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Effect of Na-deficiency on the spin-Peierls transition in α'-NaV_2O_5

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Abstract

We have investigated the phase diagram of $Na_xV_2O_5$ in the composition range $0.7 \leq x \leq 1.5$ and the effect of Na-deficiency on the spin-Peierls transition in the quasi-one-dimensional (1D) magnet α'-NaV_2O_5. The α'-NaV_2O_5 phase exists in the composition range $0.80 \leq x \leq 1.00$. The spin-Peierls transition is suppressed by Na-deficiency and disappears around $x = 0.97$. The Curie-like increase of magnetic susceptibility was observed in α'-NaV_2O_5 at low temperature. Any evidence for a magnetic order in α'-$Na_xV_2O_5$ has never been observed in contrast to the Zn-doped $CuGeO_3$ or $SrCu_2O_3$. The electric resistivity decreases with Na-deficiency, although α'-$Na_xV_2O_5$ remains semiconductive in $0.80 \leq x \leq 1.00$. The temperature dependence of conductivity for the Na-deficient samples seems to be consistent with a variable range hopping in the 1D system. This suggests that the carriers are doped into the 1D chain by Na-deficiency but do not induce clean metallic behavior. We also report a low dimensional behavior in the magnetic susceptibility and a possible spin singlet state as the ground state in $Na_{1.3}V_2O_5$ (the η-phase). © 1997 Elsevier Science S.A.

Keywords: α'-NaV_2O_5; Na-deficiency; Spin-Peierls transition; Magnetic susceptibility; Electric conductivity

1. Introduction

There are many compounds, so called sodium–vanadium bronze, in the Na–V–O system. Seven phases, α $(0 < x \leq 0.02)$, β $(0.21 \leq x \leq 0.35)$, δ $(0.55 \leq x \leq 0.57)$, τ $(x = 0.64)$, α' $(0.79 \leq x \leq 1.00)$, η $(1.28 \leq x \leq 1.45)$ and κ $(1.68 \leq x \leq 1.82)$ have been reported [1–3]. The β-phase has been intensively investigated because of its quasi-one-dimensional (1D) conducting properties [4,5]. Recently we found the spin-Peierls transition in α'-NaV_2O_5 [6]. This is the second example of the inorganic spin-Peierls compound following $CuGeO_3$ [7]. The schematic crystal structure of α'-NaV_2O_5 is shown in Fig. 1. α'-NaV_2O_5 crystallizes in an orthorhombic cell with space group $P2_1mn$ [8]. It consists of layers formed by VO_5 square pyramids which share edges and corners. Sodium ions are located in the sites between the layers. There are two crystallographic vanadium sites which form two kinds of VO_5 chain (A and B in Fig. 1) along the *b*-axis and they are assigned to $V^{4+}O_5$ and $V^{5+}O_5$ chains, respectively. Therefore α'-NaV_2O_5 is expected to be a quasi-1D spin system because the magnetic $V^{4+}O_5$ chains are isolated by the non-magnetic $V^{5+}O_5$ chains in the structure. Actually we reported that the temperature dependence of magnetic susceptibility shows a good fit to the equation for a $S = 1/2$ antiferromagnetic Heisenberg linear chain and furthermore this compound shows the spin-Peierls transition at 35 K [6,9,10].

Recently a low-dimensional spin system with a spin gap and its doping or substitution effect have received much attention due to quantum effects of interest.

