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Magnetic, Electric and Structural Properties of β-$A_xV_2O_5$ (A = Na, Ag)

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Physical properties of β-$A_xV_2O_5$ (A = Na, Ag) have been systematically reconsidered from structural, electric, and magnetic points of view. We prepared samples, both powder and single crystal, with precise composition for this purpose. The single crystals have been successfully grown by a self flux method using NaV_3O_8 as a flux. The precise adjustment of x was performed by embedding the as-grown crystals in a large amount of powder and heating them. β-$Na_{0.33}V_2O_5$ was not a conventional semiconductor but a possible anisotropic metal at higher temperatures. It exhibited a metal-insulator transition at 136 K, suggesting a charge ordering. The ordered structure underwent a magnetic ordering with T_c = 24 K. We also observed a development of $1 \times 2 \times 1$ superstructure below 230 K, suggesting an ordering of the intercalated ion. Those transitions similarly occurred in β-$Ag_{0.33}V_2O_5$. The deviation from $x = 0.33$ drastically decreased the transition temperatures or magnitudes of anomalies at the transitions, and both metallic behavior in the high temperature phase and magnetic ordering were lost.

KEYWORDS: vanadium bronze, β-$Na_xV_2O_5$, β-$Ag_xV_2O_5$, single crystal growth, self flux method, metal-insulator transition, charge ordering, magnetic ordering

§1. Introduction

A member of vanadium bronzes, β-$A_xV_2O_5$ has long been known as a quasi-one-dimensional conductor. This compound family has attracted considerable interests since Chakraverty *et al.* explained the transport phenomena in β-$Na_{0.33}V_2O_5$ in terms of a bipolaron formation from low temperature specific heat measurements.[1)] Magnetic Resonance or X-ray diffraction (XRD) data were also interpreted from this point of view.[2-4)] Aside from these previous efforts, we emphasize for the following reasons that it is significant to investigate the β phase from other aspects.

First, β phase has a unique crystal structure with magnetic ions.[5,6)] It adopts a monoclinic structure with 2-fold axis of b. As is shown in Fig. 1, there are three different sites for vanadium (V1,V2,V3) atoms. The A^+ ions are intercalated in a tunnel formed by V_2O_5 framework and form a pair of chains along the b axis. Many kinds of cations such as Na, Ag, Li, or K can be inserted on A1 site. Cu ion can be also inserted in the tunnel, but located on a different site, so that its crystal structure is discriminated as β' phase. The three kinds of vanadium sites form a double chain described as follows. V1 forms an infinite zigzag chain along the b axis by sharing the edges of VO_6 octahedron. V3 also forms an infinite zigzag chain, but has five-fold square pyramidal coordination. On the other hands, V2 forms an infinite ladder chain by sharing the corners of VO_6 octahedron. This low dimensional nature in crystal structure is generally found in vanadium bronze system. It reminds us of recently discovered quantum spin systems, the most remarkable example of which is spin-Peierls compound α'-NaV_2O_5.[7)] Therefore it is reasonable to expect in the β phase exotic phase transitions coupled with spin and charge or lattice.

