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<th>Growth and Electrical Properties of V[n]O₂[n]₋₁ (n=3, 4, ..., 8) Single Crystals</th>
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<tr>
<td>Author(s)</td>
<td>Nagasawa, Koichi; Bando, Yoshichika; Takada, Toshio</td>
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Kyoto University
Growth and Electrical Properties of $V_nO_{2n-1}$
($n=3, 4, ..., 8$) Single Crystals

Koichi NAGASAWA*, Yoshichika BANDO** and Toshio TAKADA**

Received October 6, 1971

Single crystals of the intermediate vanadium oxides between $V_2O_3$ and $VO_2$ with the general formula $V_nO_{2n-1}$ ($n=3, 4, ..., 8$) were grown by the chemical transport reaction using $TeCl_4$ as a transport agent. The reactions were carried out in sealed tubes. The sizes of the crystals produced were about $1-10$ mm. The temperature dependence of magnetic susceptibility, electrical resistivity and thermoelectric power were measured on single crystals. $V_3O_5$ having monoclinic structure was n-type semiconductor at the temperature ranging from $150^\circ K$ to room temperature. On $V_4O_7$, $V_5O_9$, $V_6O_{11}$ and $V_8O_{15}$ having triclinic structure, metal-semiconductor transitions occurred at $250^\circ K$, $135^\circ K$, $177^\circ K$ and $70^\circ K$, respectively. These transition temperatures were coincident with those of the anomaly in magnetic susceptibility. $V_7O_{13}$ having triclinic structure showed metallic conduction below room temperature.

INTRODUCTION

There have been many investigations on the intermediate vanadium oxides between $V_2O_3$ and $VO_2$. These phases, which are expressed by general formula $V_nO_{2n-1}$ ($n=3, 4, ..., 8$), were found by Andersson$^{1}$ and except $V_3O_5$ commonly called Magnéli phases after the main investigator. Burdes$^{2}$ and Grossman et al.$^{3}$ confirmed Andersson's results. Kosuge$^{4}$ studied the phase relation between $V_2O_3$ and $V_3O_5$ in a closed system and so proposed the phase diagram combined with the results which Kachi and Roy$^{5}$ obtained. In addition to the phase studies mentioned above, Katsura et al.$^{6,7}$ measured the equilibrium oxygen pressure for each phase at $1600^\circ K$ and $1800^\circ K$. Furthermore, Okinaka et al.$^{8}$ recently determined the stability range of each phase as a function of the oxygen pressure and temperature from $800^\circ K$ to $1600^\circ K$.

The structures of Magnéli phases have been investigated by S. Andersson et al.$^{9,10}$ Based on the crystal structure of $Th_2O_3$, one of titanium Magnéli phases, S. Andersson showed that the structures could be explained by introducing periodic shear plane to the rutile structure. The structure of $V_3O_5$ has been determined by Åbrink et al.$^{11}$

Moreover, there has been recently considerable interest in the magnetic and electrical properties on these phases. Kosuge$^{4}$ measured the temperature dependence of magnetic susceptibility and showed that the magnetic susceptibilities of $V_3O_5$, $V_4O_7$, $V_5O_9$ and $V_6O_{11}$ had the large anomalies at $133^\circ K$, $250^\circ K$, $139^\circ K$ and $177^\circ K$,
respectively. Mössbauer effect measurements revealed that the phase transformation in \( V_{107} \) and \( V_{109} \) was not a usual magnetic transition from paramagnetic to antiferromagnetic but a crystallographic transformation like \( VO_2 \). Kachi et al. measured the temperature dependence of electrical resistivity using sintered samples of these phases, and observed small anomaly on only \( V_{109} \) at about 140°K. Single crystals of \( V_{n}O_{2n-1} \) were necessary in order to investigate further the electrical properties. However, single crystals of \( V_{n}O_{2n-1} \) except \( V_{103} \) have not been obtained, because each phase is stable in the narrow range of oxygen pressure at high temperature, as shown in Fig. 1.