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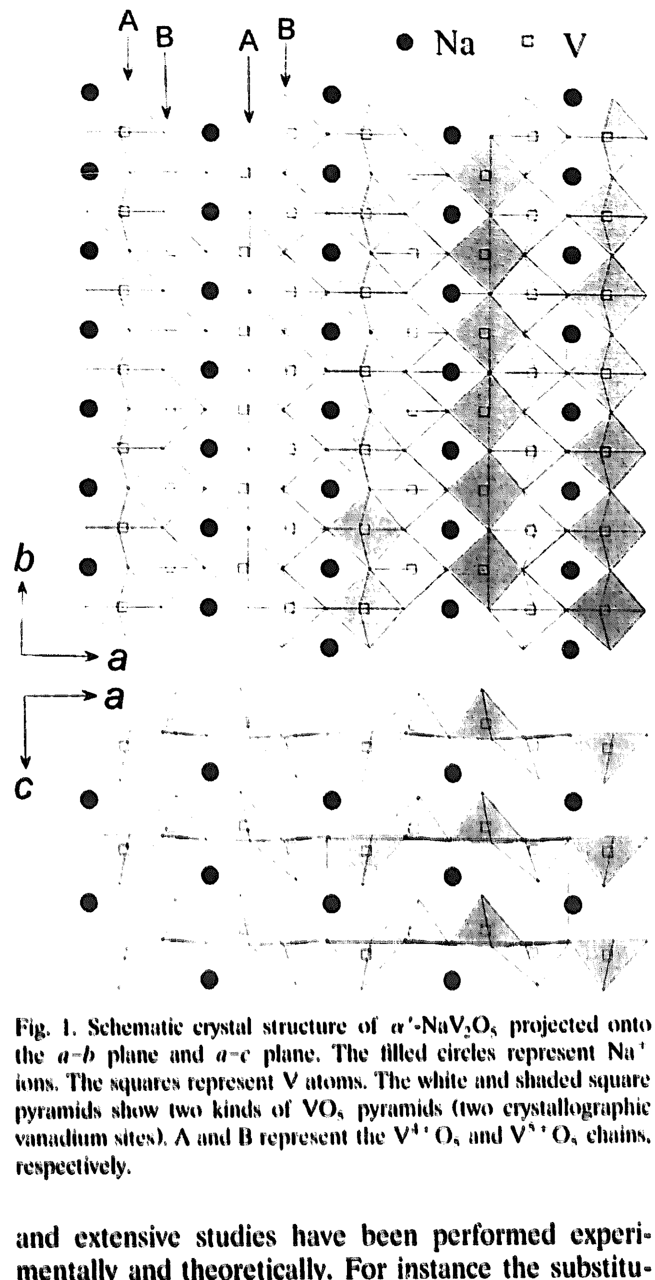

Fig. 1. Schematic crystal structure of α'-NaV_2O_5 projected onto the a–b plane and a–c plane. The filled circles represent Na^+ ions. The squares represent V atoms. The white and shaded square pyramids show two kinds of VO_5 pyramids (two crystallographic vanadium sites). A and B represent the $V^{4+}O_5$ and $V^{5+}O_5$ chains, respectively.

and extensive studies have been performed experimentally and theoretically. For instance the substitution of a small amount of Zn for Cu in the spin-ladder compound $SrCu_2O_3$ and the spin-Peierls compound $CuGeO_3$ leads to an antiferromagnetic long-range order [11] or the coexistence of a spin-Peierls state with a magnetically ordered state [12–14]. The doping effect in α'-NaV_2O_5 is very interesting. The previous report demonstrated the existence of Na-non-stoichiometry in α'-NaV_2O_5 (the existence of a Na-deficient compound) [6]. Sodium deficiency introduces non-magnetic V^{5+} ions in the magnetic V^{4+} linear chain. In the present study we have investigated the phase diagram of $Na_xV_2O_5$ in the composition range $0.7 \leq x \leq 1.5$ and the effect of Na-deficiency on the spin-Peierls transition in α'-NaV_2O_5. In this paper we report the magnetic and electric properties of α'-$Na_xV_2O_5$. We also report a low-dimensional behavior in the magnetic susceptibility and a possible spin singlet state as the ground state in $Na_{1.3}V_2O_5$ (the η-phase).

2. Experimental

Powder samples of $Na_xV_2O_5$ were prepared by the solid-state reaction of mixtures with appropriate molar ratios of $NaVO_3$, V_2O_3 and V_2O_5 [6]. Single crystals of α'-NaV_2O_5 were grown by the self-flux method [15]. Single crystals of α'-$Na_xV_2O_5$ were prepared by heating a small crystal of stoichiometric α'-NaV_2O_5 embedded in a large quantity of the powder sample of α'-$Na_xV_2O_5$ in an evacuated silica tube at 650°C for 1 week. By measuring the magnetic susceptibility, it was checked that the composition of the single crystals were identical to that of powder samples. The magnetic susceptibility was measured using a Quantum Design SQUID magnetometer. The electric resistivity measurements were made by an ordinary four-probe method using single crystals.

3. Result and discussion

The composition range of the α'-phase was $0.80 \leq x \leq 1.00$ in $Na_xV_2O_5$ in the present work, which was in agreement with the previous report [2]. This means that α'-NaV_2O_5 shows Na-deficiency but does not accommodate excess Na in the structure. Above $x = 1.0$ the η-phase coexisted with the stoichiometric α'-NaV_2O_5 and it existed as the single phase around $x = 1.3$. The η-phase seemed not to have a Na-non-stoichiometric region, which was different from the previous results [1]. The compositional dependence of lattice constants in the α'-phase is shown in Fig. 2. The a- and b-axis show a little change while the c-axis significantly decreases with an increase of Na-deficiency. Since Na ions lie between layers, the Na-deficiency mostly affects the interlayer distance.

