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Magnetism of 1D Quantum Ferrimagnets, $A_3Cu_3(PO_4)_4$ with A = Ca, Sr

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Neutron and high field magnetization measurements are reported for one-dimensional (1D) quantum ferrimagnets, $A_3Cu_3(PO_4)_4$ with A = Ca, Sr in which the metal network is characterized by intertwining double chains of Cu(II) ions. High field magnetization up to 40 T at 4.2 K shows a clear signature of 1D ferrimagnets, i.e., a characteristic intermediate quantum state with a so-called 1/3 magnetization plateau. Neutron diffraction on powder samples of $Sr_3Cu_3(PO_4)_4$ at 70 mK in the magnetically ordered state reveals weak magnetic peaks. The fact that the intensity of the magnetic peaks are very weak, compared with those of the nuclear peaks, suggests that the quantum nature of the spins to essential for the ordering process of the system with discrete quantum energy levels.

KEYWORDS: neutron diffraction, high field magnetization, one dimensional, quantum spin, ferrimagnet

§1. Introduction

Quantum antiferromagnetism in low dimensional systems has been a subject of intense study in recent years. Much of the recent interest in this field has been focused on the magnetic properties of generalized one-dimensional magnets with peculiar topologies of the exchange pathways, giving rise to interesting quantum and spin frustration effects. The crystal structure of $A_3Cu_3(PO_4)_4$ with A = Ca, Sr is monoclinic and the metal network is characterized by intertwining double chains of Cu(II) ions as shown in Fig. 1(a).[1] In the figure, filled circles denote two kinds of Cu(II) ions with different coordinations, either Cu(1) or Cu(2). Open ovals represent oxygen atoms. As a result, the system may be viewed as $S = 1/2$ zig-zag chains of triangular units, consisting of one s_m spin at the kink site and two spins, S_{2n} and S_{2n+1}, at the corner sites, with relevant exchange interactions J_1, J_2 and J_3, by focusing on the metal ions and bridging oxygen network, as sketched in Fig. 1(b). This topological situation brings us a variety of interesting model systems described by the following Hamiltonian,

$$\begin{aligned}\mathcal{H} = \sum \{ & J_1 s_m (S_{2n-2} + S_{2n+1}) \\ & + J_2 s_m (S_{2n-1} + S_{2n}) \\ & + J_3 S_{2n} S_{2n+1} \\ & + g\mu_B H (s_m + S_{2n} + S_{2n-1}) \}\end{aligned}$$

For instance, a highly frustrated situation occurs due to competing exchange interactions in the triangular units of the chain when all couplings are antiferromagnetic. Interesting enough, it has been proposed that the system is characterized by a 1D ferrimagnet due to peculiar topologies of the exchange pathways, although only one kind of metal is involved and all the couplings are antiferromagnetic. Magnetic susceptibility measurements, reported by Drillon *et al.*,[2] show a clear signature of 1D ferrimagnet, i.e. a characteristic rounded minimum

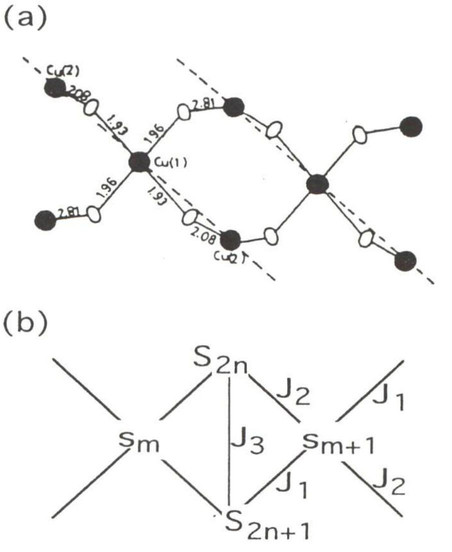

Fig. 1. (a)Metal network characterized by intertwining double chains of Cu(II) ions. (b)Relevant exchange pathways denoted by J_1, J_2 and J_3.

of χT around 25 K, indicating the existence of dominant antiferromagnetic interaction in a chain, and a strong divergence upon cooling down, showing the growth of non-compensated net moments. At very low temperature, $Ca_3Cu_3(PO_4)_4$ orders ferromagnetically at $T_C = 0.8$ K, while $Sr_3Cu_3(PO_4)_4$ exhibits an antiferromagnetic ordering at $T_N = 0.9$ K, due to the effect of inevitable interchain interactions. In order to interpret the susceptibility results, Drillon *et al.* have proposed an interesting 1D ferrimagnet model based on the antiferromagnetically coupled trimers (the largest interaction being J_1).[3)]

In order to clarify the magnetic state of this unique system, it is of particular interest to study the magnetic behaviors in sufficiently high magnetic fields since the high field will induce the different states, if any, due to competition between the Zeeman energy and the relevant antiferromagnetic coupling energies. Moreover, the ordered magnetic structure below T_N has not been investigated. A determination of the magnetic structure will give us important information on the couplings, including interchain interactions.

