

Two new quantum spin compounds: $S=1/2$ alternating chain system, high pressure form of $(\text{VO})_2\text{P}_2\text{O}_7$ and 2D spin trimer compound $\text{La}_4\text{Cu}_3\text{MoO}_{12}$

Masaki AZUMA, Takashi SAITO and Mikio TAKANO

Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611-0011, Japan

(Received December 20, 1999)

Magnetic properties of recently found two quantum spin compounds are discussed. $(\text{VO})_2\text{P}_2\text{O}_7$, known as a quantum spin chain compound, was found to undergo a structural transition when treated at 2 GPa and 700° C. The high-pressure phase comprises a unique kind of $S = 1/2$ Heisenberg alternating antiferromagnetic chain, in contrast with the ambient pressure phase containing two crystallographically different chains. Magnetic susceptibility, high-field magnetization and inelastic neutron scattering data showed the presence of only one spin gap as expected from the structure. This result confirms the recent assertion based on magnetization and NMR measurements that the two kinds of alternating chains of the AP phase have single independent spin gaps. $\text{La}_4\text{Cu}_3\text{MoO}_{12}$ is a 2D compound with an average structure of YAlO_3 type. In the Cu_3MoO_4 layer of this compound, 1/4 of Cu^{2+} (spin-1/2) forming a triangular lattice is replaced with nonmagnetic Mo^{6+} as in the Kagome lattice. However the arrangement of the nonmagnetic ions are different from Kagome. Triangular clusters (trimers) of Cu^{2+} form an orthorhombic sublattice, so there is no frustration between the trimers. Susceptibility data showed that each Cu^{2+} had spin-1/2 above room temperature, but the magnetic moment decreased to spin-1/2 per trimer at lower temperatures because of the strong intra-trimer antiferromagnetic interaction. The moments localized on the trimers got antiferromagnetically ordered at 2.7 K. This ordering was broken by applying a magnetic field higher than 20 T. After the spin flip, the magnetization data showed a plateau at a saturation moment of 1 μ_B per trimer.

KEYWORDS: $S = 1/2$ Heisenberg alternate chain, susceptibility, specific heat, magnetization, spin trimer

§1. Introduction

Dimensionality and arrangement of the spins affect the ground state of a quantum magnet in various fashion. High- T_c superconductivity occurs in a doped 2 dimensional (2D) CuO_2 plane where Cu^{2+} ions ($S=1/2$) form an antiferromagnetic (AF) square lattice. Spin singlet ground states with spin gaps are found in several 1D AF systems such as $S=1/2$ alternating bond chains,¹⁾ $S=1/2$ 2-leg ladders²⁾ and $S=1$ chains (Haldane systems).³⁾ The findings of the inorganic model compounds such as CuGeO_3 (spin-Peierls),⁴⁾ Y_2BaNiO_5 (Haldane),⁵⁾ SrCu_2O_3 ⁶⁾ and $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ ⁷⁾ (ladders) in a past decade have accelerated the keen interest because of the large antiferromagnetic interactions (J) and the thermal stability which made it rather easy to finely tune the electronic properties by means of chemical doping. Spin gaps are also found in 2D systems such as CaV_4O_9 ⁸⁾ and $\text{SrCu}_2(\text{BO}_3)_2$.⁹⁾ In the ground states of these spin gap compounds, two $S=1/2$ spins form a spin singlet. $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{Cl}\cdot 6\text{H}_2\text{O}$ and $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{Cl}\cdot 6\text{H}_2\text{O}$ ¹⁰⁾ comprise triangle clusters of $S=3/2$ and $5/2$, respectively. For both systems, the strong intra-triangle AF interactions make the spin multiplet with $S=1/2$ ($S_{\text{total}}=1/2$) the ground state. As results these salts behave as paramagnets with $S=1/2$ at low temperatures. In this manuscript, we report the recent study on two quantum spin magnets, $S=1/2$ alternating chain system, high pressure form of $(\text{VO})_2\text{P}_2\text{O}_7$

and 2D spin trimer compound $\text{La}_4\text{Cu}_3\text{MoO}_{12}$

§2. High Pressure Phase of $(\text{VO})_2\text{P}_2\text{O}_7$

2.1 AP and HP phases of $(\text{VO})_2\text{P}_2\text{O}_7$

$(\text{VO})_2\text{P}_2\text{O}_7$ (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.*¹¹⁾ A recent neutron scattering study on single crystals¹²⁾ 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.¹³⁾ However, this compound comprises two slightly different chains^{14,15)} 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.¹⁶⁾

