

RANDOM MAGNET OF QUASI-ONE DIMENSIONAL CONDUCTOR  $\text{Na}_{0.2}\text{V}_2\text{O}_5$   
BRONZES

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The susceptibility of  $\text{Na}_{0.2}\text{V}_2\text{O}_5$  showed a power law dependence on the temperature:  $\chi \propto T^{-\alpha}$ . This behavior of the susceptibility and the magnetic field dependence of the specific heat for the same crystal is explained by the exchange-coupled pair model.

## 1. Introduction

The  $\beta$ -phase vanadium bronze  $\text{Na}_x\text{V}_2\text{O}_5$  is a non-stoichiometric compound and has a monoclinic structure with double chains of vanadium ions [1]. There are three inequivalent vanadium sites labeled  $V_1$ ,  $V_2$  and  $V_3$  [2].  $V_1$  and  $V_2$  sites have a deformed octahedral oxygen environment and  $V_3$  site has a nearly bipyramidal oxygen environment.  $V_1$ ,  $V_2$  and  $V_3$  sites construct different two double chains which are parallel to the monoclinic  $b$  axis. These chains surround tunnels which can accommodate sodium ions. Each sodium ion has donated its valence electron to a neighbouring vanadium ion making this a magnetic  $V^{4+}$  ion [3]. Chains of  $V^{4+}$  ions exhibit one dimensional transport properties parallel to the  $b$ -axis [4].

Recently, Chakraverty et al. [5] proposed a bipolaron model and explained a linear term in temperature of the specific heat of nonmetallic vanadium bronzes by a tunneling motion of these non-magnetic bipolarons to nearly equivalent neighboring sites.

However, Schlenker et al. [6] found a weak ferromagnetic phase transition at  $\sim 20$  K for  $\text{Na}_{0.33}\text{V}_2\text{O}_5$  single crystal and suggested antiferromagnetic couplings along the  $b$ -axis and ferromagnetic couplings in the  $a$ - $c$  plane.

To understand the magnetic properties of  $\text{Na}_x\text{V}_2\text{O}_5$  in more detail, Amarasekara et al. [7] measured the specific heat of  $\text{Na}_x\text{V}_2\text{O}_5$  ( $x=0.2, 0.25, 0.3, 0.36$  and  $0.41$ ) with and without the magnetic field. They explained the results by taking account of magnetically coupled spin pairs and isolated spins.

We will discuss below the magnetic properties of  $\text{Na}_x\text{V}_2\text{O}_5$  in terms of the exchange-coupled pair model of Clark and Tippie [8].

## 2. Experiment

Single crystals of  $\text{Na}_x\text{V}_2\text{O}_5$  were grown by a Bridgman method. The largest crystal ( $0.5 \times 2 \times 10 \text{ mm}^3$ ) grew for  $x=0.33$  and for  $0.20$  it was difficult to grow single crystals larger than tiny needle of about ( $0.5 \times 0.5 \times 5 \text{ mm}^3$ ). This susceptibility was measured with a torsion balance to study the magnetic behavior in a wide temperature range. Fig. 1 shows the susceptibility of

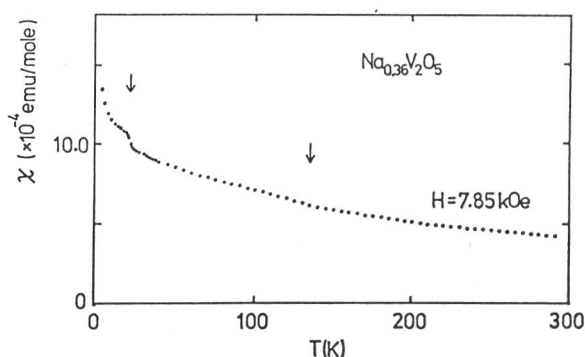


Fig. 1. The magnetic susceptibility measured by a torsion balance. The arrows indicate a structural phase transition ( $\sim 130$  K) and a weak ferromagnetic phase transition ( $\sim 20$  K) temperatures.

the susceptibility of pure  $V_2O_5$  powder and obtained that

$$\chi = \frac{(2.7 \pm 1) \times 10^{-3}}{T} + 3 \times 10^{-4} \text{ (emu/mole).}$$

It is very difficult to separate the magnetic contribution of impurities and vacancies contained in pure  $V_2O_5$  from the magnetic behavior of donated  $S=1/2$  spin system in  $Na_xV_2O_5$ . Therefore, in this paper, all measurements include the contributions of magnetic impurities and vanadium vacancies.