Here we report on the high field magnetization measurements for both compounds up to 40 T at 4.2 K and the neutron diffraction measurements for $Sr_3Cu_3(PO_4)_4$ down to 70 mK below T_N.

§2. High Field Magnetization

High field magnetization was measured on powder samples at 4.2 K in pulsed magnetic field up to 40 T available at ISSP, using an induction method. Examples of magnetization curves are shown in Figs. 2 and 3 for $Sr_3Cu_3(PO_4)_4$ and $Ca_3Cu_3(PO_4)_4$, respectively. The magnetization increases steeply and saturates around 20 T for Sr-compound and around 10 T for Ca-compound. It should be noted that the absolute value of about 0.4 μ_B/Cu^{2+} for the saturated magnetization is far from the expected value of $M_S = 1.15$ μ_B for $S = 1/2$ and $g = 2.3$ determined from ESR[4)] but just 1/3 of the fully aligned ferromagnetic state. The observed saturated state, therefore, should be regarded as an intermediate quantum state with a so-called 1/3 magnetization plateau.

In the first step of analysis, we employ a model of trimeric chain. In the limit of isolated trimer made up of three $S = 1/2$ spins in a line with antiferromagnetic intra-trimer interaction J_1, the quantum energy states are $E_0 = 0$ ($S_T = 1/2$), $E_1 = 2|J_1|$ ($S_T = 1/2$) and $E_2 = 3|J_1|$ ($S_T = 3/2$) where S_T is the total spins of an isolated trimer. In the 1D model of weakly coupled trimers described by $|J_1| \gg |J_2|, |J_3|$, the low-lying energy states are considered to form narrow bands in the vicinity of the isolated trimer eigenvalues. From this simple model, the zero magnetization state at zero field corresponds to the degenerated ground doublets with $S_T^z = \pm 1/2$, the intermediate state with $M = (1/3)M_S$ corresponds to the state with $S_T^z = 1/2$ in which all the s_m spins at the kink sites of the intertwining double chains (see Fig. 1(b)) are down($\downarrow$) and all the S_{2n} and S_{2n+1} spins at the corners are up($\uparrow$), and the transition to the fully saturated state with $S_T^z = 3$ in which all the spins are up($\uparrow$) is expected to occur at $g\mu_B H = 3|J_1|$, by considering the energy difference between the $S_T = 1/2$ ground doublet and the $S_T = 3/2$ excited quartet. Unfortunately, the fully aligned ferromagnetic state was not observed in our available field up to 40 T but the observation of full alignment is our future challenging task for more intense magnetic field.

§3. Neutron Diffraction

Measurements of neutron diffraction were performed on powder samples of $Sr_3Cu_3(PO_4)_4$ at 4.2 K above T_N and at 70 mK well below $T_N = 0.9$ K, using the Kinken powder neutron diffractometer HERMES for high efficiency and high resolution measurements installed at the T1-3 beam port of JRR-3M, JAERI, Tokai. This multi-detector system has a large solid angle of detectors of 0.13 sr and gives quite high counting efficiency. Instrumental details of HERMES is given in Ref. 5. Figure 4 shows a diffraction pattern of $Sr_3Cu_3(PO_4)_4$ at 4.2 K above T_N. Observed powder pattern was best fitted by Rietveld refinement procedure by means of RIETAN-97β. Since we used the known accurate positional parameters of the heavy atoms determined by X-ray diffraction[1)] as

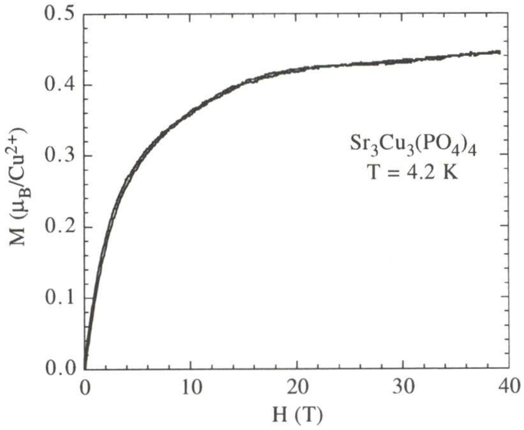

Fig. 2. High field magnetization of $Sr_3Cu_3(PO_4)_4$ powder sample at 4.2 K in pulsed magnet fields up to 40 T.