We found that this compound undergoes a pressure-induced transition to a similar but simplified structure with a unique kind of chain.¹⁷⁾ 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 AP form viewed along the b axis (see Fig. 1 (c)) 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 the other 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. 1 (b) 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 sample¹⁴) and eight in the monoclinic structure ($P2_1$) for a single crystal.¹⁵) 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 (HP) phase seems to be a good example of spin-1/2 Heisenberg AF chain with a weak alternation ($J_2/J_1 \sim 1$).

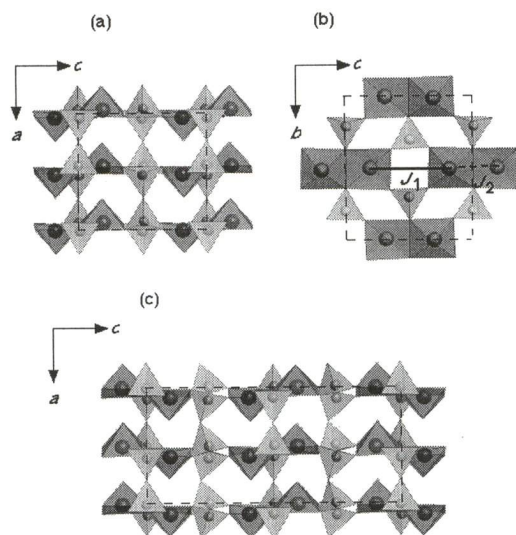


Fig. 1. Crystal structures of HP $(VO)_2P_2O_7$ illustrated along the a -axis (a) and the b -axis (b). The large and small spheres represent V and P ions, respectively. Crystal structure of the AP phase along the b axis is also shown for comparison (c).

2.2 Experimental

The powder 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 $NH_4H_2PO_4$. High pressure powder X-ray diffraction (XRD) was performed using a cubic-anvil type high pressure apparatus (SMAP 1800) installed at BT14B1 of SPring-8, Japan Synchrotron Radiation Research Institute. White beam

X-ray from the synchrotron radiation was injected to the sample through the high pressure cell and was detected by the solid state detector fixed at $2\theta = 4^\circ$. Single crystals were grown by cooling the melt from 1200 °C to 600 °C in 60 h at 3 GPa. The magnetic susceptibility was measured in an external magnetic 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. The inelastic neutron scattering data were collected on the TOPAN triple axis spectrometer at the JRR3M reactor, Japan Atomic Energy Research Institute.

2.3 Single crystal growth at 3 GPa

Figure 2 shows the XRD patterns taken at various conditions. When the pressure was applied, the peak shifted to the high energy direction indicating the shrinkage of the lattice. The peak broadening was due to the strain in the particles. The peaks sharpened again with increasing the temperature and new peaks corresponding to (2 2 1), (1 1 3) and (2 3 1) reflections of the HP phase appeared at 500 °C. This clearly showed that the transition to the HP phase took place between 400 and 500 °C. Finally at 1150 °C the sample melted and all the peaks disappeared except for those of characteristic X-rays of lead.

