New S = 1/2 Alternating Chain Compound - High Pressure Form of (VO)2P2O7 - (SOLID STATE CHEMISTRY-Multicomponent Materials)

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New S = 1/2 Alternating Chain Compound - High Pressure Form of $(VO)_2P_2O_7$-

Masaki Azuma, Takashi Saito, Zenji Hiroi, and Mikio Takano

Crystal structure and magnetic properties of the high pressure phase of $(VO)_2P_2O_7$ were investigated, and it was found that this compound comprised S = 1/2 Heisenberg alternating antiferromagnetic chains. The magnetic susceptibility and the high-field magnetization data consistently showed the presence of a spin gap of about 25 K. Single crystals were grown by slowly cooling the stoichiometric melt in the high pressure cell.
Keywords: 1 dimensional magnet, Spin gap, High pressure synthesis

The unexpected discovery of high-T_C superconductivity in cupric oxides has strongly stimulted the research of the quantum mechanical interplay of the electronic spin, charge, and orbital degrees of freedom in 3*d* transition metal (*M*) oxides. The interplay is composition- and structure-sensitive, and hence it is meaningful to try to increase the variety of the *M* - O lattice and also the variety of the counter-cations and counter-anions that would finely tune the electronic state of the *M* - O lattice even by using unconventional synthesizing techniques. In this respect we have reported the high-pressure (HP) synthesis of a pair of spin-ladder cupric oxides, $SrCu_2O_3$ (two-legged) and $Sr_2Cu_3O_5$ (three-legged), the HP synthesis of oxides containing Fe^{4+} and Ru^{4+} exhibiting interesting metal-insulator transitions, and others. Described below is a recent study of a new one-dimensional (1D) system in which the spin degree of freedom is killed quantum mechanically.

No doubt it is interesting to study how to control the electronic degrees of freedom. For example, if the ground state of a condensed system is the spin singlet state, where the spin degree of freedom is killed, there opens a way to create the freedom by mixing the excited magnetic state using an external field. In this sense there has been a growing interest in antiferromagnetic (AF) systems having a spin gap. Spin gap is the energy gap between the singlet ground state and the lowest magnetic excited state. Such a gap has been found mainly in one dimensional (1D) systems like spin-1/2 alternating

SOLID STATE CHEMISTRY — Multicomponent Materials —

Scope of research

Novel inorganic materials that have new, useful or exotic features such as superconductivity, ferromagnetism and quantum spin ground state are synthesized by novel methods. Recent topics are:

- *High-T_c superconducting copper oxides with higher T_c or J_c.*
- *Perovskite-based compounds with unusual magnetic and electronic properties.*
- *Low-dimensional spin system showing dramatic quantum effects.*

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chains, spin-1 chains (called the Haldane system) and spin-1/2 ladders like $SrCu_2O_3$ discovered by us.

$(VO)_2P_2O_7$ has long been known as an active catalyst for the selective oxidation of butane to maleic anhydride. The V^{4+} ions in this compound possess spin-1/2. A neutron scatteritng experiment [1] revealed that this compound was best described as a spin-1/2 alternating chain system in which the magnitude of AF interaction changes alternatingly as $-V^{4+}-(J_1)-V^{4+}-(J_2)-V^{4+}-(J_1)-V^{4+}-(J_2)-V^{4+}-$. However, unfortunately, the structure is too complex to study the intersting magnetism in detail [2].

We recently found that this compound undergoes a pressure-induced transition to a similar but much simpler structure [3]. And the measurements of magnetic susceptibility, high-field magnetization, and specific heat have indicated consistently and unambiguously that the HP phase is a good example of the spin-1/2 Heisenberg alternating AF chain system having a spin gap.

The HP phase was obtained by treating the ambient pressure (AP) phase at 2 GPa and 700 °C for 30 min. using a cubic-anvil type HP apparatus. The structure determined by means of X-ray diffraction and neutron diffraction is illustrated in Fig. 1. As known through the neutron scattering study on the AP phase [1], the strongest AF interaction (J_1) is mediated by the PO_4 tetrahedra, while the second strongest one (J_2) works between a pair of edge-sharing VO_5 pyramids. These interactions alternate along the c axis as can be seen in Fig. 1b.

Figure 2a shows the temperature dependence of magnetic susceptibility. After subtracting a paramagnetic contribution due to an impurity V^{4+} of 2.6 %, the data showed an exponential decay toward zero as expected for a spin gap system. The data could be well fitted to the alternating chain model with parameters J_1= 136 K, J_2/J_1 = 0.9, and g = 1.98, from which the spin gap was estimated to be about 25 K.

Figure 2b shows the magnetization measured at 0.4 K using a pulsed magnetic field. The Brillouin-function like behavior below 15 T is due to the impurity ions. Above 20 T, the data increases steeply indicating that the singlet ground state and the triplet excited state cross each other. Assuming that the gap between these states changes as $\Delta(H) = \Delta(0) - g\mu_B H$, $\Delta(0)$ = 26 K has been obtained, which is in good agreement with the susceptibility data mentioned above.

Single crystals were obtained by slowly cooling the molten liquid from 1200 to 600 °C in 40 h at 3GPa. More detailed studies on these powder and single crystal samples by means of NMR, μSR, ESR, Ramman scattering, and neutron scattering are in progress.

This work is one of a variety of researches being carried out using the HP technique and also a film technique in the present laboratory for the purpose of discovering new fundamental and practical properties of 3*d* transition metal oxides.

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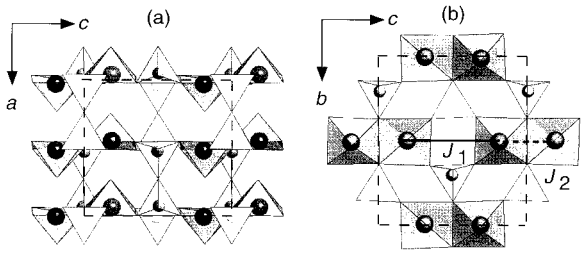

Figure 1. High-pressure phase of $(VO)_2P_2O_7$ viewed along the *b*-axis (a) and the *a*-axis (b). Large and small spheres represent V and P ions, respectively. The alternation of the AF interaction along the *c* axis can be seen in (b).

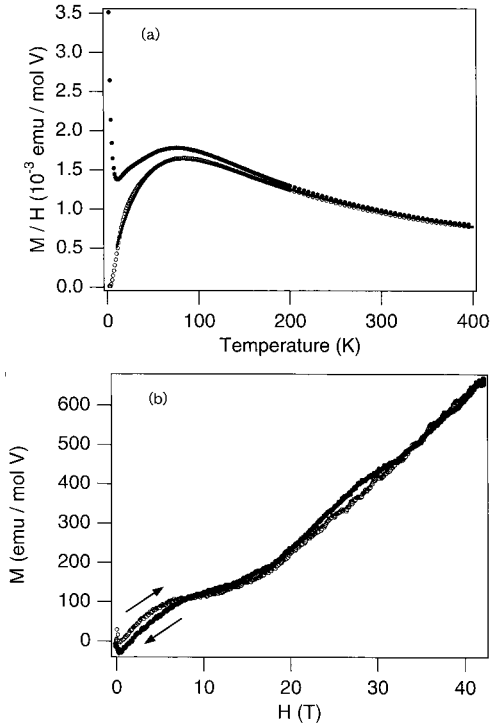

Figure 2. Temperature dependence of magnetic susceptibility (a). The data before and after the subtraction of the impurity contribution are shown with closed and open circles, respectively. The solid line is a fit to the alternation chain model. The field dependence of magnetization at 0.4 K (b).