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Magnetic Susceptibility of Quasi-One-Dimensional Compound α'-NaV_2O_5 —Possible Spin-Peierls Compound with High Critical Temperature of 34 K—

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Stoichiometric powder samples of α'-NaV_2O_5 were synthesized and the magnetic susceptibility was measured in the temperature range from 2 K to 700 K. The magnetic susceptibility has a good fit to the equation for an $S = 1/2$ antiferromagnetic Heisenberg linear chain with $J/k_B =$ 280 K and $g = 2$ above 34 K. Below 34 K the magnetic susceptibility rapidly decreases with decreasing temperature to a constant value of 1.49×10^{-4} emu/V^{4+}-mol which is reasonable for spin-singlet V^{4+}–V^{4+} pairs. This rapid reduction of the spin susceptibility below 34 K suggests the existence of a spin-Peierls transition. α'-NaV_2O_5 is a possible spin-Peierls compound with the highest critical temperature yet observed.

KEYWORDS: α'-NaV_2O_5, magnetic susceptibility, $S = 1/2$ antiferromagnetic Heisenberg linear chain, spin-Peierls transition

The magnetic properties of low-dimensional systems have attracted considerable interest recently. The spin-Peierls transition, which is one of the interesting phenomena in one-dimensional (1-D) systems, has been found in organic compounds.[1] It is one of the quantum phenomena in an $S = 1/2$ antiferromagnetic Heisenberg linear chain which couples to a lattice system. Below the critical temperature, a finite energy gap opens in the magnetic excitation spectrum accompanying with a lattice distortion (lattice dimerization) and the spin system is in a spin-singlet (nonmagnetic) state. The first inorganic compound in which a spin-Peierls transition was observed was $CuGeO_3$.[2] Spin-gap behavior without any lattice distortion was observed in $(VO)_2P_2O_7$[3] and $SrCu_2O_3$[4] which have a quasi-1-D ladder structure, and also in CaV_4O_9[5] which has a quasi-2-D structure. Recently we observed a similar spin-gap behavior in CaV_2O_5[6] which has a ladder-type structure. The structure of α'-NaV_2O_5 is similar to that of CaV_2O_5. CaV_2O_5 is a tetravalent vanadium oxide while α'-NaV_2O_5 is a mixed-valence ($V^{4+}/V^{5+} = 1$) oxide.

α'-NaV_2O_5 is one of the compounds in the $Na_xV_2O_5$ system. Five bronze phases, α ($0 < x \leqq 0.02$), β ($0.22 \leqq x \leqq 0.40$), α' ($0.70 \leqq x \leqq 1.00$), η ($1.28 \leqq x \leqq 1.45$), and χ ($1.68 \leqq x \leqq 1.82$), have been reported.[7] Of these, the β-phase has been intensively investigated because of its quasi-1-D conducting properties.[8,9] There are few reports on the physical properties of other phases. α'-NaV_2O_5 crystallizes in an orthorhombic cell with space group $P2_1mn$.[10] The schematic crystal structure of α'-NaV_2O_5 is shown in Fig. 1. It consists of layers of VO_5 square pyramids which share edges and corners with sodium ions lying between the layers. There

