0	1	2.7546	2.7557	3	0	0	6	1.4830	1.4834	5
1	1	2	2.7360	2.7377	3	3	1	5	1.4713	1.4714	1
2	0	-3	2.6663	2.6637	1	0	2	4	1.4120	1.4121	<1
3	1	-1	2.5593	2.5595	2	1	1	-6	1.3675	1.3677	<1
3	1	1	2.5416	2.5421	2	6	2	0	1.3314	1.3312	<1
0	0	4	2.2240	2.2251	35	4	2	-5	1.1736	1.1738	<1
2	0	-4	2.0920	2.0915	1	4	0	7	1.1579	1.1578	1
3	1	3	1.9709	1.9695	<1	3	1	-7	1.1527	1.1529	1
6	0	0	1.9431	1.9435	1	3	1	7	1.1419	1.1419	1
5	1	1	1.9138	1.9135	1	1	1	8	1.0584	1.0583	<1
6	0	-1	1.9054	1.9059	1	3	3	-4	1.0328	1.0326	<1
1	1	-4	1.8800	1.8804	2	3	1	8	1.0221	1.0220	<1
0	2	0	1.8263	1.8272	1						

^a *I*/*I*₀ is not corrected for the influence of the mylar film over the sample.

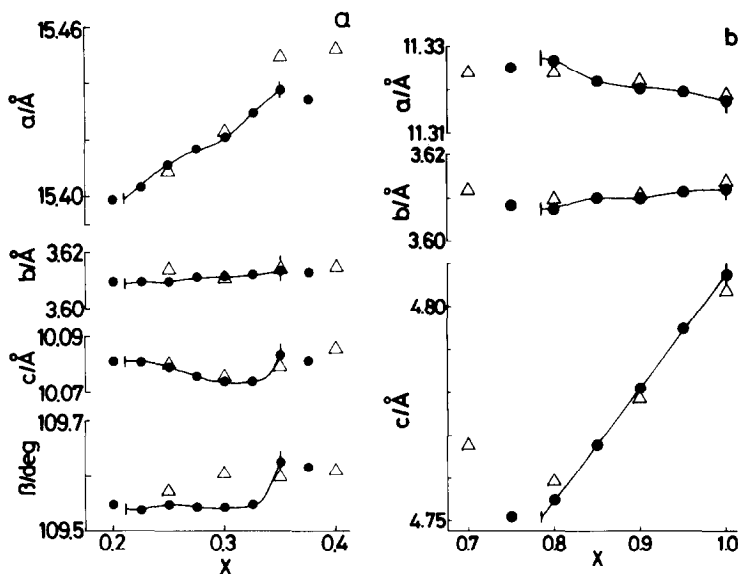


FIG. 2. Lattice parameters versus *x* for the systems (a) β-Na_{*x*}V₂O₅, (b) α'-Na_{*x*}V₂O₅. (●) this work, (Δ) from Ref. (3).

cess Na ions beyond the limit. The abrupt changes in the cell parameters may be caused by the excess Na ions. In the α' -phase, all lattice parameters change smoothly with x and parameter c , in particular, shows a steep linear increase with x .

NaV₂O₅-V₂O₄-V₂O₅ System

Phase relation on the system V₂O₄-V₂O₅ has been established at temperatures from 773 to 924 K (12) and at temperatures from 873 K to 1073 K (13). Both experiments indicated that V₃O₇ and V₆O₁₃ exist while V₄O₉ is not stable at 923 K. In this study, however, V₃O₇ never appeared. Instead, V₄O₉ formed in the V₂O₅-V₆O₁₃-Na_{*x*}V₁₂O₂₉ region. Although the reason for this result is not clear at present, one possible explanation is that V₄O₉ was formed as a metastable phase due to the presence of Na ion.

A new compound, Na_{*x*}V₁₂O₂₉ ($0.55 \leq x \leq 0.65$) (monoclinic with space groups *Cm*, *C2*, or *C2/m*) was found. Although its single crystal has not yet been obtained, the powder X-ray pattern, listed in Table II, indicates that it has essentially the same structure as *M_xV₁₂O₂₉* (*M* = Li, Cu) (5, 6). The cell parameters are shown in Table IV. In the three samples having nominal compositions Na_{*x*}V₁₂O₂₉, $x = 0.5, 0.6, 0.7$, only the product with $x = 0.6$ was single-phase. However, the powder X-ray pattern of the phase shifted slightly but obviously in the three samples. From this result, we conclude that the phase has a homogeneity region with respect to the Na content and estimate the range to be $0.55 \leq x \leq 0.65$.