![Graph](image-url)

**Fig. 1.** Plot of log \( P_{O_2} \) versus \( 10^4/T \) for the \( V_{2}O_3, V_{5}O_9, V_{6}O_{11}, V_{2}O_{2}, V_{n}O_{2n-1} \) (\( n \geq 7 \)), \( V_{5}O_5, V_{6}O_{11}, V_{7}O_{23} \), and \( VO_2 \) respectively.
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Chemical transport reaction in a closed system may be suitable for growing single crystals of these phases which are stable under such conditions, because the equilibrium oxygen pressure of an oxide can be automatically controlled in a tube. Recently, Niemyski et al. prepared highly pure single crystals of TiO₂ by chemical transport reaction using TeCl₄. Bando et al. also prepared VO₂ single crystals by the same method. Moreover, single crystals of V₅O₂n₋₁ have been recently grown by Nagasawa et al. In the experiment, the postulated reaction of the type,

\[ V₅O₂n₋₁(s) + \left( n - \frac{1}{2} \right) TeCl₄(g) \]

\[ \rightleftharpoons (n-2) VC₁₄(g) + 2VC₁₃(g) + \left( n - \frac{1}{2} \right) TeO₂(g) \]

was used, where (s) shows solid state and (g) gaseous state.

The present paper aims to examine the conditions for the preparation of V₅O₂n₋₁ single crystals to investigate the electrical properties from the measurements of electrical resistivity and thermoelectric power, and aims to find the relation of the phase transformation and the structure having periodic shear plane.

Some parts of this investigation were already reported in short note. In this paper, the detailed results are reviewed and summarized.

**EXPERIMENTALS**

1. **Growth procedures**

The sealed tube for the chemical transport reaction was made by the following way. V₅O₂n₋₁ powder of about 1 gram as the starting material was loaded into the end of transparent silica tube of 13 mm in diameter and 170 mm in length. In the case of V₅O₁₅, VO₂ and V₆O₁₁ mixed in mole ratio of 1.9 and 2.0 were used as the starting one. And then TeCl₄ powder as a transport agent was added into the silica tube in the dry box. After the tube was evacuated to 10⁻⁶ mmHg, it was sealed off. The tube was inserted in the horizontal electric furnace, where the source zone with the starting material was kept at 1050°C and the crystallization zone at 950°C. The tube was heated for 72 hr. The reaction was stopped by quenching the tube in water. The tube was broken out, and the crystals at the crystallization zone were removed from the wall of silica glass. Chemical transport yielded many crystals which were 0.5~10 mm in length and 0.5~2 mm in width. The crystals were washed in diluted aqueous HCl solution, and TeCl₄ was dissolved. And then crystals were washed in water and dried. In order to measure the transport rate, the crystals obtained at the crystallization zone were weighed. The V/O ratios of the crystals obtained were volumetrically determined by Zinc-Amalgam method. Spectroscopic analysis for starting material V₅O₂ and the crystals obtained was performed.

2) **Phase identifications and measurements**

The phases of crystals were identified by x-ray diffraction analysis and measurements of magnetic susceptibility. The x-ray powder patterns were taken using Ni-filtered
Growth and Electrical Properties of $V_nO_{2n-1}$ ($n=3, 4, ..., 8$) Single Crystals

Cu-K radiation. The magnetic susceptibility was measured with many crystals of 0.5~5 mm in size. In order to confirm the crystal to be a single crystal, Laue photograph was taken of the growth plane for a crystal of 5~10 mm in width, using W radiation. The crystal system and lattice constant of $V_nO_{2n-1}$ single crystals were determined by the x-ray precession photographs and 4-circle x-ray diffractometer, using Mo-K radiation.

The measurements of electrical resistivity were carried out along the growth axis of a rod-like crystal by means of four point method using a d.c. potentiometer. On $V_3O_5$, the measurements were done, in the directions parallel and perpendicular to the growth axis, by four point method and two point method.

To measure the thermoelectric power, both ends of a rod-like crystal were firmly clamped to two copper blocks between which it was about 5 mm. One copper block was jointed to a heater. Cu-AuCo thermocouple and copper wire were attached to both ends of a crystal using silver paste. The temperature difference between both ends was measured by the two thermocouples. At the same time, the difference of potential between both copper wires was measured by micro voltage meter. The temperature difference between both ends of a crystal was kept to be 2~4°C by controlling the current of heater.