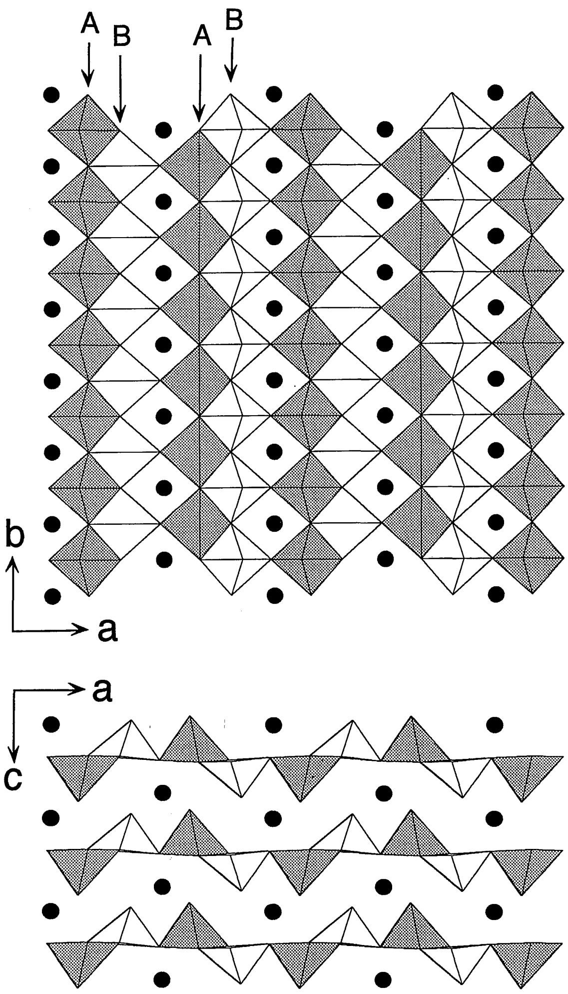

Fig. 1. Schematic crystal structure of α'-NaV_2O_5 projected onto the *a*-*b* plane and *a*-*c* plane. The filled circles represent Na^+ ions. The white and shaded square pyramids show two kinds of VO_5 pyramids (two crystallographic vanadium sites). A and B represent the $V^{4+}O_5$ and $V^{5+}O_5$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

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are two crystallographic vanadium sites, which form two kinds of VO_5 chain (A and B in Fig. 1) along the b-axis. Analysis of the V-O bond length and Na–V distance indicated that the A and B chains are possibly $V^{4+}O_5$ and $V^{5+}O_5$ chains, respectively.[10] Therefore α'-NaV_2O_5 is expected to be a quasi-1-D spin system because the magnetic $V^{4+}O_5$ chains are isolated by the nonmagnetic $V^{5+}O_5$ chains in the structure. The static susceptibility was measured by Carpy *et al.* in the temperature range from 80 K to 397 K.[11] They reported that the susceptibility has a broad maximum at around room temperature. Ogawa *et al.* studied α'-NaV_2O_5 as a quasi-1-D conducting system by means of EPR and NMR.[12] They measured the EPR susceptibility down to 12 K and proposed a spin-singlet state based on the bipolaron model as the ground state, although no anomalous behavior was observed in the temperature dependence of EPR susceptibility. They also suggested the existence of a V^{4+} zigzag chain, rather than a linear chain. We have prepared powder samples of α'-NaV_2O_5 with attention to the stoichiometry and carefully measured the static magnetic susceptibility in the temperature range from 2 K to 700 K.

In this letter, we report that α'-NaV_2O_5 is a typical $S = 1/2$ 1-D antiferromagnetic Heisenberg linear chain system. We also report a rapid decrease in the magnetic susceptibility below 34 K and therefore a possible spin-Peierls transition in α'-NaV_2O_5. $CuGeO_3$ is the only inorganic spin-Peierls compound yet found. α'-NaV_2O_5 is possibly not only the second inorganic spin-Peierls compound found but also the spin-Peierls compound with the highest critical temperature among organic and inorganic compounds.

Powder samples were prepared by the solid-state reaction of mixtures with appropriate molar ratios of $NaVO_3$, V_2O_3 and V_2O_5. The weighed mixtures were pressed into pellets and heated at 650°C in an evacuated silica tube for several days with one intermediate grinding. A blue-black product of α'-NaV_2O_5 was obtained. The starting compounds V_2O_3 and V_2O_5 were prepared by reducing NH_4VO_3 in H_2 gas at 900°C for 2 days and by decomposing it in O_2 gas at 600°C for 2 days, respectively. $NaVO_3$ was prepared by heating mixture of Na_2CO_3 and V_2O_5 in air at 550°C for 2 days. The prepared samples were characterized by powder X-ray diffraction. In our experiments they were of single phase in the composition range from $x = 0.9$ to 1.02 in $Na_xV_2O_5$. The lattice constants of the sample with the nominal composition of $x = 1.02$ are $a = 1.130(8)$ nm, $b = 0.361(1)$ nm and $c = 0.480(1)$ nm at room temperature. This sample was considered to be the stoichiometric one, because sodium had a tendency to be slightly sublimated during the reaction.