The magnetic susceptibility of α'-NaV_2O_5 is relatively small comparing with that of other transition metal oxides and therefore it is influenced by the magnetic impurities accidentally included or a method of measurement. We have made an effort to improve the quality of the sample. Fig. 3 shows the most reliable data of the magnetic susceptibility measured using the powder sample. The magnetic susceptibility rapidly decreases with decreasing temperature below the spin-Peierls transition temperature of 35 K, as shown in the inset of Fig. 3. Above 35 K, the magnetic susceptibility shows a good fit to the Bonner–Fisher curve with $J/k_B = 560$ K and $g = 2$ [6]. Fig. 4 shows the magnetic susceptibility of the powdered α'-$Na_xV_2O_5$ below 80 K. The spin-Peierls transition is suppressed by Na-deficiency and vanishes around $Na_{0.97}V_2O_5$. The spin-Peierls transition was very sensitive to Na-deficiency. Mila et al. did not observe the

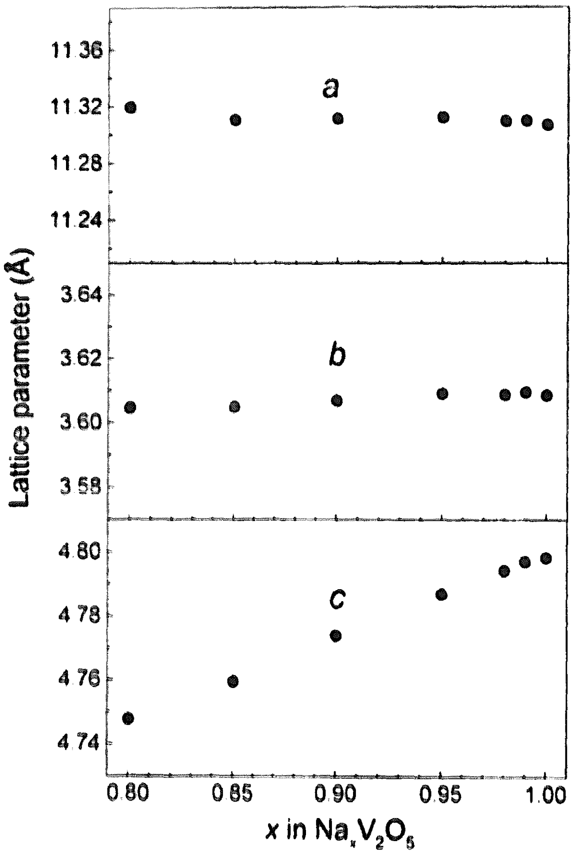

Fig. 2. Compositional dependence of lattice constants for α'-$Na_xV_2O_5$.

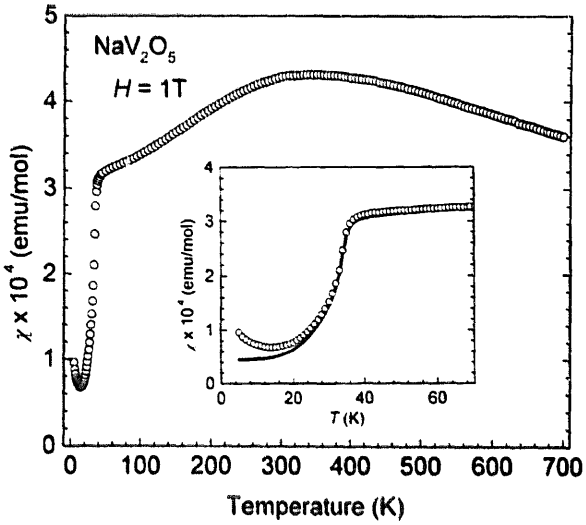

Fig. 3. Magnetic susceptibility of α'-NaV_2O_5 measured in a field of 1 T. The inset shows magnetic susceptibility of α'-NaV_2O_5 in the temperature range from 5 K to 700 K. The solid line shows the susceptibility derived by subtracting the Curie contribution.