The Na_{*x*}V₉O₂₂ did not appear in the present study. It has been known that formation of *M_xV₉O₂₂* (*M* = Li, Cu) is rather sluggish, but they can be obtained at 923 K within ca. 2 weeks as a single phase (6). Contrary to this report, no peaks for Na_{*x*}V₉O₂₂ were observed in the powder X-ray pattern even after two weeks firing at 923 K during this study, indicating that Na_{*x*}V₉O₂₂ does not exist at 923 K.

In the Cu_{*x*}V₁₂O₂₉, x ranges from 1.0 ~ 1.9 while it ranges from 1.05 ~ 1.80 and 2.05 ~ 2.15 in the β - and β' -Li_{*x*}V₁₂O₂₉, respectively (5, 6). These values are significantly larger compared with those of the present Na-based compound (0.55 ~ 0.65). As pointed out in the previous paper (6), the maximum x becomes 2.0 for the β -Li_{*x*}V₁₂O₂₉ and 3.0 for the Cu_{*x*}V₁₂O₂₉ or β' -Li_{*x*}V₁₂O₂₉, if we count available *M*⁺ sites in the structures. If we consider, on the other hand, the number of available V⁴⁺ sites, the maximum value becomes 2.0 for every *M_xV₁₂O₂₉*. Indeed, above-mentioned Li- or Cu-containing phases have the maximum x -values around 2.0. From the structural view point, therefore, a value of x up to 2.0 is expected to be allowed also for Na_{*x*}V₁₂O₂₉. The observed range, $0.55 \leq x \leq 0.65$, in Na_{*x*}V₁₂O₂₉ is far less than the expected maximum. It is interesting to find out which positions are occupied by Na and how such a structure with the minimal Na content is stabilized.

NaV₂O₅-V₂O₃-V₂O₄ System

In the V₄O₇-V₂O₄ system, four Magnéli phases, V₅O₉, V₆O₁₁, V₇O₁₃, and V₈O₁₅, have been reported (14). These four phases are expected to appear in the Na V₂O₅-V₄O₇-V₂O₄ region. We could not, however, determine them because of the broad and weak powder X-ray patterns.

De Roy *et al.* synthesized NaV₆O₁₁ for the first time by electrolytic reduction of molten NaVO₃ at 973 K and described its structure in hexagonal space group $P\bar{6}2c$ (9). The compound was obtained in the present study as well; however, our structure refinement gave somewhat different results (15). Its powder X-ray pattern indexed by means of the electron diffraction patterns and Weissenberg photographs is shown in Table III and the cell parameters are shown in Table IV. Of the four experimental compositions, Na_{0.9}V₆O₁₁, Na_{1.0}V₆O₁₁, Na_{0.75}V₅O₉, and Na₂V₁₀O₁₉, only the Na_{1.0}V₆O₁₁ was single-