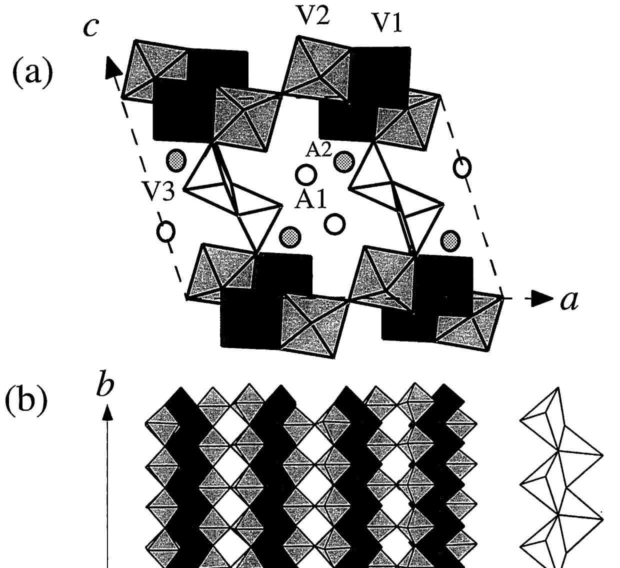

Fig. 1. (a) Crystal structure of β-$A_xV_2O_5$ projected on ac plane. V1-3 indicate crystallographically independent vanadium sites. A1 and A2 indicate A sites for the β phase. The A1 site is preferably occupied. (b) Arrangement of the three kinds of VO_x polyhedra along the b axis.

Second, β-$A_xV_2O_5$ is one of the best conductors among vanadium bronze system. Therefore we consider that investigations of electric properties of β-$A_xV_2O_5$

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may not only lead to a discovery of new phenomena such as a charge ordering or a metal-insulator transition but also give a key to understand unique characters in V^{4+}-V^{5+} mix valency.

We are systematically investigating the β and β' phase. In this paper we report the single crystal growths and physical properties of β-$Na_xV_2O_5$ and β-$Ag_xV_2O_5$. Although there are many reports on their physical properties, the ambiguity in composition (x) has been inevitable. The most characteristic point in our study is that we have succeeded in obtaining samples, both powder and single crystal, with arbitrary and precise composition. The detail is discussed in §2. In §3 we report the physical properties of β-$Na_xV_2O_5$ and β-$Ag_xV_2O_5$, especially focussing on phase transitions occurring in β-$Na_{0.33}V_2O_5$ and β-$Ag_{0.33}V_2O_5$. The comparison between them and the effects of Na nonstoichiometry on the physical properties are also discussed.

§2. Experimental

2.1 Syntheses of powder samples and characterizations

Powder samples of β-$Na_xV_2O_5$ ($0.23 < x < 0.35$ in our study) and β-$Ag_xV_2O_5$ ($0.23 < x < 0.41$) were synthesized by a solid state reaction in evacuated silica tubes. The source material was a mixture of AVO_3 (A = Na, Ag), V_2O_3, and V_2O_5. The reaction temperature was chosen to be 600°C and 500°C for β-$Na_xV_2O_5$ and β-$Ag_xV_2O_5$, respectively. AVO_3 was synthesized by a solid state reaction of 1:1 molar ratio of A_2CO_3 and V_2O_5 in air. V_2O_3 was synthesized by a reduction of V_2O_5 in H_2 atmosphere.

The prepared samples were characterized with powder X-ray diffraction (Cu-Kα, 10–300 K). Magnetic susceptibilities were measured using a Quantum Design SQUID magnetometer. Electric resistivities were measured by an ordinary four-probe method using single crystals. Specific heat measurements were carried out by an AC technique.

2.2 Single crystal growths of β-$Na_x V_2 O_5$

In order to obtain reliable data on electric resistivity, single crystal growth is essential. However one of the most serious problems in the single crystal growth in the β phase is that β-$A_xV_2O_5$ does not congruently melt, producing a mixture of liquid and vanadium oxide (VO_2 etc.) at the melting point. Those resultant solids not only remain in crystals as impurities but also decrease the size of the single crystal. Therefore we adopted a self flux method.

The single crystal of β-$Na_{0.33}V_2O_5$ was successfully grown by a self flux method using NaV_3O_8 as a flux. The mixture of NaV_3O_8 and β-$Na_{0.33}V_2O_5$ (NaV_6O_{15}) can be regarded as a pseudo binary system. NaV_3O_8 was prepared by a solid state reaction of $NaVO_3$ and V_2O_5 at 500°C. The single crystal with a typical size of 4 mm × 0.5 mm × 0.2 mm was obtained by melting 1:30 (weight ratio) mixture of $Na_{0.33}V_2O_5$ and NaV_3O_8 in vacuum at 740°C and cooling it from 700°C to 600°C with a rate of 0.5°C/h. The flux was removed with dilute hydrochlolic acid. It was confirmed that the as-grown crystal is β-$Na_{0.33}V_2O_5$. The single crystals with $x \neq 0.33$ were prepared by a subsequent treatment as described below. The as-grown crystals ($Na_{0.33}V_2O_5$) were embedded into a large amount of powder sample with a certain Na concentration. The whole mixture was heated in vacuum for several days. The heat treatment was performed at 600°C when $x > 0.33$, namely for Na insertion into crystals, and 640°C for Na deintercalation ($x < 0.33$). It has been found that the Na concentration of the single crystal is the same as that of the powder.