The magnetic susceptibility (χ) was measured using a Quantum Design SQUID magnetometer in the temperature range from 2 K to 700 K. The sample was sealed into an originally designed quartz capillary with He gas for measurements above 300 K. No significant difference was observed between the data measured on heating after cooled under zero-field and 1 T. The raw data of χ for the best sample ($x = 1.02$) measured at $H = 1$ T are

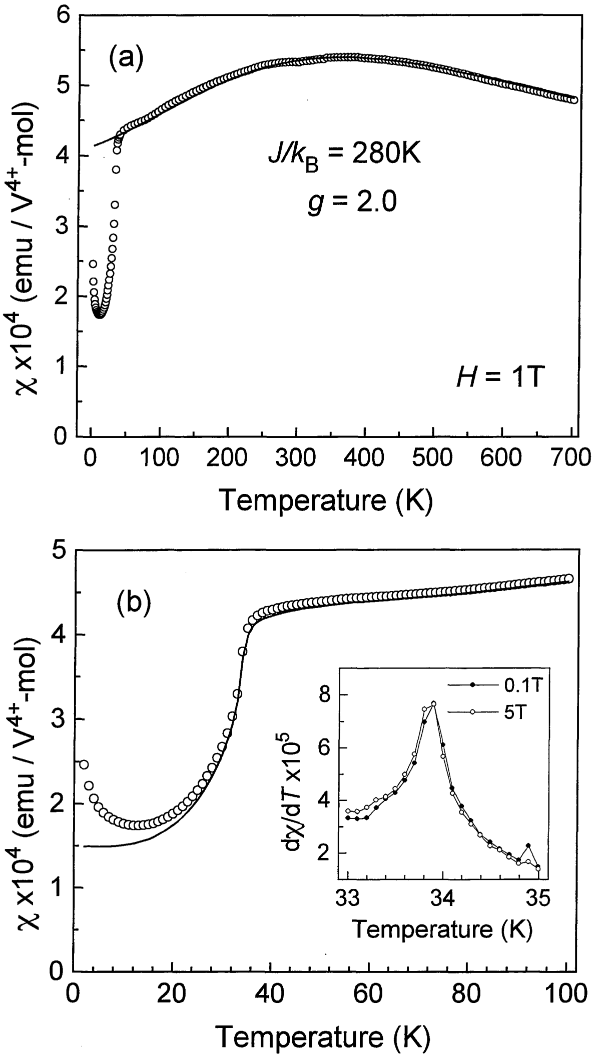

Fig. 2. (a) Raw data of magnetic susceptibility of α'-NaV_2O_5 measured in a field of 1 T. The solid line represents the fit to the equation for the $S = 1/2$ 1-D Heisenberg model (see text). (b) Magnetic susceptibility of α'-NaV_2O_5 in the temperature range from 2 K to 100 K. The solid line shows the susceptibility derived by subtracting the Curie contribution (see text). The inset shows $d\chi/dT - T$ plots.

shown in Figs. 2(a) and 2(b) as a function of temperature (T). χ has a broad maximum at around room temperature, which reflects the low-dimensional nature of the spin system and is consistent with the characteristics of the structure. Furthermore, χ rapidly decreases below 34 K with decreasing temperature, showing a slight upturn below 12 K. The upturn of χ below 12 K was considered to be due to the existence of impurities and/or free ions caused by defects. Assuming impurities with $S = 1/2$, the concentration was estimated to be less than 0.1%. The subtraction of this Curie contribution gives a constant value of about 1.49×10^{-4} emu/V^{4+}-mol below 12 K, as can be seen in Fig. 2(b). This value is comparable to χ ($\sim 1.2 \times 10^{-4}$ emu/V^{4+}-mol) of the insulating phase of VO_2 in which the well-known spin-singlet V^{4+}-V^{4+} pairs are formed.[13] This indicates the formation of a spin-singlet state at low temperature in α'-NaV_2O_5. The existence of a spin-singlet state was also inferred from the effect of Na deficiency on χ, as described below. χ at low temperature increased in proportion to the degree of Na deficiency. For example the large increase in χ at low temperature in $Na_{0.9}V_2O_5$ masked the reduction of χ at around 34 K. Na deficiency results in additional V^{5+} ions. The nonmagnetic V^{5+} ions themselves have no influence on the spin susceptibility but are expected to have a significant effect on it when the spin system is in a spin-singlet state, because the additional V^{5+} ions disturb the formation of V^{4+}-V^{4+} spin pairs and free magnetic V^{4+} ions are produced in the spin-singlet V^{4+}-V^{4+} chains.