TABLE II
 POWDER X-RAY PATTERN OF $\text{Na}_{0.6}\text{V}_{12}\text{O}_{29}$

h	k	l	$d_{\text{obs}}/\text{\AA}$	$d_{\text{calc}}/\text{\AA}$	I/I_0	h	k	l	$d_{\text{obs}}/\text{\AA}$	$d_{\text{calc}}/\text{\AA}$	I/I_0
2	0	0	13.677	13.760	2	9	1	1	2.1996	2.1994	<1
0	0	1	9.900	9.935	18	8	0	3	2.1802	2.1798	<1
2	0	-1	8.927	8.938	1	12	0	1	2.1435	2.1434	10
2	0	1	7.386	7.390	<1	10	0	-4	2.0576	2.0575	<1
4	0	0	6.864	6.880	100	11	1	0	2.0576	2.0569	<1
4	0	-1	6.260	6.267	4	6	0	4	2.0234	2.0227	2
4	0	1	5.188	5.195	1	4	0	-5	2.0184	2.0184	1
0	0	2	4.960	4.967	4	6	0	-5	1.9712	1.9711	7
6	0	-1	4.514	4.519	2	14	0	0	1.9651	1.9657	1
2	0	2	4.4022	4.4021	2	11	1	1	1.9515	1.9521	<1
6	0	1	3.8845	3.8819	<1	7	1	-4	1.9515	1.9505	<1
4	0	2	3.6943	3.6950	2	12	0	2	1.9405	1.9410	1
8	0	-1	3.4689	3.4700	1	2	0	5	1.9130	1.9137	<1
8	0	0	3.4393	3.4399	13	8	0	-5	1.8899	1.8903	1
1	1	-1	3.3980	3.3983	3	12	0	-4	1.8810	1.8807	<1
1	1	1	3.3456	3.3428	<1	13	1	-1	1.8535	1.8536	<1
0	0	3	3.3102	3.3115	1	9	1	-4	1.8462	1.8458	<1
4	0	-3	3.2440	3.2456	2	13	1	0	1.8270	1.8265	<1
2	0	3	3.0828	3.0837	4	13	1	-2	1.8175	1.8179	<1
8	0	1	3.0675	3.0681	21	0	2	0	1.8062	1.8067	1
5	1	0	3.0203	3.0206	<1	11	1	2	1.7995	1.7996	<1
6	0	-3	2.9789	2.9794	27	10	0	-5	1.7867	1.7877	<1
4	0	3	2.7752	2.7767	<1	4	2	0	1.7484	1.7474	<1
10	0	0	2.7517	2.7519	1	12	0	3	1.7317	1.7317	1
5	1	-2	2.7156	2.7152	1	16	0	0	1.7200	1.7200	1
3	1	2	2.6975	2.6949	<1	14	0	-4	1.7155	1.7155	1
8	0	-3	2.6632	2.6638	1	7	1	-5	1.7052	1.7053	<1
10	0	-2	2.6396	2.6389	<1	0	2	2	1.6969	1.6979	<1
2	0	-4	2.5326	2.5334	4	2	0	-6	1.6836	1.6839	<1
7	1	-2	2.4886	2.4881	<1	6	0	-6	1.6666	1.6664	<1
7	1	1	2.4886	2.4879	<1	0	0	6	1.6556	1.6558	<1
5	1	2	2.4646	2.4647	<1	11	1	3	1.6320	1.6322	<1
1	1	-3	2.4646	2.4637	<1	2	0	6	1.6065	1.6066	1
6	0	-4	2.3912	2.3913	2	8	2	0	1.5993	1.5995	<1
2	0	4	2.3635	2.3637	2	16	0	-4	1.5667	1.5666	<1
10	0	-3	2.3582	2.3585	1	11	1	-5	1.5612	1.5618	<1
9	1	-1	2.3516	2.3528	<1	8	2	1	1.5564	1.5568	<1
12	0	-1	2.3391	2.3383	<1	18	0	-2	1.5501	1.5501	2
12	0	0	2.2927	2.2933	<1	6	2	-3	1.5453	1.5449	<1
3	1	3	2.2791	2.2780	<1	4	0	6	1.5420	1.5418	<1
9	1	-2	2.2474	2.2473	<1						

phase. Moreover, X-ray peaks due to the $\text{NaV}_6\text{O}_{11}$ did not shift in the X-ray patterns, indicating no detectable solid-solution range.

A structure refinement (15) revealed that

the $\text{NaV}_6\text{O}_{11}$ is essentially isostructural with $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$ and $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$ (16), compounds related to magnetoplumbite. Cadée *et al.* (16) found many isostructural phases $M(M', M'')_6\text{O}_{11}$ with $M = \text{Ba}^{2+}$ and Sr^{2+} . The