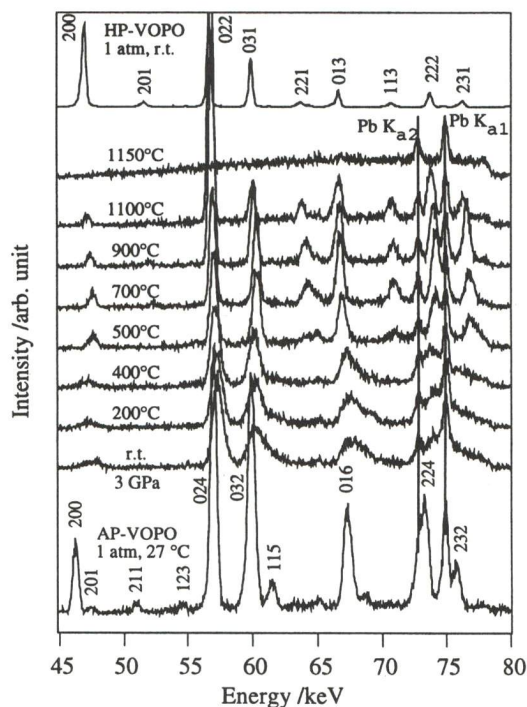


Fig. 2. Powder XRD patterns taken at various pressures and temperatures. The data collected with $Cu-K\alpha$ radiation were converted in the energy scale and plotted at the top for comparison. The 2 solid lines correspond to the characteristic X-ray of lead from the beam stopper.

Single crystals were grown by slowly cooling the melt at

3 GPa.¹⁸⁾ About 2 g of the AP phase sample was packed in a platinum capsule of 9.6 mm diameter and 15 mm high and compressed using a cubic anvil type high pressure apparatus. The sample was first heated to 1200 °C and then cooled to 600 °C in 60 h. Green transparent crystals of the typical size of 1 mm × 0.5 mm × 0.2 mm were obtained. The magnified view of the crystals is shown in Fig. 3.

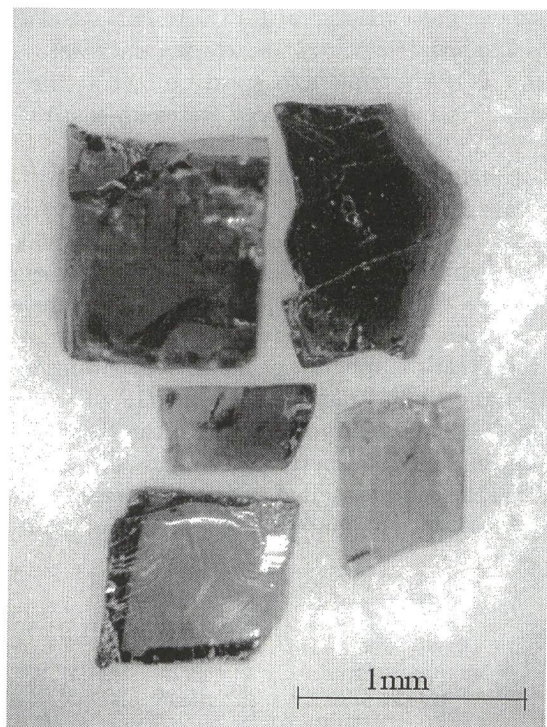


Fig. 3. Single crystals of the HP VOPO obtained by cooling the melt from 1200° to 600° in 60 h at 3 GPa.

2.4 Observation of a spin gap

Figure 4 shows temperature dependence of magnetic susceptibility taken on the crushed powder of the single crystals. One can see a broad maximum centered around 90 K suggesting the 1D nature in magnetism followed by a sudden decrease reflecting the spin gap.

Below 5 K, the data increased because of the paramagnetic free moments generated by defects like the edges of the chains. The data were fitted to an analytical equation for the spin $S = 1/2$ antiferromagnetic alternating-exchange Heisenberg chain as determined using quantum Monte Carlo simulations and transfer-matrix density-matrix renormalization group calculations for $0.01 \leq T/J \leq 10$ and $0 \leq \alpha \leq 1$.^{18,19)} The result of the fit is shown in Fig. 4 with a solid line. After the subtraction of the contribution of the impurity spins of 1.3 % of V^{4+} spin susceptibility remained and was plotted with dots. The fit yielded the following parameters, $g = 1.95$, $J_1 = 135.2$ K and $\alpha = 0.873$. Applying the relation between J_1 , α and the magnitude of the spin gap (Δ),²⁰⁾ $\Delta = 33.7$ K was derived.

