Sample quality and magnetic properties of Ca$_{1-x}$Na$_x$V$_2$O$_4$

Hiroya Sakurai$^1$, Hiroyuki Takeya$^2$, and Kazuo Hirata$^2$

$^1$ National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan
$^2$ National Institute for Materials Science, 1-2-1 Sengen, Tsukuba 305-0047, Japan

E-mail: sakurai.hiroya@nims.go.jp

Abstract. Ca$_{1-x}$Na$_x$V$_2$O$_4$ shows a variety of physical properties depending on temperature, magnetic field and the composition. We made the $x = 1/6$, 1/3 and 1/2 samples under a high pressure of 6 GPa and grew single crystal of CaV$_2$O$_4$ at ambient pressure using floating-zone technique. The samples of the solid-solution system were found to be of high quality. On the other hand, antiferromagnetic transition temperature, $T_N$, of the single crystal was $T_N = 66$ K, which is significantly lower than that of the raw materials ($T_N = 78$ K) as reported previously. This is probably because Ca content of the single crystal is slightly smaller than that of the powder. Electron probe microanalysis indicated that the true composition of the single crystal is Ca$_{0.99}$V$_2$O$_4$.

1. Introduction

AV$_2$O$_4$ (A = Ca or Na) crystallizes in calcium ferrite type structure, which is composed of the double chains of VO$_6$ octahedra, as shown in Fig. 1. Because low-dimensional electron correlations and geometrical frustration are expected in the compounds, much effort has recently been made to clarify their physical properties. The double chains in CaV$_2$O$_4$, which is electrically insulating, can be identified as Haldane chains at a high temperature and as spin ladders at a low temperature, and it finally settles in antiferromagnetic (AF) ordered state below $T_N = 51 - 78$ K [1, 2, 3, 4]. In the magnetic behavior, the orbital degree of freedom plays an important role [2, 3, 4]. On the other hand, NaV$_2$O$_4$ shows AF ordering at $T_N = 140$ K maintaining metallic conductivity [5]. Photoemission spectroscopy measurement revealed the suppression of the spectral density of state and the power law behavior, as expected for the Tomonaga-Luttinger liquid, indicating one-dimensional nature of the compound [6]. Due to neutron diffraction measurements, incommensurate spin-density-wave state with magnetic moment perpendicular to the chains is thought to be the most probable magnetic ground state [7]. Interestingly, the AF phase can be divided into, at least, three subphases of AF1, AF2, and AF3, depending on the temperature and the magnetic field [8]. AF1 phase covers the small area of high temperature and low field, AF2 phase is stabilized under a high field in a wide temperature range below $T_N$, and AF3 phase, including the ground state, is seen at a low-temperature and low-field region. Magnetization, electrical resistivity and specific heat measurements indicated that, when Na ions are substituted with Ca ions, the $T_N$ value decreases and AF1 phase becomes dominant as seen in Fig. 2. Below a certain Na content, the compound exhibits metal-insulator transition at the temperature where the magnetic susceptibility shows a peak. As the Na content
further decreases, the metal-insulator transition becomes obscure and finally disappears [8]. This complex phase diagram has been confirmed by muon spin rotation/relaxation (μSR) [9, 10], $^{51}$V and $^{23}$Na nuclear magnetic resonance (NMR) [11, 12], and optical conductivity measurements [13]. Pressure effect was also studied [14]; $T_N$ and $T_{n1}$, the temperature of the phase boundary between AF1 and AF2, decrease with increasing pressure under the magnetic field of 1 T at the suppression rates of 5.2 K/GPa and 4.2 K/GPa, respectively, which is very consistent with μSR results at 1.7 GPa [9, 10]. However, it is strange that AF3 phase becomes stable at 1.7 GPa at 3 K for Ca$_{1/6}$Na$_{5/6}$V$_2$O$_4$, in which at ambient pressure only AF1 phase was observed down to 1.8 K [9, 10], although for NaV$_2$O$_4$ $T_{n2}$, the temperature of the phase boundary between AF2 and AF3, decreases more rapidly with increasing pressure above 0.4 GPa under 1 T than $T_N$ or $T_{n1}$.

![Figure 1. Structure of AV$_2$O$_4$ (A = Ca or Na) (a) and the double chain (b) The octahedra and the circle represent VO$_6$ octahedra and A, respectively.](image)

2. Experimental

Powder CaV$_2$O$_4$ was obtained by reduction reaction of CaV$_2$O$_6$, which was in advance made from the stoichiometric mixture of CaCO$_3$ and V$_2$O$_5$ at 700°C in air. The reaction was performed in flowing H$_2$ gas at 1000°C for 6 hours. Single crystal of CaV$_2$O$_4$ was grown from the powder by conventional floating-zone method in flowing 5% H$_2$/Ar gas. White powder appeared very thinly on the lining of the quartz tube of the floating-zone furnace. The crystal was annealed in flowing H$_2$ gas at 1000°C for 2 hours and then cooled slowly in the furnace.