RESULT AND DISCUSSION

1) Crystal growth

Crystals obtained at the crystallization zone were bright and black in color, rod-like or plate-like in shape and up to 12 mm in size. Figure 2 shows the photograph of the crystals obtained. Table 1 shows the representative transport conditions for $V_3O_5$, $V_4O_7$, $V_5O_8$, $V_6O_{11}$, $V_7O_{13}$ and $V_8O_{15}$, transport rates, phases of the starting

![Fig. 2. Photographs of typical crystals obtained in the crystallization zone.](image)

(a) $V_7O_{13}$   (b) $V_3O_5$   (c) $V_6O_{11}$

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Table 1. Representative Conditions for Growth of $V_xO_{2n-1}$ Single Crystals and Phases of Products.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Starting material (before reaction)</th>
<th>TeCl$_4$ weight (mg/cc)</th>
<th>Transport rate (mg/hr)</th>
<th>Starting material (after reaction)</th>
<th>Crystals obtained (after reaction)</th>
<th>Results of chemical analysis for crystals obtained ($x$ in VO$_x$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>$V_3O_5$</td>
<td>2</td>
<td>0.4</td>
<td>$V_3O_5$</td>
<td>$V_2O_5^{**}$</td>
<td>Observed = 1.65, Calculated = 1.67</td>
</tr>
<tr>
<td>A-2</td>
<td>$V_3O_5$</td>
<td>4</td>
<td>1.0</td>
<td>$V_6O_5^*$</td>
<td>$V_2O_5^{**}$</td>
<td>—</td>
</tr>
<tr>
<td>A-3</td>
<td>$V_5O_5$</td>
<td>6</td>
<td>3.6</td>
<td>$V_6O_5^*$</td>
<td>$V_2O_5^{**}$</td>
<td>—</td>
</tr>
<tr>
<td>A-4</td>
<td>$V_3O_5$</td>
<td>8</td>
<td>4.1</td>
<td>$V_6O_5^*$</td>
<td>$V_2O_5^{**}$</td>
<td>—</td>
</tr>
<tr>
<td>B-1</td>
<td>$V_2O_7$</td>
<td>8</td>
<td>4.3</td>
<td>$V_4O_7^*$</td>
<td>$V_4O_7^{**}$</td>
<td>Observed = 1.74, Calculated = 1.75</td>
</tr>
<tr>
<td>C-1</td>
<td>$V_3O_9$</td>
<td>8</td>
<td>4.4</td>
<td>$V_6O_9^*$</td>
<td>$V_2O_5^{**}$</td>
<td>Observed = 1.80, Calculated = 1.80</td>
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<tr>
<td>C-2</td>
<td>$V_5O_9$</td>
<td>8</td>
<td>4.3</td>
<td>$V_6O_9 + V_6O_{11}^{**}$</td>
<td>$V_2O_5 + V_6O_{11}^{**}$</td>
<td>Observed = 1.81 —</td>
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<tr>
<td>D-1</td>
<td>$V_6O_{11}$</td>
<td>8</td>
<td>4.5</td>
<td>$V_6O_{11}$</td>
<td>$V_6O_{11}^{**}$</td>
<td>Observed = 1.82, Calculated = 1.83</td>
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<tr>
<td>E-1</td>
<td>$V_2O_{13}$</td>
<td>8</td>
<td>4.1</td>
<td>$V_7O_{13}$</td>
<td>$V_7O_{13}^{**}$</td>
<td>Observed = 1.86, Calculated = 1.86</td>
</tr>
<tr>
<td>F-1</td>
<td>$VO_2 + V_6O_{13}$ (1:9:1)</td>
<td>8</td>
<td>4.0</td>
<td>$V_8O_{15}^{**}$</td>
<td>$V_8O_{15}^{**}$</td>
<td>Observed = 1.87, Calculated = 1.88</td>
</tr>
<tr>
<td>F-2</td>
<td>$VO_2 + V_6O_{13}$ (2:0:1)</td>
<td>8</td>
<td>4.5</td>
<td>—</td>
<td>$V_8O_{15} + V_6O_{15}^{***}$</td>
<td>—</td>
</tr>
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</table>

The phase was identified by x-ray analysis, x-ray analysis and magnetic susceptibility measurement or x-ray precession photograph.

The transport rate for each phase increased with amount of TeCl$_4$ in the tube. For instance, the rate of $V_3O_5$ increased with amount of TeCl$_4$ per unit volume of the tube, as shown in Table 1. TeCl$_4$ of 8 mg per unit volume yielded the largest crystals in comparison with less amount. The crystal growth under the amount above 8 mg of TeCl$_4$ per unit volume was not done because the tube exploded owing to high pressure of TeCl$_4$ gas. The explosion was also found in the growth experiment of $V_4O_7$, $V_5O_9$, $V_6O_{11}$, $V_7O_{13}$ and $V_8O_{15}$.