§3. Results and Discussion

3.1 Phase transitions in β-$A_{0.33}V_2O_5$ (A=Na, Ag)

In this section we report phase transitions occurring in β-$A_{0.33}V_2O_5$ (A = Na, Ag). In the following four paragraphs we discuss physical properties of β-$Na_{0.33}V_2O_5$. The comparison between β-$Na_{0.33}V_2O_5$ and β-$Ag_{0.33}V_2O_5$ is discussed in the next, and we finally give a possible explanation in this system.

Figure 2 shows the temperature dependences of the magnetic susceptibility (χ) of β-$Na_{0.33}V_2O_5$ with an applied magnetic field of 10^4 and 10^2 Oe. A jump in the $\chi(T)$ curve below 24 K is attributed to the magnetic transition which was first reported by Schlenker *et al.*[8] As they reported, the behavior below T_c was quite different between the measurement with zero field cooled (ZFC) and field cooled (FC) when the applied field was low enough. The behavior seems spin glass like, but they explained the magnetic transition in terms of a long-range magnetic ordering from a largely anisotropic behavior below T_c. They argued that there exist an antiferromagnetic interaction along the b axis and weaker couplings in the ac plane. Our preliminary NMR studies have revealed that the magnetic transition is a long-range magnetic ordering:[9] at least a possibility of spin glass can be discarded. At first sight it seems strange that the long-range magnetic ordering occurrs in such a low Na concentration, because only one sixth of the vanadium ions is magnetic in this case. Therefore, in order to cause

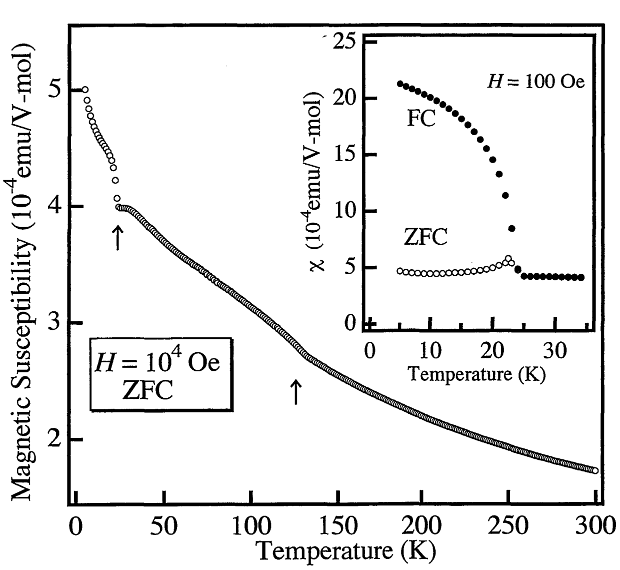

Fig. 2. Temperature dependence of magnetic susceptibility of powder β-$Na_{0.33}V_2O_5$ with an applied magnetic field (H) of 10^4 Oe. Inset shows the magnetic susceptibility measured with H = 100 Oe. They are normalized per vanadium (V) mol.