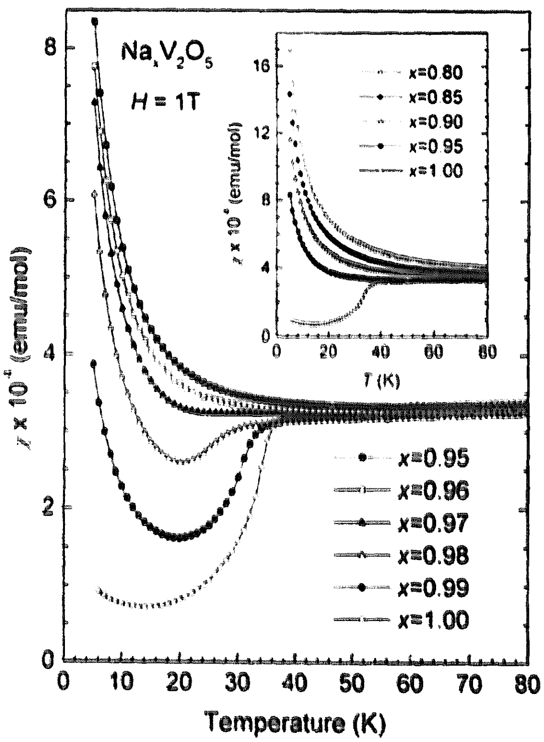

Fig. 4. Magnetic susceptibility of α'-$Na_xV_2O_5$ with $x = 0.95 \sim 1.00$ measured in a field of 1 T in the temperature range from 5 K to 80 K. The inset shows magnetic susceptibility of α'-$Na_xV_2O_5$ with $x = 0.80 \sim 1.00$.

spin-Peierls transition in α'-NaV_2O_5 [16]. This could be due to the deviation from stoichiometry in their samples. Sodium deficiency introduces non-magnetic V^{5+} ions in the magnetic V^{4+} linear chains and cuts the chains. The Curie-like increase of magnetic susceptibility which was in proportional to Na-deficiency was observed in α'-$Na_xV_2O_5$ at low temperature. Any evidence for a magnetic order, however, has never been observed in contrast to the Zn-doped $CuGeO_3$ or $SrCu_2O_3$. This indicates that α'-NaV_2O_5 is an ideal 1D magnetic system and the magnetic interchain interaction is very weak. The Curie constant obtained from fitting the magnetic susceptibility to the Curie–Weiss law between 5 K and 15 K is given in Fig. 5 as a function of y in $Na_{1-y}V_2O_5$. In this fitting, the obtained Weiss temperatures were in $0 \sim -0.9$ K in all samples. The dotted lines represent the $y/2$ and $y/12$ dependence, assuming free ion with $S = 1/2$ associated with Na-non-stoichiometry. At first the Curie constant increases with a proportion of $y/2$ and then $y/12$ above $y = 0.03$. The turning point of $y = 0.03$ corresponds to the composition at which the spin-Peierls transition disappears. The introduction of a non-magnetic ion into a magnetic linear chain affects the magnetic properties in a different manner in the spin-Peierls state and the magnetic 1D chain, respectively. Such an effect may be more remarkable in the state with a spin-gap than in the magnetic linear chain without a spin gap. Some theories predict that the compositional dependence of the Curie constant lies between $y/4$ and $y/12$ in the spin-ladder system with spin gap [17].

The electric resistivity of α'-$Na_xV_2O_5$ was measured along the b-axis (the linear chain direction)

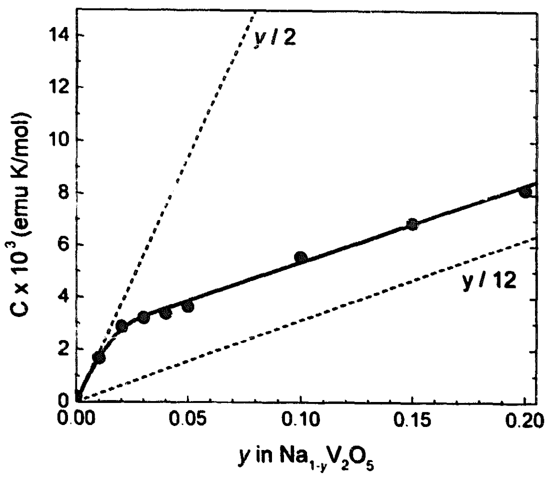

Fig. 5. Compositional dependence of Curie constant in α'-$Na_{1-y}V_2O_5$. The Curie constant was obtained from fitting the magnetic susceptibility to the Curie-Weiss low between 5 K and 15 K. The dotted lines represent the $y/2$ and $y/12$ dependence, respectively.