TABLE III
POWDER X-RAY PATTERN OF NaV₆O₁₁

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs} /Å	<i>d</i> _{calc} /Å	<i>I</i> / <i>I</i> ₀	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs} /Å	<i>d</i> _{calc} /Å	<i>I</i> / <i>I</i> ₀
0	0	2	6.538	6.549	100	4	0	0	1.2368	1.2369	1
1	0	0	4.938	4.948	4	2	1	8	1.2318	1.2319	1
1	0	1	4.626	4.628	9	3	1	5	1.2155	1.2156	1
1	0	2	3.9506	3.9478	18	4	0	2	1.2155	1.2154	1
0	0	4	3.2747	3.2748	63	1	1	10	1.1910	1.1907	5
1	1	0	2.8575	2.8565	10	4	0	3	1.1903	1.1901	4
1	0	4	2.7309	2.7308	77	3	1	6	1.1614	1.1618	1
1	1	2	2.6180	2.6183	41	1	0	11	1.1575	1.1578	1
2	0	0	2.4740	2.4738	6	2	0	10	1.1575	1.1576	1
2	0	1	2.4311	2.4308	3	2	1	9	1.1487	1.1486	<1
2	0	2	2.3142	2.3142	21	4	0	5	1.1183	1.1185	1
0	0	6	2.1829	2.1832	1	3	2	2	1.1183	1.1184	1
1	1	4	2.1526	2.1526	24	3	1	7	1.1066	1.1066	<1
1	0	6	1.9974	1.9974	4	0	0	12	1.0913	1.0916	5
2	0	4	1.9742	1.9739	1	4	1	0	1.0795	1.0796	1
2	1	1	1.8514	1.8512	2	2	2	8	1.0764	1.0763	11
2	1	2	1.7980	1.7981	2	4	0	6	1.0764	1.0762	11
1	0	7	1.7502	1.7503	2	2	1	10	1.0727	1.0729	4
2	1	3	1.7190	1.7190	1	3	2	4	1.0727	1.0725	4
3	0	0	1.6487	1.6492	2	4	1	2	1.0655	1.0653	1
0	0	8	1.6371	1.6374	70	3	0	10	1.0257	1.0257	2
2	0	6	1.6371	1.6369	70	2	0	12	0.9986	0.9987	<1
2	1	4	1.6240	1.6239	15	4	0	8	0.9870	0.9869	1
3	0	2	1.5994	1.5993	4	3	3	0	0.9522	0.9522	<1
1	0	8	1.5548	1.5545	1	3	1	10	0.9474	0.9475	2
2	1	5	1.5218	1.5520	1	5	0	4	0.9474	0.9472	2
2	0	7	1.4919	1.4924	<1	4	0	9	0.9424	0.9425	1
3	0	4	1.4727	1.4729	2	3	3	2	0.9424	0.9422	1
2	2	0	1.4281	1.4282	19	0	0	14	0.9356	0.9356	1
1	1	8	1.4206	1.4205	3	4	2	1	0.9326	0.9326	<1
2	1	6	1.4206	1.4202	3	5	0	5	0.9257	0.9257	1
1	0	9	1.3959	1.3963	1	4	2	2	0.9257	0.9256	1
3	0	5	1.3959	1.3957	1	1	0	14	0.9195	0.9194	1
2	0	8	1.3653	1.3654	6	3	3	4	0.9144	0.9143	<1
3	1	2	1.3432	1.3430	1	4	2	3	0.9144	0.9143	<1
2	1	7	1.3229	1.3227	1	4	1	8	0.9012	0.9013	<1
2	2	4	1.3092	1.3091	2	5	0	6	0.9012	0.9013	<1
3	1	3	1.3092	1.3091	2	3	1	11	0.8994	0.8994	<1
1	0	10	1.2660	1.2663	8	4	0	10	0.8994	0.8993	<1
3	1	4	1.2660	1.2656	8	3	2	9	0.8950	0.8950	<1
2	0	9	1.2543	1.2544	1						

TABLE IV
UNIT CELL PARAMETERS FOR THE NEWLY DISCOVERED COMPOUNDS

Compound	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	<i>β</i> /deg
δ-Na _{0.56} V ₂ O ₅	11.663(2)	3.6543(4)	8.9019(6)	91.03(1)
Na _{0.6} V ₁₂ O ₂₉	28.075(1)	3.6134(3)	10.1353(5)	101.422(4)
NaV ₆ O ₁₁	5.7129(2)		13.0990(5)	