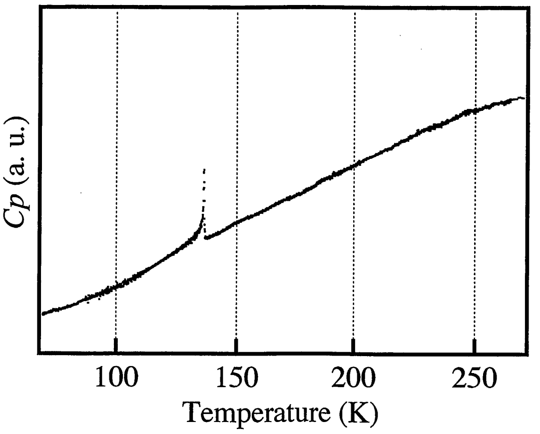

Fig. 3. Temperature dependence of specific heat of β-Na$_{0.33}$V$_2$O$_5$.

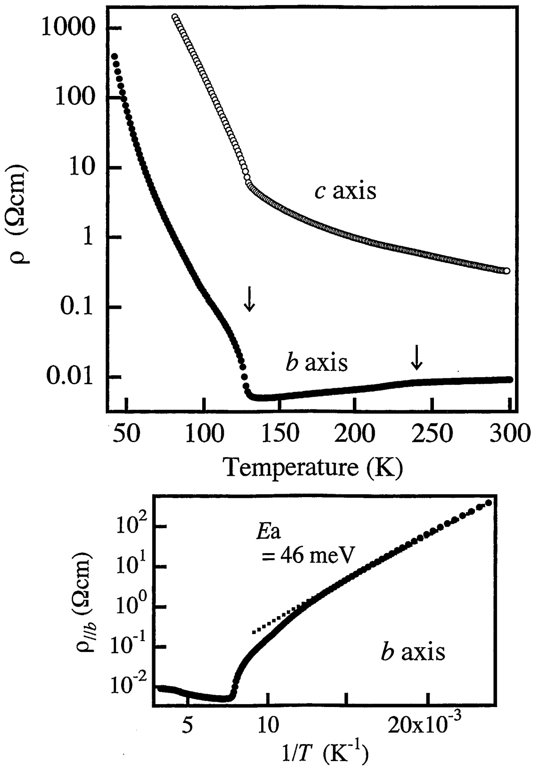

Fig. 4. (upper) Temperature dependences of electric resistivity of β-Na$_{0.33}$V$_2$O$_5$ measured along the b and c axis. (lower) Electric resistivity (∥ b) of β-Na$_{0.33}$V$_2$O$_5$ plotted against reciprocal of temperature.

such a magnetic ordering, it is naturally considered that the magnetic V^{4+} ions occupy 50% of only one of the three V sites and form a highly ordered structure, for example an infinite linear chain or alternate chain.

Above the magnetic transition we observed an anomaly in $\chi(T)$ around 130 K. A sharp peak in the specific heat at 136 K which is shown in Fig. 3 suggests that a structural phase transition occurred around the temperature. Although there was no change in crystal system at the transition, temperature dependence of lattice parameters confirmed the existence of the phase transition.

Figure 4 shows the temperature dependences of the electric resistivity ($\rho(T)$) of single crystalline β-Na$_{0.33}$V$_2$O$_5$ measured along both parallel (b) and perpendicular to the chain direction. We chose the c axis as the perpendicular direction, because the sample size along the a axis was much smaller than that along the c axis. It has been found that the conductivity along the b axis is slightly metallic at higher temperatures whereas that along the c axis is always semiconducting. We observed a drastic decrease in the conductivity along the b axis at the transition. The activation energy (Ea $\equiv -d(\ln(\rho_{\|b}))/d(1/T)$) was estimated to be about 46 meV between 85 K and 42 K. We consider that the transition involves a charge ordering.[9] Although there are some reports on electric resistivities or phase transitions in that compound,[2,10,11] we emphasize that this is a first direct evidence of anisotropic metal and metal-insulator transition in this compound. Why has it been so difficult to detect them in spite of those previous works? The conductivity in the high temperature phase was strongly affected by some imperfections in samples. The metallic coductivity was observed only with the single crystals with high qualities, and even the existence of the phase transition was not detected with polycrystalline samples.