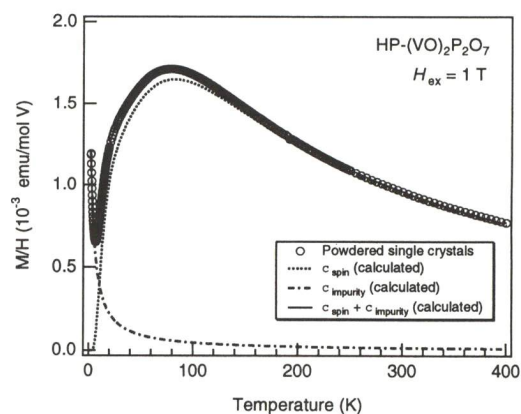


Fig. 4. Temperature dependence of magnetic susceptibility of HP (VO)₂P₂O₇ below 400 K. The solid line is the result of the fit, the dashed line is impurity spin contribution, and the dots show the spin susceptibility.

The existence of the spin gap was confirmed by means of inelastic neutron scattering. Figure 5 shows the scattering from the powder sample of (VO)₂P₂O₇ collected at 2 and 40 K. The data were taken with the incident energy of 14.7 meV and collimations 30'-30'-30'-60' at fixed $Q = 0.83 \text{ \AA}^{-1}$. The data at 2 K clearly showed a peak at 2 meV (23.2 K) in the scattering. The peak vanished in the 40 K data, indicating that this scattering was magnetic in nature and the spin gap size was 23.2 K.

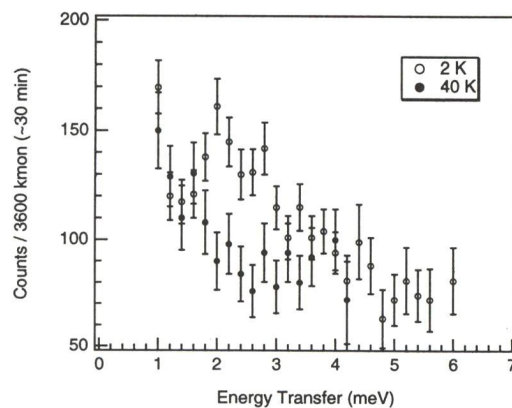


Fig. 5. Inelastic neutron scattering from HP (VO)₂P₂O₇ at $Q = 0.83 \text{ \AA}^{-1}$ with the incident energy of 14.7 meV. Open circles show the data collected at 2 K while the closed circles corresponds to the data at 40 K.

Figure 6 shows the magnetization curve taken for powder sample 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

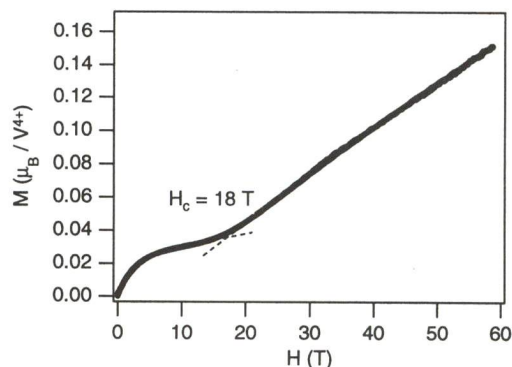


Fig. 6. Magnetization curve of HP $(\text{VO})_2\text{P}_2\text{O}_7$ measured in pulsed magnetic field at 1.3 K.

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. The magnetization increased almost linearly up to 60 T without showing such a secondary anomaly as found for the AP phase.

2.5 Discussions

The two step increase of the magnetization found for the AP phase was not observed in the present study for the HP 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. This result confirms the recent assertion based on magnetization and NMR measurements that the two kinds of alternating chains of the AP phase have single independent spin gaps.¹⁶⁾ The spin gap size estimated from the susceptibility data (33.7 K) was considerably larger than those estimated from other 2 methods (23 K), the inelastic neutron scattering and the magnetization measurements. The origin of this discrepancy is not clear at the present stage of the study, but it might be due to the effect of the inter-chain interaction. Inelastic neutron scattering study on the obtained single crystals is desired to solve this problem.

