Proceedings of the European Conference "Physics of Magnetism '99", Poznań 1999

NEW $S = 1/2$ ALTERNATING CHAIN COMPOUND — HIGH PRESSURE FORM OF $(VO)_2P_2O_7$-

M. AZUMA[a], T. SAITO[a], Z. HIROI[b], M. TAKANO[a], Y. NARUMI[c] AND K. KINDO[c]

[a]Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan
[b]Institute for Solid State Physics, University of Tokyo
Roppongi 7-22-1, Minato-ku, Tokyo 106-8666, Japan
[c]KYOKUGEN, Osaka University, Toyonaka, Osaka 560-8531, Japan

The high-pressure phase of $(VO)_2P_2O_7$ comprises a unique kind of spin-1/2 Heisenberg alternating antiferromagnetic chain, in contrast with the ambient pressure phase containing two crystallographically different chains. Magnetic susceptibility and high-field magnetization data showed the presence of a single spin gap of 23 (magnetization) $\sim$ 27 (susceptibility) K, not double as observed for the ambient pressure phase. This result shows that the two kinds of chains of the ambient pressure phase have single, different spin gaps.

PACS numbers: 75.10.Jm, 75.40.Cx, 75.50.Ee

There is a growing interest in one dimensional (1D) antiferromagnetic (AF) quantum spin systems with spin gaps like spin-1/2 alternating chains [1], spin-1 chains (Haldane systems) and spin-1/2 spin ladders [2]. $(VO)_2P_2O_7$ (VOPO) comprises vanadium ions in the 4+ oxidation state with spin-1/2. The singlet ground state of this compound was first found by Johnston et al. [3]. A recent neutron scattering study on single crystals [4] showed the validity of the alternating chain model with a major AF interaction (J_1) between a pair of VO_5 pyramids bridged by PO_4 tetrahedra and a minor one (J_2) between a pair of edge sharing VO_5 pyramids. Interestingly, the data also revealed the existence of a second energy gap of about twice as large as the first one as predicted theoretically [5]. However, this compound comprises two slightly different chains [6, 7], making it difficult to determine whether these chains have single but different spin gaps or have the same double gaps. High-field magnetization and NMR studies have shown the former is the case [8].

We found that this compound undergoes a pressure-induced transition to a similar but simplified structure with a unique kind of chain [9]. The crystal structures of the high-pressure (HP) and the ambient-pressure (AP) phases are illustrated in Fig. 1. Both these are made of edge-sharing pairs of VO_5 pyramids and PO_4 tetrahedra, while the arrangement is simpler in the HP phase. In the

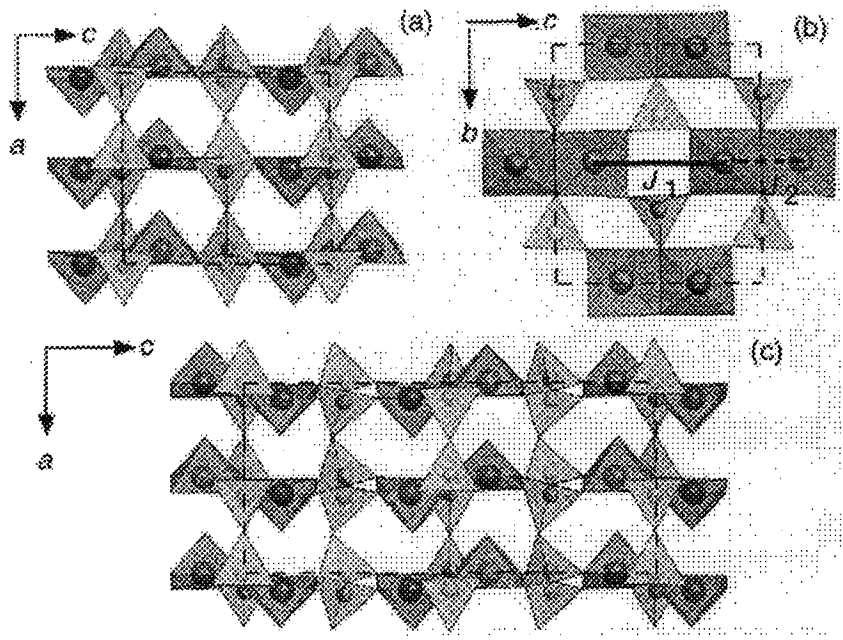

Fig. 1. Crystal structures of HP $(VO)_2P_2O_7$ illustrated along the a-axis (a) and the b-axis (b). The large and small spheres represent V and P ions, respectively. Crystal structure of the AP phase along the a-axis is also shown for comparison (c).