Another characteristic point in the resistivity data is that there is a slight change in the curvature below 240 K. It suggests an existence of another broad phase transition, although there was no anomaly in the magnetic susceptibility. We performed XRD measurements and observed satellite peaks indicative of the twofold lattice constant along the b axis below ca. 230 K. They gradually increased the intensities with decreasing temperature, which is a similar result to the data in ref. 4 except a small difference in the transition temperature. According to ref. 4, this is an evidence of a bipolaron ordering which has been suggested by previous researchers.[1,3,12] If the origin of the transition at 230 K is attributed to such a phenomenon, there must be a drastic change in the electric resistivity or magnetic susceptibility. Moreover the intensities of the superstructure reflections were strong enough to observe with ordinary powder XRD measurements, namely they were too strong to attribute their origin to the simple ordering of V^{4+}. Therefore the development of the satellite peaks should be explained in terms of an ordering of the intercalated Na$^+$ ion. All Na$^+$ ions preferably occupy the same site (A1, Fig. 1(a)) until x reaches 0.333, when the site is 50% occupied. It is impossible for the site to accomodate more ions, because the two Na chains along the b axis in one tunnel is very close to each other (2.3 Å). It is never allowed to occupy the two nearest-neighboring sites at the same time. Therefore Na$^+$ ions can form a zigzag chain along the b axis if a displacement of the ion occurs, when the $1 \times 2 \times 1$ superstructure appears. It is not yet known whether the low temperature structure involves a more complicated structure, i.e. a superstructure along a or c axis. The structural analysis with the single crystal is now in preparation.

Figure 5 shows the magnetic susceptibility of β-Ag$_{0.33}$V$_2$O$_5$. The magnetic properties of β-Ag$_{0.33}$V$_2$O$_5$ were quite similar to those of β-Na$_{0.33}$V$_2$O$_5$, which suggests that the above discussion can be applied to β-

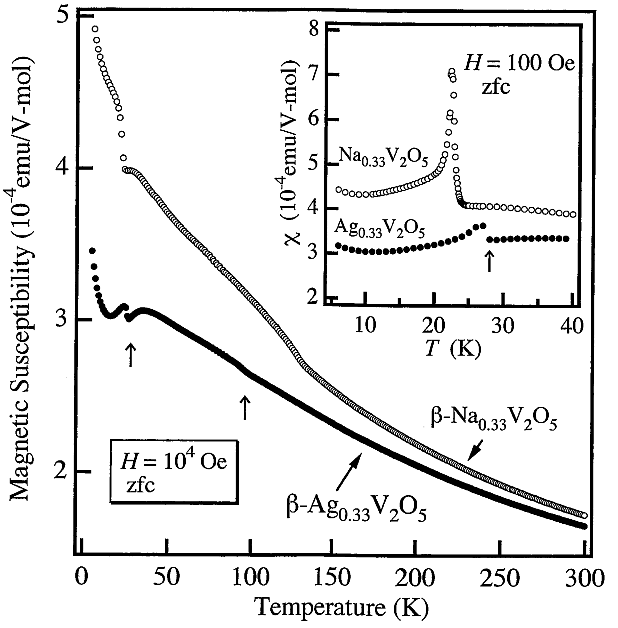

Fig. 5. Temperature dependences of magnetic susceptibility of powder β-$Ag_{0.33}V_2O_5$ measured with $H = 10^4$ and 10^2 Oe.

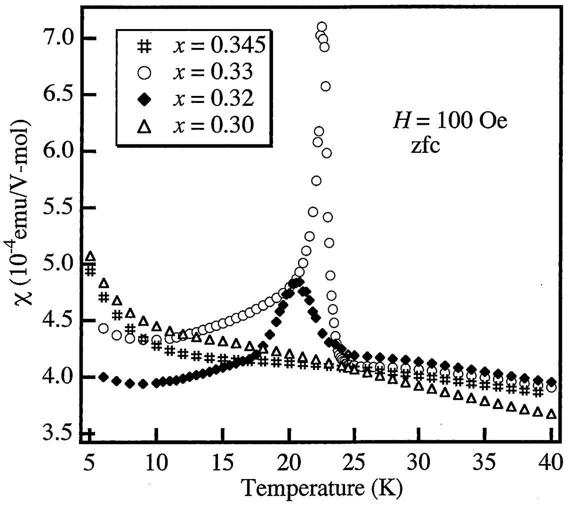

Fig. 6. Effect of Na nonstoichiometry on the magnetic transition: temperature dependences of magnetic susceptibility of β-$Na_xV_2O_5$ ($x = 0.30, 0.32, 0.33, 0.345$) measured with $H = 100$ Oe.