§3. Spin Trimer Compound $\text{La}_4\text{Cu}_3\text{MoO}_{12}$

3.1 Crystal structure

$\text{La}_4\text{Cu}_3\text{MoO}_{12}$ is a 2D compound with an average structure of YAlO_3 type.²¹⁾ In the Cu_3MoO_4 layer of this compound as shown in Fig. 7, 1/4 of Cu^{2+} ions forming a triangular lattice is replaced with nonmagnetic Mo^{6+} ions as in the Kagome lattice. However the arrangement of the nonmagnetic ions is different from Kagome. These make an orthorhombic sublattice so that the remaining Cu^{2+} ions form triangular clusters. The average Cu-O bond length within the triangle is 1.982 Å while that between the triangles is 2.690 Å. This suggests that the intra-triangular antiferromagnetic interactions are considerably stronger than the inter-triangular ones. So, the system can be regarded as weakly coupled $S=1/2$

triangle clusters.

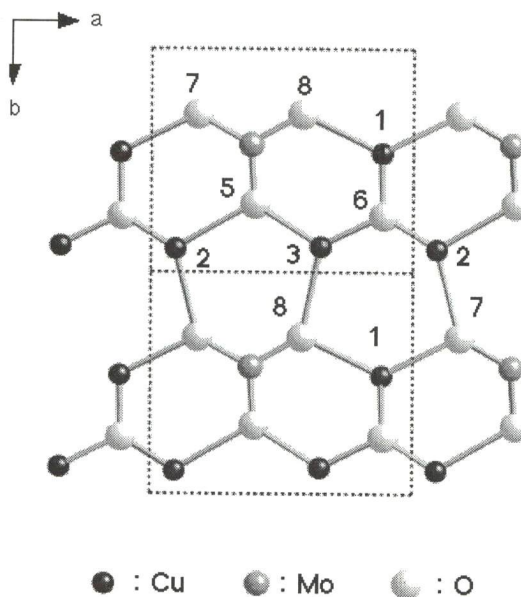


Fig. 7. Cu_3MoO_4 plane of $\text{La}_4\text{Cu}_3\text{MoO}_{12}$. The numbers show the crystallographic sites. The solid line represent the triangle clusters.

3.2 Experimental

Powder sample was prepared by a solid state reaction of La_2O_3 , CuO and MoO_3 . These are mixed in a proper ratio, pressed into pellet and heated at 1025 °C in the air for 4 days with 2 intermittent grindings. Finally the sample was slow-cooled at 36°C⁻¹ in the furnace. Magnetic susceptibility was measured with SQUID magnetometers (Quantum Design MPMS equipped with a sample space oven and MPMS XL). Specific heat data were taken by means of a pulse relaxation method using a commercial calorimeter (Quantum Design PPMS). The high field magnetization was measured in a pulsed magnetic field up to 60 T by an induction method using a multilayer pulse magnet at KYOKUGEN, Osaka University.

3.3 Results and discussions

Figure 8 shows the temperature dependence of the magnetic susceptibility and the inverse plot of the data from 5 to 800 K taken on heating in an external field of 1 T. The susceptibility above 400 K was fitted well to the Curie-Weiss law assuming $\mu_{\text{eff}} = 1.81$ ($g = 2.09$) and Weiss temperature of -558 K. On the other hand, the slope of the $1/\chi - T$ plot below 250 K decreased to 0.39 of the high-temperature value. This was indicative that each triangle cluster had a total spin $S_{\text{total}} = 1/2$. Above the room temperature, such spin trimers broke because of the thermal fluctuation. The large intra-trimer AF interaction gave a large Weiss constant at high temperatures. Below the room temperature, the clusters form spin-trimers with $S_{\text{total}} = 1/2$ because of the strong AF intra-trimer interactions. The inter trimer interactions

are weakly antiferromagnetic as indicated by the small Weiss constant of -16 K. In the data measured in the field of 0.1 T as shown in the inset of Fig. 8, a cusp was found at 5 K suggesting an AF ordering. As shown in Fig. 7, there is no frustration between the trimers, so it is reasonable to assume that the $S_{\text{total}} = 1/2$ spins got ordered.