Now we can estimate χ_0 (the sum of the diamagnetic and Van Vleck paramagnetic parts) of α'-NaV_2O_5 to be 1.49×10^{-4} (emu/V^{4+}-mol). Using χ_0 we tried to fit χ to the following equation for the $S = 1/2$ 1-D (infinite linear chain) model:[14]

$$\chi = \frac{Ng^2\mu_B^2}{k_BT} \cdot \frac{A + BX^{-1} + CX^{-2}}{1 + DX^{-1} + EX^{-2} + FX^{-3}} + \chi_0,$$

where $X = k_BT/|J|$, g is the powder-averaged g-factor, and J the exchange constant. The following coefficients which were obtained by fitting the 1-D equation to a theoretical calculation for the $S = 1/2$ Heisenberg system[14] were used in our calculation: $A = 0.25$, $B = 0.14995$, $C = 0.30094$, $D = 1.9862$, $E = 0.68854$ and $F = 6.0626$. The result is shown by the solid line in Fig. 2(a). The good fit indicates that α'-NaV_2O_5 is a typical $S = 1/2$ 1-D antiferromagnetic Heisenberg linear chain system. The best fit to the equation was obtained with $J/k_B =$ 280 K and $g = 2.0$.

The rapid reduction of the spin susceptibility below 34 K strongly suggests the existence of a spin-Peierls transition. The critical temperature is estimated to be 33.9 K from $d\chi/dT - T$ plots which are shown in the inset of Fig. 2(b). We carried out powder X-ray diffraction measurement at low temperature. The lattice constants are shown in Fig. 3 as a function of temperature. The lattice constants smoothly change with temperature and tend to become constant below 50 K without any significant discontinuous change. No discontinuous change of lattice constants has been observed in $CuGeO_3$ by powder X-ray diffraction originally because the change in atomic position is slight.[15] A detailed structural analysis using single crystals should be carried out in order to confirm the lattice dimerization. The field dependence of the critical temperature in $CuGeO_3$ was reported as evidence of the spin-Peierls transition.[2] We examined the critical temperature under fields of 0.1 T and 5 T which was the maximum field obtainable using our apparatus. The temperature at the maximum of $d\chi/dT$ appears to be slightly lower at 5 T than at 0.1 T, as shown in the inset of Fig. 2(b). However a field of 5 T is too low to determine the change in the critical temperature, we believe, because the critical temperature (34 K) in α'-NaV_2O_5 is much higher than that (14 K) in $CuGeO_3$.

In summary, we synthesized stoichiometric powder samples of α'-NaV_2O_5 and measured the magnetic susceptibility in the temperature range from 2 K to 700 K. The magnetic susceptibility has a maximum at around room temperature and below 34 K rapidly decreases with decreasing temperature to the constant value χ_0. The