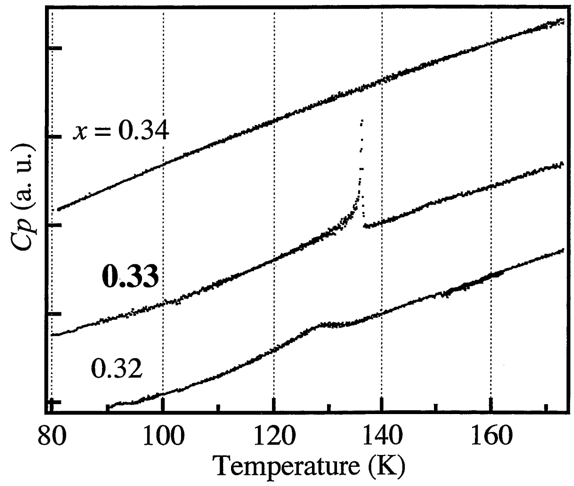

Fig. 7. Effect of Na nonstoichiometry on the metal-insulator transition: temperature dependence of specific heat of β-$Na_xV_2O_5$ ($x = 0.32, 0.33, 0.34$).

$Ag_{0.33}V_2O_5$. The magnetic transition occurred at 27 K and another transition was observed at 90 K. The satellite reflections were also similarly observed below 220 K. However, in spite of those similarities, the intensities of the superstructure reflections were much larger than those observed in β-$Na_{0.33}V_2O_5$. That supports our speculation that the superstructure is caused by the ordering of the cation, because the atomic scattering factor of Ag is larger than that of Na.

In summary, the possible scenario in an anisotropic metal β-$A_{0.33}V_2O_5$ is as follows. With decreasing temperature the intercalated A^+ ions gradually form a superstructure. Then a charge ordering occurs, when the metallic conductivity becomes semiconducting. The ordered structure finally undergoes a magnetic ordering. There is no need to take into accounts a bipolaron formation because of the absence of a spin-singlet state.

3.2 Effect of Na nonstoichiometry on the phase transitions

We investigated effects of Na deficiency/excess on the magnetic transition and the metal-insulator transition in β-$Na_{0.33}V_2O_5$.

The effect on the magnetic transition is shown in Fig. 6. It has been found that the magnetic transition is so sensitive to Na nonstoichiometry that the deviation from $x = 0.33$ in β-$Na_xV_2O_5$ significantly decreases both T_c and magnitude of the anomaly. The magnetic transition was undetectable in $x = 0.30$ or 0.345. It seems that the positive deviation (Na excess) was more effective than the negative (Na deficiency), if one considers that 0.345 is as near 0.333 as 0.320. The suppression similarly occurred in the metal-insulator transition, which was most clearly seen in the specific heat data shown in Fig. 7. As x deviated from 0.33, the sharp peak in the specific heat was significantly broadened and the transition temperature decreased. The close correlation between the two transitions supports our speculation on the phase transition around 130 K: it corresponds to a charge ordering and consequently a magnetic long-range ordering occurs.

Finally we speculate on the observations that the positive deviation was more effective than the negative. This unsymmetrical effect may be explained from the positions of intercalated alkali metal.[5,6] As discussed above with Fig. 1(a), 50% of the A1 site is occupied in β-$Na_{0.33}V_2O_5$. It is never allowed for more ions to occupy the A1 site. Therefore the additional ions must occupy another site (A2) when x is above 0.333. It is possible to consider that these additional ions on the minor site affect the magnetic or electric state much more significantly.