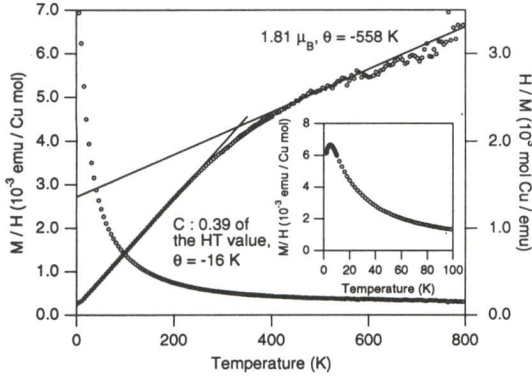


Fig. 8. Temperature dependence of the magnetic susceptibility of $\text{La}_4\text{Cu}_3\text{MoO}_{12}$ in the external field of 1. The solid lines correspond to the fit to the Curie-Weiss law. The inset shows the data taken at 0.1 T.

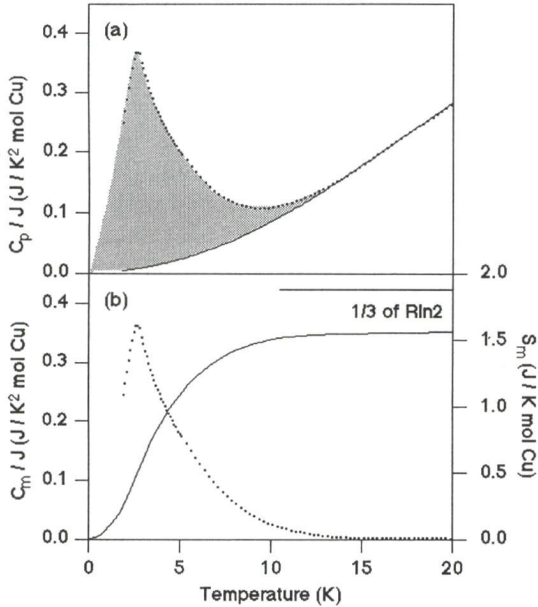


Fig. 9. Total specific heat divided by temperature C_p/T vs T (a). The solid line stands for the lattice contribution. The magnetic specific heat divided by temperature (C_m/T , dots) and the magnetic entropy (solid line) are also plotted (b).

Specific heat data were taken in a zero field to investigate the ordering in more detail. Figure 9 (a) shows the total specific heat divided by the temperature plotted against the temperature. The sharp λ -type anomaly at

2.7 K confirmed the AF transition. This temperature is slightly lower than the peak temperature of the susceptibility, but the reason is not clear at this stage. Probably, the susceptibility made a peak above the Néel temperature because of the development of the AF correlations. The solid line in the figure is the estimation of lattice contribution to the specific heat $C_l = \beta_1 T^3 + \beta_2 T^5$ where $\beta_1 = 9.0 \times 10^{-4} \text{ J / K}^4 \text{ mol Cu}$, $\beta_2 = -4.9 \times 10^{-7} \text{ J / K}^6 \text{ mol Cu}$. This β_1 value gives a Debye temperature of 243 K. The entropy is given by $S = \int \frac{C}{T} dT$, so the shaded area in Fig. 9(a) surrounded by C_p/T and C_l/T corresponds to the entropy change at the AF ordering. The magnetic specific heat and the entropy are thus estimated and plotted in Fig. 9 (b). The ground states of a equilateral triangle cluster are degenerate two $S_{\text{total}} = 1/2$ states. In that case, the entropy change at the AF ordering is expected to be $1/3 R \ln 4$ (J/K mol Cu). If there is no degeneracy, the entropy change should be $1/3 R \ln 2$ (J/K mol Cu). In the present case, the entropy change, 1.56 J/K mol Cu is much smaller, even smaller than $1/3 R \ln 2$ (J/K mol Cu). This shows that the energy levels of the doublet are separate because of a slight distortion of the triangle. The deviation of the data from $1/3 R \ln 2$ is probably due to the over estimation of the lattice contribution to the specific heat.