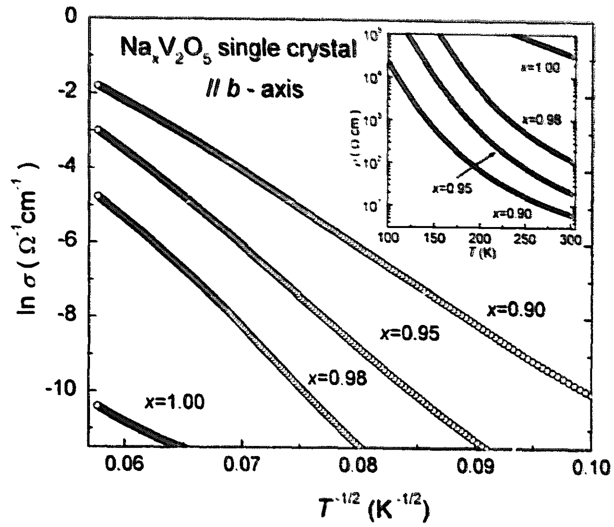

Fig. 6. Logarithm of the electric conductivity vs. $1/T^{-1/2}$ of α'-$Na_xV_2O_5$. The inset shows the resistivity of α'-$Na_xV_2O_5$ as a linear function of temperature.

using single crystals. The inset of Fig. 6 shows the resistivity of α'-$Na_xV_2O_5$ as a linear function of temperature. The resistivity of the stoichiometric sample was so high for our apparatus that the manner of temperature dependence was hardly determined. The resistivity in α'-$Na_xV_2O_5$ decreases with Na-deficiency but is semiconductive in all samples. The temperature dependence of conductivity in Na-deficient samples does not obey any activation-type behavior. Fig. 6 shows the plot of the logarithm of conductivity ($\ln\sigma$) vs. $1/T^{-1/2}$, where one can see a linear relation. The temperature dependence of Na-deficient samples seems to be consistent with a variable range-hopping in the 1D system. This suggests that the carriers are doped into the 1D chain by Na-deficiency but do not induce clean metallic behavior, because an arbitrary small concentration of defects often leads to localization in a 1D material. This is a significant point of difference from the doping effect in $CuGeO_3$ and $SrCu_2O_3$ where the doping or substitution of another cation for Cu has never resulted in the carrier doping but a long-range magnetic order.

Fig. 7 shows the magnetic susceptibility of η-$Na_{1.3}V_2O_5$. The magnetic susceptibility has a maximum around 110 K and decreases down to a small value at the lowest temperature, which indicates for η-$Na_{1.3}V_2O_5$ to be a low-dimensional magnetic system. The low magnetic susceptibility at the lowest temperature suggests a spin singlet state as the ground state. The origin of the anomaly around 110 K has not been discovered. That may be due to a trace of the Magnéli-phase vanadium oxides included in the sample. The structure of η-$Na_{1.3}V_2O_5$ has not been de-

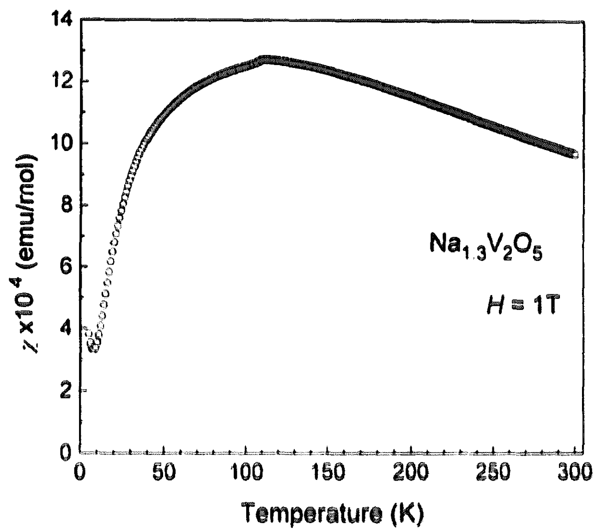

Fig. 7. Magnetic susceptibility of η-$Na_{1.3}V_2O_5$ measured in a field of 1 T.

termined yet and we cannot discuss the observed magnetic property in relation to the structure. Fortunately, we obtained a small single crystal. Studies of its structure and physical properties are now in progress.

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