3.3 Electric and magnetic properties of β-$Na_xV_2O_5$

In §3.2 we reported the x dependence of the physical properties at the transitions. In this section we discuss

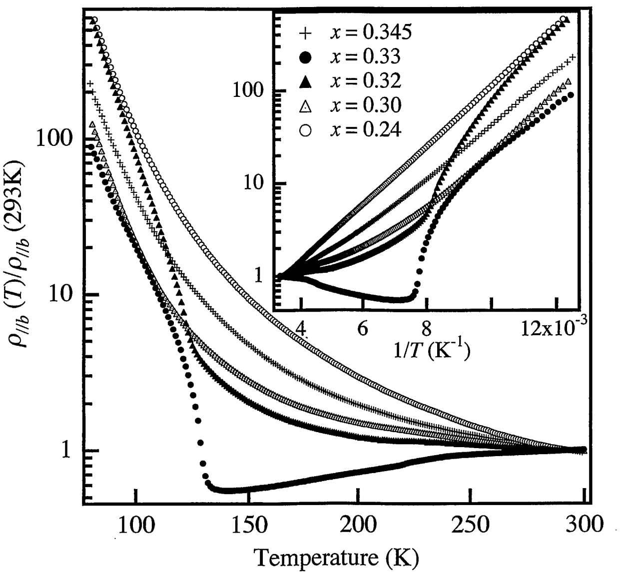

Fig. 8. Temperature dependences of electric resistivity of β-$Na_xV_2O_5$ ($x = 0.24, 0.30, 0.32, 0.33, 0.345$) normalized with the value at room temperature (293 K). Inset shows the replotting against reciprocal of temperature.

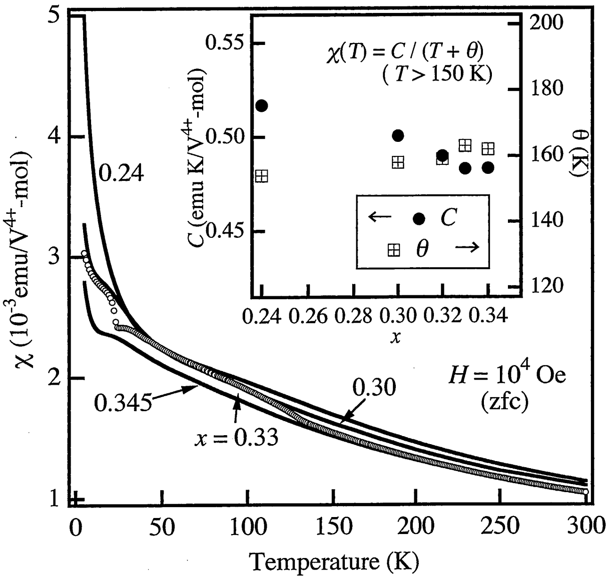

Fig. 9. Temperature dependences of magnetic susceptibility (χ) of β-$Na_xV_2O_5$ ($x = 0.24, 0.30, 0.33, 0.345$) normalized per V^{4+} (= Na) mol. The applied magnetic field is 10^4 Oe. Inset shows the x dependence of Curie and Weiss constants when χ is fitted to the Curie-Weiss law above 150 K.

the dependence above and below the transitions.

Figure 8 shows the resistivities of β-$Na_xV_2O_5$ plotted against temperarture and reciprocal of temperature. The resistivities were measured along the b axis. The data are normalized with ρ(293 K). The deviation of x from 0.33 made unclear the bending in $\rho(T)$, which agreed well with the specific heat data. Most importantly, the conductivity in the high temperature phase was significantly decreased and the metallic behavior was lost by the deviation. The resistivity of β-$Na_{0.24}V_2O_5$ obeyed an equation $\rho(T) = A\exp(-E\text{a}/T)$ with $E\text{a} = 62$ meV over a wide temperature range. Since the temperature dependence of the resistivity at lower temperatures was not so dependent on x, we are apt to misunderstand that the low temperature phase becomes stabilized by the deviation from $x = 0.33$. Needless to say, it is the high temperature phase that was stabilized, because the specific heat or the magnetic susceptibility data has indicated that the transition temperature is significantly decreased by the deviation.