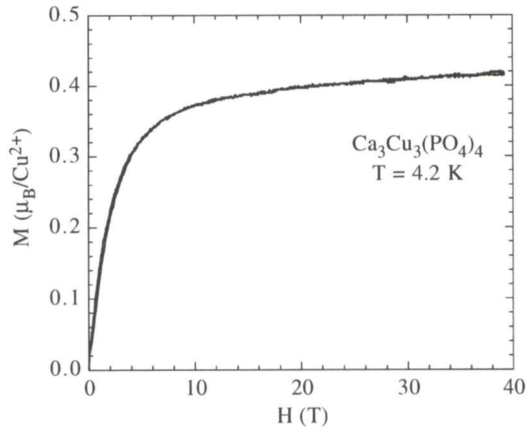

Fig. 3. High field magnetization of $ca_3Cu_3(PO_4)_4$ powder sample at 4.2 K in pulsed magnet fields up to 40 T.

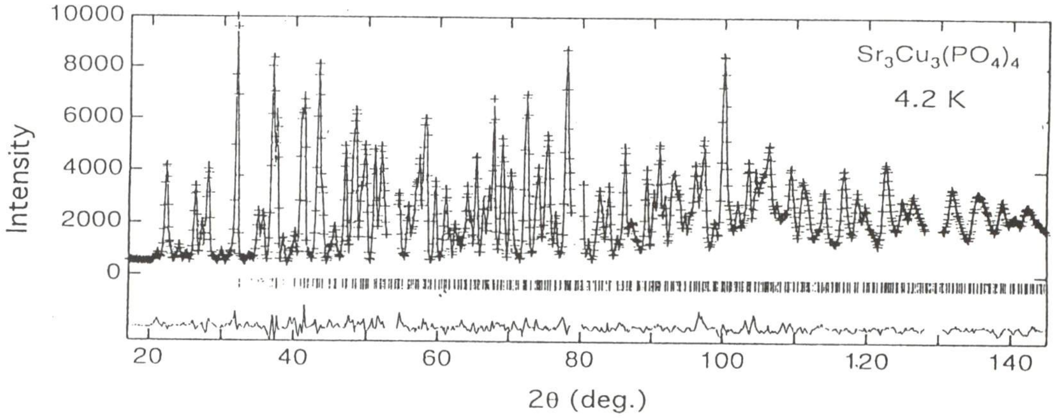

Fig. 4. Neutron diffraction pattern of $Sr_3Cu_3(PO_4)_4$ at 4.2 K.

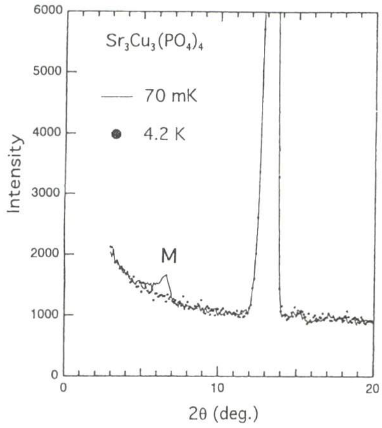

Fig. 5. Neutron diffraction patterns of $Sr_3Cu_3(PO_4)_4$ at 4.2 K and 70 mK, showing the very weak magnetic Bragg peak denoted by M.

the initial values of the fitting procedure, we were able to obtain quite good results of Rietveld analysis as shown in Fig. 4, although almost all of the peaks are overlapped in the pattern. This result indicates that it is possible to refine rather complicated structures with low symmetry using HERMES, when reliable initial values are given, as has been noticed already by Ohoyama.[6] The atomic parameters are not tabulated here since the structural refinement is beyond our purpose and, instead, we note the fact that our sample has a good quality without appreciable impurity phases.

Figure 5 shows the comparison between the 4.2 K data and the 70 mK data in the magnetically ordered state. A very weak magnetic peak was observed around $2\theta \simeq 6.5°$. This angle suggests that the ordered magnetic structure is described predominantly by two-fold periodic superstructure along the chain-axis. Although we can not deduce a meaningful result of ordered magnetic structure from the present work, we note the fact that the intensity of the magnetic peaks are very weak, compared with those of the nuclear peaks. The origin is not clear but it is worth mentioning here that the quantum nature of the spin is essential for the unique ordering process of the system with discrete quantum energy levels. In the weakly coupled trimer system, the two energetically higher levels, the excited doublet and quartet, do not participate with the ordering, because they are not populated at low temperatures. In other words, the Cu^{2+} spins are partially quenched and the ordering of Cu^{2+} spins is not complete in the sense that the ordering is restricted to the space of ground doublet with $S_T = 1/2$. The total spin within the trimer has an expectation value of 1/2 in the ordered state. Accordingly, the spin of individual sites is only 1/3 of the real spin, giving rise to a strong reduction of magnetic intensity of the order of 1/10. Detailed investigations are necessary in order to determine the magnetic structure and the magnitude of the magnetic moment.

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