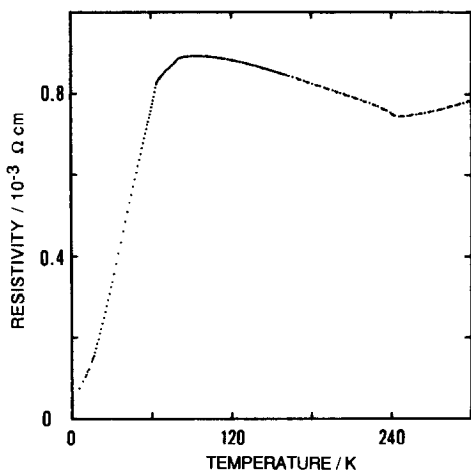


FIG. 3. The dc conductivity of a single crystal of the $\text{NaV}_6\text{O}_{11}$ along the (001) plane as a function of temperature.

present study indicates that the monovalent cation Na^+ is also acceptable as the M ion in their chemical formula.

In the $\text{NaV}_6\text{O}_{11}$, O atoms form hexagonally close packed layers. One-quarter of the O atoms in every three layers is substituted by Na atoms. One-sixth of the V atoms is placed in trigonal-bipyramidal sites located in the Na-containing layers and the remaining V atoms are placed in octahedral sites. Detailed results of structure refinement will be reported elsewhere (15).

Figure 3 shows the resistivity perpendicular to the c -axis of a single crystal of the $\text{NaV}_6\text{O}_{11}$ at 5–298 K. The resistivity, ρ , varied from 7.3×10^{-5} to $8.9 \times 10^{-4} \Omega \text{ cm}$ in this range and showed very complicated behavior. The value of $d\rho/dT$ is positive below 80 K and above 246 K. It is negative

between 80 and 246 K. In addition, there is an anomaly at ~ 64 K. Magnetic measurements on $\text{NaV}_6\text{O}_{11}$ and related compounds are in progress. Preliminary results for $\text{NaV}_6\text{O}_{11}$ indicate that there is a magnetic transition at ~ 60 K, corresponding to the anomaly in resistivity.

References

1. M. POUCHARD, A. CASALOT, J. GALY, AND P. HAGENMULLER, *Bull. Soc. Chim. Fr.* **11**, 4343 (1967).
2. A. HARDY, J. GALY, A. CASALOT, AND M. POUCHARD, *Bull. Soc. Chim. Fr.* **4**, 1056 (1965).
3. J. GALY, A. CASALOT, M. POUCHARD, AND P. HAGENMULLER, *C. R. Acad. Sci. Paris* **262C**, 1055 (1966).
4. A. D. WADSLEY, *Acta Crystallogr.* **8**, 695 (1955).
5. E. TAKAYAMA-MUROMACHI, AND K. KATO, *J. Solid State Chem.* **71**, 274 (1987).
6. Y. KANKE, E. TAKAYAMA-MUROMACHI, AND K. KATO, *J. Solid State Chem.* **83**, 69 (1989).
7. K. KATO, AND E. TAKAYAMA-MUROMACHI, *Naturwissenschaften* **73**, S.499 (1986).
8. M. POUCHARD, A. CASALOT, L. RABARDEL, AND P. HAGENMULLER, *Bull. Soc. Chim. Fr.* **7**, 2742 (1968).
9. M. E. DE ROY, J. P. BESSE, R. CHEVALIER, AND M. GASPERIN, *J. Solid State Chem.* **67**, 185 (1987).
10. S. ANDERSSON, *Acta Chem. Scand.* **19**, 1371 (1965).
11. Y. KANKE, K. KATO, E. TAKAYAMA-MUROMACHI, AND M. ISOBE, *Acta Crystallogr., C* **46**, 536 (1990).
12. H. ENDO, M. WAKIHARA, AND M. TANIGUCHI, *Chem. Lett.*, 905 (1974).
13. T. TODA, K. KOSUGE, AND S. KACHI, *Nippon Kagaku Zasshi* **87**, 1311 (1966).
14. H. ENDO, M. WAKIHARA, M. TANIGUCHI, AND T. KATSURA, *Bull. Chem. Soc. Japan* **46**, 2087 (1973).
15. Y. KANKE, K. KATO, E. TAKAYAMA-MUROMACHI, AND M. ISOBE, submitted for publication.
16. M. C. CADÉE AND D. J. W. IJDO, *J. Solid State Chem.* **52**, 302 (1984).