X-ray powder patterns showed that the phases of the crystals obtained in run A-4, B-1, C-1, D-1, E-1 and F-1 were of $V_3O_5$, $V_4O_7$, $V_5O_9$, $V_6O_{11}$, $V_7O_{13}$ and $V_8O_{15}$, respectively.

Figure 3 shows the temperature dependence of magnetic susceptibility for the crystals obtained. Susceptibility of $V_3O_5$ crystals had a smooth peak at 130°K but, that of $V_4O_7$, $V_5O_9$, $V_6O_{11}$ and $V_7O_{13}$ crystals had a marked kink at about 250°K, 135°K, 170°K and 70°K, respectively. Susceptibility of $V_8O_{15}$ crystals increased with decreasing temperature. These results were approximately coincident with Kosuge’s results for $V_3O_5$, $V_4O_7$, $V_5O_9$, $V_6O_{11}$ and $V_7O_{13}$ except $V_8O_{15}$. The susceptibility vs temperature curve for a sample consisting of two phases had two kinks corresponding to the transition temperature of each phase. The crystals in C-2 were found to be two phases consisting of $V_3O_5$ and $V_4O_7$. It must be concluded by this method that the crystals in A-4, B-1, C-1, D-1, E-1 and F-1 are a single phase of $V_3O_5$, $V_4O_7$, $V_5O_9$, $V_6O_{11}$, $V_7O_{13}$ and $V_8O_{15}$, respectively.

As shown in Table 1, the V/O ratio of the single crystals determined by chemical analysis approximately agreed with the value expected from $V_xO_{2n-1}$. (326)
X-ray Laue photograph seemed to show that the crystal was single. However, it was often observed by precession photograph that crystals were twinned. Figure 4 shows the precession photograph of a V₈O₁₅ single crystal. The precession photo-

Fig. 3. Temperature dependence of the magnetic susceptibility of V₈O₂₉₋₁ crystals.

Fig. 4. Precession photograph of V₈O₁₅. The superstructure reflections which divide the interval of the main reflections into eight parts are found along the direction shown by the arrows.
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Table 2. Crystal System and Lattice Constant in Reduced Lattice. Åsbrink et al's 11 and Andersson et al's 10 Results are shown in the Bracked.

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<thead>
<tr>
<th>sys</th>
<th>a(A)</th>
<th>b(A)</th>
<th>c(A)</th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>V(A³)</th>
</tr>
</thead>
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<tr>
<td>V₃O₅</td>
<td>mono.</td>
<td>9.854</td>
<td>5.040</td>
<td>6.990</td>
<td>90</td>
<td>109.5</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>(9.86)</td>
<td>(5.04)</td>
<td>(6.99)</td>
<td>(90)</td>
<td>(109.5)</td>
<td>(90)</td>
<td>(327.4)</td>
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<tr>
<td>V₄O₇</td>
<td>tric.</td>
<td>6.778</td>
<td>7.007</td>
<td>5.504</td>
<td>109.2</td>
<td>104.6</td>
<td>64.2</td>
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<td></td>
<td>(6.72)</td>
<td>(7.01)</td>
<td>(5.51)</td>
<td>(109.0)</td>
<td>(104.6)</td>
<td>(64.3)</td>
<td>(220.1)</td>
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<tr>
<td>V₅O₉</td>
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<td>7.005</td>
<td>8.353</td>
<td>5.470</td>
<td>104.9</td>
<td>109.0</td>
<td>69.5</td>
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<td></td>
<td>(6.99)</td>
<td>(8.34)</td>
<td>(5.47)</td>
<td>(104.9)</td>
<td>(109.0)</td>
<td>(69.5)</td>
<td>(278.7)</td>
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<td>V₆O₁₁</td>
<td>tric.</td>
<td>6.998</td>
<td>9.569</td>
<td>5.448</td>
<td>100.6</td>
<td>108.9</td>
<td>90.0</td>
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<td></td>
<td>(6.99)</td>
<td>(9.56)</td>
<td>(5.44)</td>
<td>(100.7)</td>
<td>(108.9)</td>
<td>(90.1)</td>
<td>(337.1)</td>
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<td>V₇O₁₃</td>
<td>tric.</td>
<td>7.005</td>
<td>11.115</td>
<td>5.439</td>
<td>91.2</td>
<td>109.0</td>
<td>84.0</td>
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<td>(7.00)</td>
<td>(11.11)</td>
<td>(5.43)</td>
<td>(91.1)</td>
<td>(108.9)</td>
<td>(84.1)</td>
<td>(397.4)</td>
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<tr>
<td>V₈O₁₆</td>
<td>tric.</td>
<td>7.02</td>
<td>13.10</td>
<td>5.42</td>
<td>95.7</td>
<td>109.5</td>
<td>100.2</td>
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<tr>
<td></td>
<td>(6.199)</td>
<td>(13.79)</td>
<td>(5.43)</td>
<td>(98.0)</td>
<td>(109.0)</td>
<td>(99.5)</td>
<td>(455.1)</td>
</tr>
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</table>