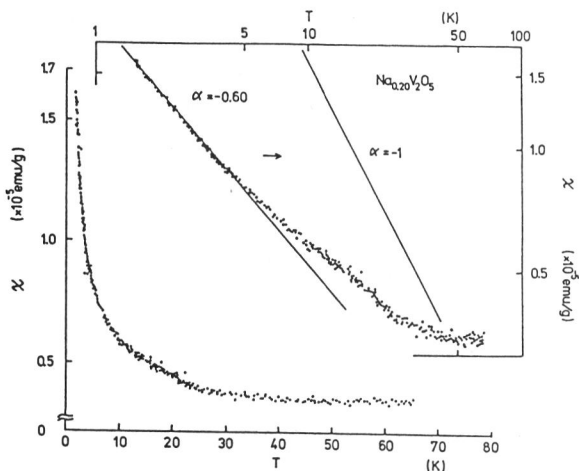


Fig. 2. The magnetic susceptibility measured by Hartshorn bridge.

$V^{4+}$  ions will make different sizes of magnetic clusters. The susceptibility of  $Na_xV_2O_5$  single crystals was first studied by Schlenker *et al.* [6]. They found a weak ferromagnetic ordering for  $Na_{0.33}V_2O_5$  around 20 K and no phase transition for the crystals except  $x=0.33$ .

Here, we will discuss the magnetic properties of  $Na_xV_2O_5$ , especially  $Na_{0.2}V_2O_5$ , from the point of view that  $Na_xV_2O_5$  is a random exchange magnet. The magnetic behavior of random-exchange Heisenberg antiferromagnetic chain was studied on conductive N-methyl-phenazinium tetracyanoquinodimethanide (NMP-TCNQ), quinolinium (TCNQ)<sub>2</sub>, acridinium-(TCNQ)<sub>2</sub>, phenazine-TCNQ [9] [10]

powdered  $Na_{0.36}V_2O_5$ . Anomalous changes in the susceptibility were observed at  $\sim 130$  K and at  $\sim 20$  K. A change at  $\sim 130$  K and a jump at  $\sim 20$  K come from a first order structural phase transition [8] and weak ferromagnetic phase transition [6], respectively. The concentration  $x=0.36$  was determined by a chemical analysis. The composition is not exactly  $x=0.33$  and therefore a sharp transition was not observed. The susceptibility increases below 20 K. The main reason is considered to come from isolated spins due to random distribution of magnetic  $V^{4+}$  ions, because  $x$  deviates from 0.33. Pure  $V_2O_5$  powder contains small amounts of magnetic impurities. We measured

Fig. 2. shows the susceptibility of  $Na_{0.20}V_2O_5$ . The susceptibility does not obey a simple Curie-Weiss law and seems to diverge following a power law of the form  $T^{-\alpha_x}$  as temperature  $T$  decreases, although the exponent  $\alpha_x$  changes slightly in the measured temperature region. The behavior that  $\chi T^{-\alpha_x}$  will be explained by the exchange-coupled pair model [9] [10].