AP form viewed along the b-axis (see Fig. 1c) the pyramids are lined along the c-axis in a manner of -up-up-down-down-up-up- and so are the tetrahedra. In contrast, the mode is up-down-up-down- for the HP phase. Accordingly the c-axis of the HP form is about a half of the AP phase. The AP phase has two major AF interactions along the c-axis, one mediated by the two V–O–(P)–O–V paths (J_1) and another through the almost orthogonal V–O–V paths (J_2), where $J_2/J_1 \sim 0.8$. The alternation of these interactions along the c-axis leads to a spin-1/2 alternating chain, which seems to survive in the HP phase as marked in Fig. 2b with solid (J_1) and dashed (J_2) lines. Because of this structural similarity to the AP phase, the HP phase was also expected to be a gapped alternating AF system. Note that the HP phase has only one V^{4+} site while the AP phase with multiple sites, four in the orthorhombic ($Pca2_1$) structure for a powdered sample [6] and eight in the monoclinic structure ($P2_1$) for a single crystal [7]. Therefore, the HP phase comprises a unique kind of chain, in contrast with the ambient pressure phase containing two crystallographically different chains. This high pressure phase seems to be a good example of spin-1/2 Heisenberg AF chain with a weak alternation ($J_2/J_1 \sim 1$).

The sample was prepared by treating the AP phase at 2 GPa and 700°C for 30 min in a conventional cubic-anvil type HP apparatus. The starting material, the AP form of VOPO, was prepared by a simple solid state reaction from NH_4VO_3 and $NH_4H_2PO_4$. The magnetic susceptibility was measured in an external magnetic

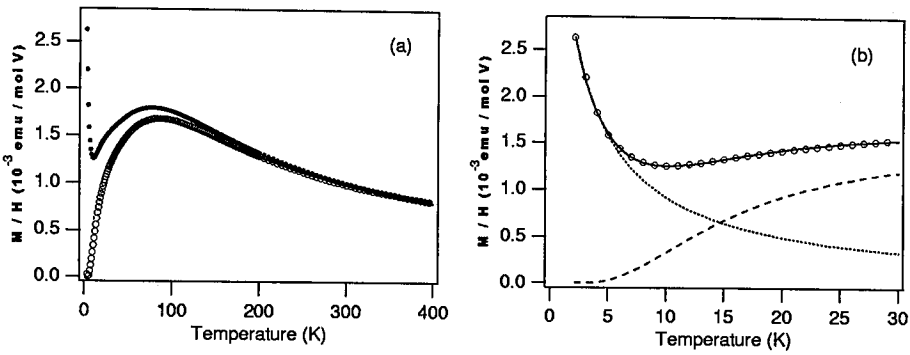

Fig. 2. Temperature dependence of magnetic susceptibility of HP $(VO)_2P_2O_7$ below 400 K (a). The closed circles are the experimental raw data, while the data after subtraction of the Curie component are shown with open circles. The solid line represents the fit to the alternation chain model. The data below 30 K were fit to the equation given in the text (b). The solid line represents the result of the fit, the long-dashed line is the spin susceptibility and the short-dashed line is the Curie term.

field of 0.1 T from 2 to 400 K on heating after zero-field cooling with a SQUID magnetometer (Quantum Design MPMS XL). The high field magnetization was measured in a pulsed magnetic field up to 60 T at 1.3 K by an induction method using a multilayer pulse magnet at KYOKUGEN, Osaka University.

Figure 2a shows temperature dependence of magnetic susceptibility of the HP phase. One can see a broad maximum centered around 90 K suggesting the 1D nature in magnetism. Below 10 K, the data increased because of the paramagnetic free moments generated by defects like the edges of the chains. The data below 30 K were fitted to an equation $\chi(T) = \chi_0 + C/(T-\theta) + aT^{-1/2}\exp(-\Delta/T)$ as seen in Fig. 2b, where χ_0 is the T-independent term, $C/(T-\theta)$ is a Curie–Weiss term owing to the free moments and the $aT^{-1/2}\exp(-\Delta/T)$ term is the susceptibility of a 1D system with a spin gap Δ [10]. The best fit was obtained for the following set of parameters, $\chi_0 = -2.0 \times 10^{-5}$ emu/(mol V), $C = 1.15 \times 10^{-2}$ emu/(K mol V), $\theta = -2.2$ K, $a = 1.6 \times 10^{-2}$, and $\Delta = 27$ K. This C value is corresponding to free spins of 3.1% of V^{4+}. The data above 30 K could be well fitted to an analytical equation given by Hatfield et al. [11] which is valid for a temperature range $T \geq 0.25J_1$, and we obtained $J_1 = 137$ K, $\alpha = 0.9$, and $g = 2.01$. We could estimate the spin gap as $\Delta = 27$ K using a theoretical relation of $\Delta = 0.2J_1$ for $\alpha = 0.9$ as well [1, 7]. This is in good agreement with the value estimated from the low temperature data mentioned above.