graph revealed the existence of superstructure along the special direction. The interval of the main reflections was equally divided into eight parts along the special direction. Generally, the photographs of VₙO₂ₙ₋₁ except V₃O₅ showed the division of the interval of the main reflections into n parts. The crystal system and lattice constant were determined with 4-circle diffractometer. The lattices obtained above were reduced by using UTRDCL28 and their results are shown in Table 2. The lattice constants which could be obtained by transforming Åsbrink et al's 11 and Andersson et al's 10 lattices to the type of reduced lattice are shown in the brackets of Table 2 and approximately agreed with those obtained in this experiment. Therefore, it is considered that the crystal structures proposed by Andersson et al. 9 were reasonable. The lattice constants of V₅O₉ having monoclinic structure also agreed with those obtained by transforming Åsbrink et al's 11 lattice to the reduced lattice. The detailed discussion on the crystallography of VₙO₂ₙ₋₁ based on the rutile structure will be given in other paper by Horiuchi et al. 29

From the x-ray precession photographs, it is also concluded that the crystals obtained are single crystals of VₙO₂ₙ₋₁ (n=3, 4, ..., 8), respectively. However, in C-2, the crystals with two phases of V₅O₉ and V₆O₁₁ were obtained using the starting material with a single phase. It must be considered that the starting material of V₅O₉ had been already oxidized in air, because single crystals with a single phase was generally obtained from starting material with a single phase. The stability range of V₅O₉ is very narrow, as shown in Fig. 1, and so the slight oxidization of starting material appears to cause the formation of V₆O₁₁ with V₅O₉. The starting material corresponding to the composition of V₅O₁₅, VO₂ and V₆O₁₁, mixed in mole ratio of 2:0, also yielded the crystals with two phases of V₅O₁₅ and V₆O₁₁, as mentioned later. In the consideration of the oxidization, VO₂ and V₅O₁₁, mixed in mole ratio of 1:9 were used as the starting material and single crystals of V₆O₁₁ were obtained. This suggests that V₅O₁₅ is stable only in the very narrow stability range of the equilibrium oxygen pressure. Each of VₙO₂ₙ₋₁ having in higher than 9 is considered to be stable only in the very narrow range of the equilibrium oxygen pressure at elevated temperature. Therefore, it should be noticed that single crystals of VₙO₂ₙ₋₁ (n>9) may
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Fig. 5. (a) Precession photograph showing the topotactic relation of \( V_5O_{15} \) and \( V_9O_{17} \). (b) A part of the photograph is enlarged to show the reflections from the two phases. The weak spots of \( V_9O_{17} \) are indicated by arrows.

be prepared by protecting the starting material from being oxidized by air before reaction.

To examine the structure of the crystal with two phases, the precession photograph was taken of a crystal with two phases. In the precession photograph of a crystal in F-2, as shown in Fig. 5, the weak reflections which divide the interval of the main reflections into nine parts were observed in addition to the strong reflections, which divided the interval into eight parts, corresponding to \( V_5O_{15} \). From these reflections it is apparent that \( V_9O_{17} \) topotaxially exists in the crystal of \( V_5O_{15} \). As mentioned later, the temperature dependence of electrical resistivity of a crystal in C-2 shows the two anomalies corresponding to \( V_5O_5 \) and \( V_6O_{11} \) and two phases coexist in a crystal.