### 3. Discussion

For  $x=0.33$ ,  $V^{4+}$  ions to occupy  $V_1$  sites [2] and  $V^{4+}$  and  $V^{5+}$  ions make a regular array alternately along the  $b$ -axis. A sharp magnetic phase transition occurs for  $x=0.33$ . When  $x$  deviates from 0.33, the alternate arrangement of  $V^{4+}$  and  $V^{5+}$  ions is disturbed and randomly distributed

[11] and a doped Si [12]. The susceptibility and the specific heat were given as a function of temperature  $T$ :

$$\chi_{h=0} \propto T^{-\alpha_\chi}$$

$$C_{h=0} \propto T^{1-\alpha_C}$$

where  $\alpha_\chi$  and  $\alpha_C$  are constants and  $h$  is the magnetic field.  $\alpha_\chi \approx \alpha_C$  was also found within experimental accuracy in the pioneer work. As shown in Fig. 2, the susceptibility versus temperature curve is nearly a straight line in a log-log plot. Below 5 K,  $\alpha_\chi \approx 0.6$  for  $\text{Na}_{0.2}\text{V}_2\text{O}_5$ . The specific heat,  $C$ , of the same crystal ( $\text{Na}_{0.2}\text{V}_2\text{O}_5$ ) was measured by Amarasekara *et al.* [7] and we estimated that  $\alpha_C \approx 0.5$  for the same temperature region. In  $\text{Na}_{0.2}\text{V}_2\text{O}_5$ ,  $\alpha_\chi = \alpha_C$ . This does not prevent to interpret  $\text{Na}_{0.2}\text{V}_2\text{O}_5$  as a random exchange Heisenberg antiferromagnetic chain. Recent theory suggest that the exponents  $\alpha_\chi$  and  $\alpha_C$  are different from each other and  $\alpha_\chi$  depends weakly on temperature [13].

We considered here exchange coupled pairs of  $S_1=S_2=1/2$ . Two cases are considered that the singlet ( $S=S_1+S_2=0$ ) is a lower or higher energy state than the triplet ( $S=1$ ).

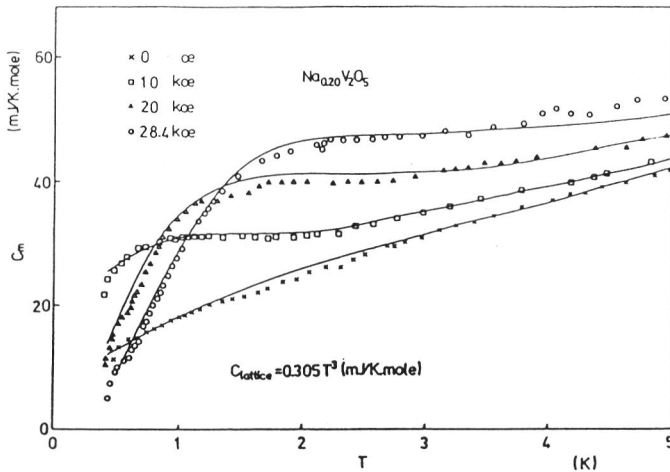


Fig. 3. The magnetic field dependence of the specific heat of  $\text{Na}_{0.2}\text{V}_2\text{O}_5$ . The solid lines show the calculation described in the text.

of exchange interaction that  $P(J) \propto J^{-\alpha}$  ( $0 < \alpha < 1$ ) in the calculation of thermodynamic properties.

Amarasekara *et al.* obtained the magnetic specific heat linear in temperature, especially for the crystals of  $x \gtrsim 0.2$ . As they suggested, this linear term has been observed in many kinds of substances, for example in real glasses, spin glasses, conductive materials and antiferromagnetic linear chains. We demonstrated here one explanation for the magnetic properties of  $\text{Na}_{0.2}\text{V}_2\text{O}_5$ .

The magnetic field dependence of the specific heat is explained quantitatively as shown in Fig. 3 by assuming that the singlet is lower than the triplet for 98.5 % of the exchange coupled pairs and is to the contrary for the rest (1.5%). This calculation is consistent with the result of susceptibility measurement.

The exchange-coupled pair model of Clark and Tippie is based on antiferromagnetically coupled pairs. They neglected the interaction between a pair and its next neighbouring spins. Following them, we used a distribution function

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