Figure 3 shows the magnetization curve taken at 1.3 K in a pulsed magnetic field. Below 15 T a Brillouin function-like behavior owing to the free spins was seen, while above 18 T the magnetization began to increase again almost linearly. The gap between the singlet ground state and the first triplet excitation in the presence of magnetic field is given as $\Delta(H) = \Delta - g\mu_B H$. If the gap is assumed to close at 18 T based on the field dependence of the magnetization, Δ is estimated to be about 23 K. This value seems considerably smaller than that estimated

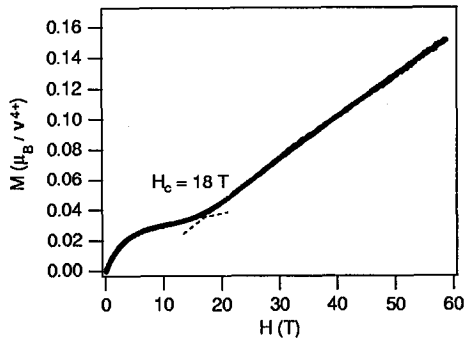

Fig. 3. Magnetization curve of HP $(VO)_2P_2O_7$ measured in pulsed magnetic field at 1.3 K.

from the susceptibility data, but magnetization data tend to give smaller values in comparison with other methods [8]. The magnetization increased almost linearly up to 60 T without showing such a secondary anomaly as found for the AP phase. It is reasonable to attribute this difference to the multiplicity of the chains: The AP phase has two kinds of chains with single, different gaps while the HP phase has a unique kind of chain with a single gap.

References

[1] J.C. Bonner, M.E. Fisher, *Phys. Rev. A* **135,** 640 (1964); J.C. Bonner, H.W.J. Blöte, J.W. Bray, I.S. Jacobs, *J. Appl. Phys.* **50,** 1910 (1997); J.C. Bonner, H.W.J. Blöte, *Phys. Rev. B* **25,** 6959 (1982).

[2] M. Azuma, Z. Hiroi, M. Takano, K. Ishida, Y. Kitaoka, *Phys. Rev. Lett.* **73,** 3468 (1994); M. Azuma, M. Takano, R.S. Eccleston, *J. Phys. Soc. Jpn.* **67,** 740 (1998).

[3] D.C. Johnston, J.W. Johnson, D.P. Goshorn, A.J. Jacobson, *Phys. Rev. B* **35,** 219 (1987).

[4] A.W. Garrett, S.E. Nagler, D.A. Tennant, B.C. Sales, T. Barns, *Phys. Rev. Lett.* **79,** 745 (1997).

[5] G.S. Uhrig, H.J. Schulz, *Phys. Rev. B* **54,** R9624 (1996).

[6] Z. Hiroi, M. Azuma, Y. Fujishiro, T. Sairo, M. Takano, F. Izumi, T. Kamiyama, T. Ikeda, submitted to *J. Solid State Chem.*

[7] P.T. Nguyen, R.D. Hoffman, A.W. Sleight, *Mat. Res. Bull.* **30,** 1055 (1995).

[8] T. Yamauchi, Y. Ueda, Y. Narumi, K. Tatani, T. Kobayashi, K. Kindo, J. Kikuchi, K. Motoya, submitted to *Phys. Rev. Lett*; J. Kikuchi, K. Motoya, T. Yamauchi, Y. Ueda, submitted to *Phys. Rev. B.*

[9] M. Azuma, T. Saito, Y. Fujishiro, Z. Hiroi, M. Takano, F. Izumi, T. Kamiyama, T. Ikeda, Y. Narumi, K. Kindo, submitted to *Phys. Rev. B.*

[10] M. Troyer, H. Tsunetsugu, D. Würtz, *Phys. Rev. B* **50,** 13515 (1994).

[11] J.W. Hall, W.E. Marsh, R.R. Weller, W.E. Hatfield, *Inorg. Chem.* **20,** 1033 (1981).