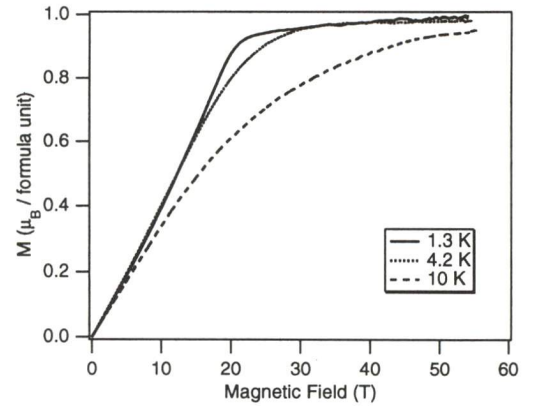


Fig. 10. Magnetization curve of HP $\text{La}_4\text{Cu}_3\text{MoO}_{12}$ measured in pulsed magnetic field at 1.3 , 4.2 and 10 K.

The inter-triangle interaction was suggested to be weak from the small Weiss constant. If so, it would be possible to flip the ordered spin by applying magnetic field. The magnetization data taken at 1.3 , 4.2 and 10 K are shown in Fig. 10. At 1.3 K, the data was concave reflecting the AF ordering below 20 T. After the spin flip at 20 T, the data tended to saturate at $1 \mu_B$ / formula unit, in other word, $1 \mu_B$ per triangle. This confirms that the system ordered antiferromagnetically keeping the ground state of the triangles, $S_{\text{total}} = 1/2$. The real saturation of the magnetization moment of this system should be $3 \mu_B$ / formula unit, so the observed saturation-like behavior is a plateau. The data at 4.2 K and 10 K also tended to saturate at the same mag-

netization, $1 \mu_B$ / formula unit. This is consistent with the susceptibility data which obeyed the Curie-Weiss law below 200 K.

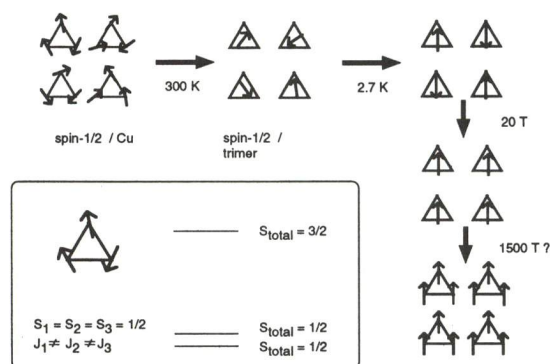


Fig. 11. Schematic drawing of the change of spin structures in $\text{La}_4\text{Cu}_3\text{MoO}_{12}$

The magnetism of this compound is schematically summarized in Fig. 11. At temperature above 400 K, $S=1/2$ spins localized on each lattice point behaved paramagnetically, so the susceptibility obeyed Curie-Weiss law. The large AF interaction within the triangles resulted as large Weiss temperature of -558 K. Each triangle formed spin trimer with $S_{\text{total}} = 1/2$ around the room temperature because of the intra-triangle interactions. Thus, the Curie constant decreased to about 1/3 of the high-temperature value. Since the inter-triangle interactions were weak, the Weiss temperature was as small as -16 K. The $S_{\text{total}} = 1/2$ spins localized on the trimers got antiferromagnetically ordered at 2.7 K. This ordering was broken by applying a magnetic field higher than 20 T, but the $S_{\text{total}} = 1/2$ state held.

§4. Acknowledgment

The authors express their thanks to Profs S. Maekawa, H. Yokoyama, H. Takagi, Drs Y. Mizuno and M. Nohara for fruitful discussions. Thanks are also due to Prof. Kindo and Dr Narumi for the magnetization measurement, to Dr. Utsumi for the help in HP XRD study, to Dr Fujita for the help in the neutron scattering study and to Prof. Johnston for the fitting of the susceptibility data. This work was partly supported by Grant-in Aid for Scientific Research of Ministry of Education, Science, Sports and Culture, Japan and CREST (Core Research

for Evolutional Science and Technology) of Japan Science and Technology Corporation (JST).