<table>
<thead>
<tr>
<th>Element</th>
<th>Starting material ( V_5O_5 ) (ppm)</th>
<th>Single crystals ( V_5O_5 ) (ppm)</th>
<th>Single crystals ( V_9O_{17} ) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Co</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ni</td>
<td>100</td>
<td>100</td>
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<td>Ti</td>
<td>Tr*</td>
<td>Tr*</td>
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<td>100</td>
</tr>
<tr>
<td>Si</td>
<td>100</td>
<td>200</td>
<td>200</td>
</tr>
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</table>

* Trace
Fig. 6. Electrical resistivity versus temperature curves of V$_3$O$_5$. From 250°K to room temperature by four point method and below 250°K by two point method.

$S_{ll} - 1$: Parallel to the growth axis of sample 1
$S_{ll} - 2$: Parallel to the growth axis of sample 2
$S_{ll} - 3$: Perpendicular to the growth axis of sample 2
The results of spectroscopic analysis are shown in Table 3. The little amounts of Te, Cl and Si were contained in single crystal.

2) **Electrical properties**

Electrical properties of as grown VₙO₂₋₁ crystals are reviewed in paragraph (A), (B), (C), (D), (E), and (F) and summarized.

(A) V₃O₅

The electrical resistivity ρ of V₃O₅ was measured from room temperature to 120°C, as shown in Fig. 6. V₃O₅ has been clarified to be semiconductive in the measured temperature range. An activation energy of the electrical conduction was about 0.4 eV above 180°C and gradually decreased below 180°C. The anisotropy of ρ in the direction parallel and perpendicular to the growth axis was hardly observed.

Thermoelectric power α are plotted against temperature from room temperature to 200°C in Fig. 7. The negative sign of α indicated that V₃O₅ was n-type semiconductor. From the slope of the α-T curve, the Fermi energy measured from the

![Graph of Thermoelectric power versus temperature curve of V₃O₅.](image)
bottom of conduction band was estimated to be about 0.1 eV. At 130°K, V$_3$O$_5$ had transition of the magnetic susceptibility $\chi$, as shown in Fig. 3. However, the sharp anomaly on $\rho$-T curve was not observed. The metal-semiconductor transition at about 160°K reported by Takei et al.\textsuperscript{14} could not be seen in the present experiment.

(B) V$_4$O$_7$

Figure 8 shows the temperature dependence of $\rho$. The V$_4$O$_7$ crystal underwent
Fig. 9. Thermoelectric power versus temperature curves of V$_4$O$_7$. 

(333)
a metal-semiconductor transition at 244°K on cooling. At the transition temperature $T_t$, $\rho$ increased by about two orders of magnitude. Upon heating, a hysteresis of about 6°K was seen before $\rho$ returned to the value of the metallic state. Transition temperature of $\rho$ agreed approximately with that of $x$ shown in Fig. 3. An activation energy of the semiconducting state decreased from 0.8 eV to 0.1 eV with decreasing temperature. The temperature dependence of $\alpha$ is shown in Fig. 9. The absolute value of $\alpha$ suddenly jumped at $T_t$ and gradually increased until about 195°K with

\begin{center}
\begin{tabular}{c c c c c c c c c}
& 330 & 250 & 200 & 160 & 130 & 110 & 100 \\
\hline
T (°K) & 6 & 5 & 4 & 3 & 2 & 1 & 0 \\
\hline
\end{tabular}
\end{center}

\begin{center}
\begin{tabular}{c}
$E_a=0.17$eV \\
$E_a=0.1$eV \\
T\text{\tiny f} of V\text{\tiny 5}O\text{\tiny 9}
\end{tabular}
\end{center}

Fig. 10. Electrical resistivity versus temperature curves of V$_5$O$_9$. (334)
decreasing temperature. From the slope, the Fermi energy measured from the bottom of conduction band was estimated to be about 0.15 eV. Below about 195°K, the absolute value of $\alpha$ decreased with decreasing temperature. In spite of the same temperature dependence of $\rho$, some sample showed the rapid increase of $\alpha$ below 120°K. The origin of these behaviors in $\alpha$ is not clear.

(C) $V_5O_9$

The $V_5O_9$ crystal underwent a metal-semiconductor transition at 129°K on cooling and at 135°K on heating, as shown in Fig. 10. This temperature corresponds with the transition temperature of $z$. At the $T_t$, $\rho$ increased by about five orders of magnitude. The value of $\alpha$ and activation energy of semiconducting state showed a little difference between two samples. Increase in the absolute value of $\alpha$ was found below 130°K, as shown in Fig. 11 and the Fermi energy was estimated to be about 0.2 eV.