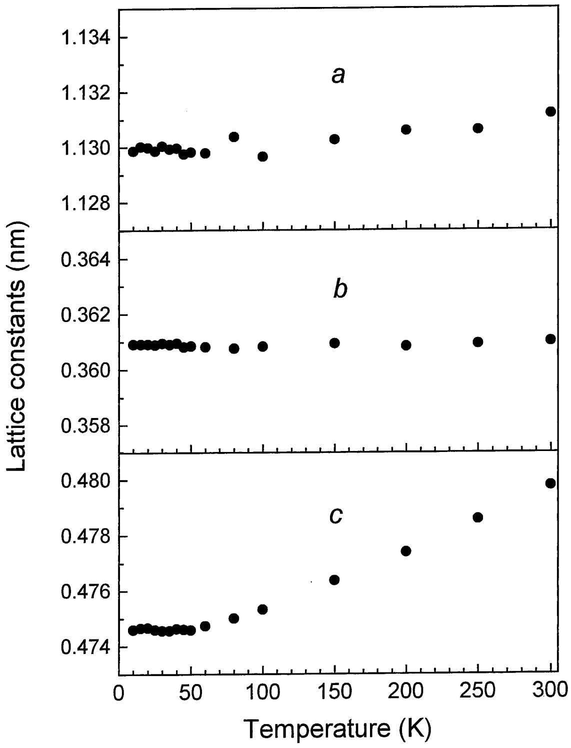

Fig. 3. Temperature dependence of lattice constants of α'-NaV_2O_5.

magnetic susceptibility above 34 K shows a good fit to the equation for an $S = 1/2$ antiferromagnetic Heisenberg linear chain with $J/k_B = 280$ K and $g = 2$. The ground state of α'-NaV_2O_5 was concluded to be a spin-singlet state because of the reasonable value of χ_0 for spin-singlet V^{4+}-V^{4+} pairs and the significant effect of Na deficiency on χ. The rapid reduction in spin susceptibility below 34 K suggests the existence of a spin-Peierls transition. α'-NaV_2O_5 is possibly the second example of a spin-Peierls inorganic compound. It should be noted that the observed critical temperature is the highest among spin-Peierls organic and inorganic compounds at present. NMR, heat capacity and more detailed diffraction studies are now being planned.

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1) See for review, S. Inagaki and H. Fukuyama: Kotai Buturi **60** (1985) 369 [in Japanese].
2) M. Hase, I. Terasaki and K. Uchinokura: Phys. Rev. Lett. **70** (1993) 3651.
3) D. C. Johnston, J. W. Johnson, D. P. Goshorn and A. J. Jacobson: Phys. Rev. B **35** (1987) 219.
4) M. Azuma, Z. Hiroi, M. Takano, K. Ishida and Y. Kitaoka: Phys. Rev. Lett. **73** (1994) 3463.
5) S. Taniguchi, T. Nishikawa, Y. Yasui, Y. Kobayashi, M. Sato, T. Nishioka, M. Kontani and K. Sano: J. Phys. Soc. Jpn. **64** (1995) 2758.
6) H. Iwase, M. Isobe, Y. Ueda and H. Yasuoka: submitted to J. Phys. Soc. Jpn.
7) M. Pouchard, A. Casalot, J. Galy and P. Hagemuller: Bull. Soc. Chim. Fr. **11** (1967) 4343.

8) Y. Kanai, S. Kagoshima and H. Nagasawa: J. Phys. Soc. Jpn. **51** (1982) 697.
9) M. Onoda, T. Takahashi and H. Nagasawa: Phys. Status Solidi B **109** (1982) 793.
10) A. Carpy and J. Galy: Acta Crystallogr. Sect. B **31** (1975) 1481.
11) A. Carpy, A. Casalot, M. Pouchard, J. Galy and P. Hagenmuller: J. Solid State Chem. **5** (1972) 229.
12) K. Ogawa, M. Onoda and H. Nagasawa: J. Phys. Soc. Jpn. **55** (1986) 2129.
13) See for reviews, J. B. Goodenough: *Progress in Solid State Chemistry* (Pergamon Press, New York, 1971) Vol. 5, p. 145; N. F. Mott: *Metal-Insulator Transition* (Taylor and Francis, London, 1974).
14) W. E. Hatfield: J. Appl. Phys. **52** (1981) 1985.
15) J. E. Lorenzo, K. Hirota, G. Shirane, J. M. Tranquada, M. Hase, K. Uchinokura, H. Kojima, I. Tanaka and Y. Shibuya: Phys. Rev. B **50** (1994) 1278.