- 1) J. C. Bonner and M. E. Fisher, Phys. Rev. **135**, A640 (1964); J. C. Bonner, H. W. J. Blöte, J. W. Bray and I. S. Jacobs, J. Appl. Phys. **50**, (1979) 1910; J. C. Bonner and H. W. J. Blöte, Phys. Rev. B **25**, 6959 (1982).
- 2) for review, see E. Dagotto and T. M. Rice, Science **271**, 618 (1996).
- 3) F. D. M. Haldane, Phys. Rev. Lett. **50**, 1153 (1983).
- 4) M. Hase, I. Terasaki and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).
- 5) J. Darriet and L. P. Regnault, Solid State Comm. **86**, 409 (1993).
- 6) Z. Hiroi, M. Azuma, M. Takano and Y. Bando, J. Solid State Chem. **95**, 230 (1991); M. Azuma, Z. Hiroi, M. Takano, K. Ishida and Y. Kitaoka, Phys. Rev. Lett. **73**, 3468 (1994); M. Azuma, M. Takano and R. S. Eccleston, J. Phys. Soc. Jpn **67**, 740 (1998).
- 7) R. S. Eccleston, M. Uehara, J. Akimitsu, H. Eisaki, N. Motoyama and S. Uchida, Phys. Rev. Lett. **81**, 1702 (1998).
- 8) S. Taniguchi, T. Nishikawa, Y. Yasui, Y. Kobayashi, M. Sato, T. Nishioka, M. Kontani and K. Sano, J. Phys. Soc. Jpn. **64**, 2758 (1995).
- 9) H. Kageyama, K. Yoshimura, R. Stern, N. V. Mushnikov, K. Onizuka, M. Kato, K. Kosuge, C. P. Slichter, T. Goto and Y. Ueda, Phys. Rev. Lett. **82**, 3168 (1999).
- 10) M. Takano and T. Shinjo, J. Phys. Soc. Jpn. **33**, 1312 (1972); M. Takano, Solid State Commun. **63**, 1945 (1987) and the references therein.
- 11) D. C. Johnston, J. W. Johnson, D. P. Goshorn and A. J. Jacobson, Phys. Rev. B **35**, 219 (1987).
- 12) A. W. Garrett, S. E. Nagler, D. A. Tennant, B. C. Sales and T. Barnes, Phys. Rev. Lett **79**, 745 (1997).
- 13) G. S. Uhrig and H. J. Schulz, Phys. Rev. B **54**, R9624 (1996).
- 14) Z. Hiroi, M. Azuma, Y. Fujishiro, T. Sairo, M. Takano, F. Izumi, T. Kamiyama and T. Ikeda, J. Solid State Chem. **146**, 369 (1999).
- 15) P. T. Nguyen, R. D. Hoffman and A. W. Sleight, Mat. Res. Bull. **30**, 1055 (1995).
- 16) T. Yamauchi, Y. Narumi, J. Kikuchi, Y. Ueda, K. Tatani, T. Kobayashi, K. Kindo and K. Motoya, Phys. Rev. Lett **83**, 3729 (1999); J. Kikuchi, K. Motoya, T. Yamauchi and Y. Ueda, submitted to Phys. Rev. B **60**, 6731 (1999).
- 17) M. Azuma, T. Saito, Y. Fujishiro, Z. Hiroi, M. Takano, F. Izumi, T. Kamiyama, T. Ikeda, Y. Narumi and K. Kindo, Phys. Rev. B **60**, 10145 (1999).
- 18) T. Saito, M. Azuma, M. Takano, T. Goto, H. Ohta, W. Uthumi, P. Bordet and D. C. Johnston, preprint.
- 19) D. C. Johnston, R. K. Kremer, M. Troyer, X. Wang, A. Klümper, S. L. Bud'ko, A. F. Panchula, and P. C. Canfield, unpublished.
- 20) T. Barnes, J. Riera, and D. A. Tennant, Phys. Rev. B **59**, 11384 (1999).
- 21) D. A. Vander Griend, S. Boudin, V. Caignaert, K. R. Poepelmerer, Y. Wang, V. P. Dravid, M. Azuma, M. Takano, Z. Hu and J. D. Jorgensen, J. Am. Chem. Soc **121**, 4787 (1999).