![Thermoelectric power versus temperature curves of $V_5O_9$.](image-url)
The $\text{V}_6\text{O}_{11}$ crystal had a metal-semiconductor transition at 175°K on cooling and at 177°K on heating, as shown in Fig. 12. An activation energy of semiconducting state was about 0.12 eV. As shown in Fig. 13, the absolute value of $\alpha$ abruptly increased at $T_t$, and decreased with decreasing temperature. Figure 14 shows the $\rho$-$T$ curve of a crystal of C-2 which has two anomalies of $V_5\text{O}_5$ and $V_6\text{O}_{11}$ on the $x$-$T$ curve. Two transitions corresponding to $V_5\text{O}_5$ and $V_6\text{O}_{11}$ were also observed. This result shows that two phases coexist in a crystal.

![Diagram showing electrical resistivity versus temperature curves of $V_6\text{O}_{11}$ and $V_7\text{O}_{13}$](image)

Fig. 12. Electrical resistivity versus temperature curves of $V_6\text{O}_{11}$ and $V_7\text{O}_{13}$.
Fig. 13. Thermoelectric power versus temperature curves of V_6O_{11} and V_7O_{15}.

(E) V_7O_{15}

The conduction of V_7O_{15} was metallic over the temperature from 4.2°K to room temperature without transition, as shown in Fig. 12. Thermoelectric power was nearly constant in the temperature range from room temperature to 125°K, as shown in Fig. 13.

(F) V_8O_{15}

The temperature dependence of \( \rho \) on V_8O_{15} showed a metal-semiconductor transition at 70°K, as shown in Fig. 15. An activation energy just below \( T_t \) was about 0.13 eV. Below \( T_t \), the abrupt increase in the absolute value of \( \alpha \) was also observed, as shown in Fig. 16.

There were metal-semiconductor transitions in all the phases except V_7O_{15}. The
Fig. 14. Electrical resistivity versus temperature curve of the crystal consisting of two phases of V$_5$O$_9$ and V$_6$O$_{11}$.

Fig. 15. Electrical resistivity versus temperature curve of V$_6$O$_{11}$.

list of various properties obtained in this experiment is given in Table 4. On all the metallic phases the electrical resistivities were $10^{-2}$~$19^{-3}$ $\Omega$·cm and the thermoelectric powers were $0$~$-20$ $\mu$V/deg. On the semiconducting phase of V$_5$O$_9$ the activation energy of electrical resistivity increased with increasing temperature. This
behavior suggests that the intrinsic conduction by electrons which jump over the band gap is dominated near the transition temperature and the conduction at lower temperature becomes to be dominated by impurity levels in the band gap. The increase in
the thermoelectric power near the transition temperature also indicates the abrupt increase in electron concentration near the transition temperature. On all of the semiconducting phases, the electrical properties may be attributable to the impurity ions in the sample or the nonstoichiometry.

The temperature of metal-semiconductor transition of all the phases except \( V_5O_5 \) corresponded to that of the transition observed in magnetic susceptibility. Already, Kosuge\(^6\) clarified for the magnetic transitions in \( V_4O_7 \) and \( V_5O_9 \) to be a transition from paramagnetic to paramagnetic. Measurement of the electrical resistivity showed a hysteresis loop. Moreover, the crackings of crystal which suggest the volume change of material at the transition were often observed. From these facts, the transitions would seem to be first order transitions like \( V_5O_5 \). However, the transition observed in \( V_5O_5 \) at 130\(^\circ\)K, which had not a metal-semiconductor transition, may be from paramagnetic to antiferromagnetic.

Figure 17 shows the transition temperature of \( V_nO_{2n-1} \) versus \( n \) except \( n = 3 \). On this figure, the following regularity may be pointed out for the transition temperature.

1) Magnéli phases are classified into two groups having even and odd \( n \) by the transition temperature.

2) The transition temperature decreases with increase of even and odd \( n \), respectively.

Magnéli phases have triclinic structure based upon the rutile structure with the periodic shear plane. And so it may be considered that the introduction of shear plane gives the large influence on the transition. The relation of periodic structure of Magnéli phases with the transitions may cast some light on the mechanism of the transition in future.
Growth and Electrical Properties of $V_nO_{2n-1}$ ($n=3, 4, \ldots, 8$) Single Crystals

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