Powder samples of Ca$_{1-x}$Na$_x$V$_2$O$_4$ ($x = 1/6$, 1/3, and 1/2) were synthesized from the stoichiometric mixtures of CaO, V$_2$O$_3$ and Na$_4$V$_2$O$_7$. CaO was prepared by decomposition of CaCO$_3$ at 1050°C in flowing Ar gas. V$_2$O$_3$ was made from V$_2$O$_5$ by being heated in flowing H$_2$ gas at 600°C for 4 hours and then at 800°C for 2 hours. Na$_4$V$_2$O$_7$ was synthesized from the stoichiometric mixture of Na$_2$CO$_3$ and V$_2$O$_5$ in air at 550°C. Because CaO and Na$_4$V$_2$O$_7$ are reactive with water and/or carbon dioxide in air, they were put in a dry box filled with Ar immediately after they were synthesized. Weighing, mixing and sealing in Au capsule were performed in the dry box. The samples were pressed in a belt-type press under 6 GPa, and heated at 1300°C for 1 hour. The pressure was released after the temperature was quenched to room temperature.

X-ray diffraction (XRD) measurements were performed on a commercial diffractometer, X’pert, Panalatica, using Cu Kα radiation. Ca contents in the CaV$_2$O$_4$ samples were determined by electron probe microanalysis (EPMA). Four pieces of single crystals taken from different parts of the crystal rod, as well as sintered pellet of the powder sample, were used for the analysis. Ca content, $y$ in Ca$_y$V$_2$O$_4$, was determined as the mean of the values obtained from more than five spots on each sample, to be $y = 1.00$ for the powder sample and $y = 0.99$ for each single crystal. Magnetic data were corrected under 1 T using a commercial magnetometer, MPMS-XL, Quantum Design.
3. Results and Discussion

XRD patterns of the samples are shown in Fig. 3. In the pattern of the \( x = 1/6, 1/3, \) or \( 1/2 \) sample, a peak from impurity is detectable at \( 2\theta = 48.3^\circ \). No other impurity peak was distinguishable from the peaks coming form \( \text{Ca}_{1-x}\text{Na}_x\text{V}_2\text{O}_4 \). The impurity is likely \( \text{CaVO}_3 \) because Varga et al. observed it in their samples [15]. We did not find \( \text{V}_2\text{O}_3 \) or \( \text{NaV}_6\text{O}_{11} \), which they found in their samples. It should be emphasized that our previous experiments [7, 8, 9, 10, 11, 12, 13] were performed using as high quality samples as these.

For \( x = 1/6 \) and \( 1/3 \) samples, the width of some peaks, for example the peak at \( 2\theta \sim 36^\circ \), is a little larger than that for \( x = 0 \) or \( 1/2 \), which is likely due to the phase separation observed by \( \mu \text{SR} \) and NMR [9, 10, 11]. Since the phase separation seems imperfect as suggested by the gradual change in the normalized weak transverse-field asymmetry [9, 10], it is possibly suppressed by more rapid thermal quenching and/or by quenching from higher temperature.

Magnetic susceptibility of \( \text{CaV}_2\text{O}_4 \) was shown in Fig. 4. The \( T_N \) values were estimated from the peaks of the differentiated curves to be \( T_N = 78 \) K for the powder sample and 66 K for the single crystal. The difference in the \( T_N \) value is most likely due to the difference in Ca content. Probably, the compound can accommodate such a amount of Ca defects (~1%) at around the melting point although it cannot below about 1200°C. This idea can explain why \( T_N \)
of the as-grown crystal is the lowest and why $V_2O_3$ inclusion appeared in the crystals annealed at 1200°C in flowing 5% $H_2/He$ gas [2]. The partial lack of Ca ions increases the V valence as in the case of the substitution of Ca with Na ions to lower $T_N$, and annealing enhances $T_N$ because the Ca defects gather to form Ca$V_2O_4$ with full Ca ions. $V_2O_3$ would be made during the annealing process because VO$_2$ is reduced by hydrogen gas.

Figure 4. Temperature dependences of magnetic susceptibility of Ca$V_2O_4$ (a) and their differentiated curves (b). The average curve was calculated as the mean of the three kinds of susceptibility.

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