Why is the metallic conductivity realized only near $x = 0.33$? Such phenomenon is rarely seen as a metal-insulator transition occurring against a composition change. This problem is complicated by an observation that the temperature dependence of χ at higher temperatures was not so dependent on x. Figure 9 indicates the tempearture dependences of the magnetic susceptibility of β-$Na_xV_2O_5$ normalized per V^{4+} mol. As previously reported, the $\chi(T)$ curve can be fitted quite well to the Curie-Weiss law, $\chi = C/(T+\theta)$ above 150 K whether $x = 0.33$ or not.[1] Pauli paramagnetic contribution was negligible. Although the Curie and Weiss constants slightly depended on x, there was no singular behavior which can be found only near $x = 0.33$.

If one looks for an idea which explaines the singularities in β-$Na_{0.33}V_2O_5$, a possible candidate may exist in structural properties. If one regards the double chain of A1 site as a ladder, every rung of the ladder always contains only one Na^+ ion when $x = 0.33$. When x is below 0.33, a vacancy is introduced, so that some rungs contain no ion. When x is above 0.33, an additional ion is introduced into A2 sites, which was discussed in §3.2. In that sense a distribution of Na^+ ion along the b axis becomes most uniform when $x = 0.33$. The deviation from $x = 0.33$ disorders the uniformity of the Na^+ chain. If the disorderedness in the crystal structure significantly affects the conductivities or the phase transitions, other related compounds such as β'-$Li_xV_2O_5$ or β'-$Cu_xV_2O_5$ will exhibit different physical properties.

In future we must distinguish the three extremes from a microscopic point of view: the high temperature phase of β-$Na_{0.33}V_2O_5$, the low temperature phase of β-$Na_{0.33}V_2O_5$ and β-$Na_{0.24}V_2O_5$. The electric properties macroscopically distinguishied the first one from others: only β-$Na_{0.33}V_2O_5$ exhibited a metallic conductivity at higher temperatures. We consider that the difference between them is attributed to a uniformity in a valency of vanadium as recently suggested by our NMR studies as mentioned above,[9] or NMR studies of α'-NaV_2O_5.[13] Further investigations, including a comparison between β-$Na_{0.33}V_2O_5$ and β-$Na_{0.24}V_2O_5$ are required and will be published elsewhere. On the other hands, the magnetic properties distinguished the second one from others: the magnetic transition was observed only near $x = 0.33$. If the difference results from a manner of charge ordering, structural analyses of the low temperature phase or determination of the magnetic structure are required.

§4. Conclusions

Single crystal of β-$Na_{0.33}V_2O_5$ has been successfully grown by a self flux method, using NaV_3O_8 as a flux. The single crystals with $x \neq 0.33$ can be prepared by a subsequent heat treatment.

We have systematically investigated physical properties of β-$Na_xV_2O_5$ as a function of x and T.

β-$Na_{0.33}V_2O_5$ is an anisotropic metal at higher temperatures. The deviation from $x = 0.33$ significantly decreases the conductivities.

The metallic β-$Na_{0.33}V_2O_5$ exhibits a metal-insulator transition at 136 K indicative of charge ordering, below which a long-range magnetic ordering occurs at 24 K. A development of the $1 \times 2 \times 1$ superstructure is observed below 230 K, suggesting an ordering of Na^+ ion. The discussions may be equally applicable to β-$Ag_{0.33}V_2O_5$. Those phase transitions are very sensitive to A nonstoichiometry. The deviation from $x = 0.33$ significantly decreases the transition temperature and magnitudes of the anomalies at the transitions.

Although β-$A_xV_2O_5$ has long been investigated in terms of a bipolaron formation, we propose reconsidering this compound family from view points of ordering of charge, hence spin and intercalated cation.

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