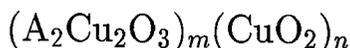


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## MAGNETIC PROPERTIES OF SPIN-LADDERS



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Magnetization  $M(T)$  and  $M(H)$  data of single crystals of the  $S = 1/2$  quasi-one-dimensional system  $(A_2Cu_2O_3)_m(CuO_2)_n$  with various  $A$ -site constituents are compared. The studied orthorhombic, incommensurate crystals are characterized by  $m/n = 5/7, 7/10$ , and  $9/13$ . The role of rare-earth ions located in  $A$ -sites is discussed.

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The investigated compounds are members of a large family  $(A_2Cu_2O_3)_m(CuO_2)_n$  of ladder compounds (where  $A$  positions are occupied by an alkaline earth or trivalent metal). Their orthorhombic structure contains two structural modules with the same  $a$  and  $b$  lattice parameters and different incommensurate  $c$  parameters. The modules  $A_2Cu_2O_3$  create a two-leg ladders plane between two layers of  $A$ -cations. The modules  $CuO_2$  represent the plane of weakly coupled  $Cu-O$  chains. A different structure of both modules along the  $c$ -axis is caused by the  $Cu-O$  squares sharing the corners and edges, respectively. In the commensurate approximation the average lattice parameter along the  $c$ -axis can be expressed as  $c = m \times c_1 = n \times c_2$  (where  $c_1$  and  $c_2$  are the  $c$  lattice parameters for the first and second modules, respectively). For the  $m/n$  values of  $5/7, 7/10$ , and  $9/13$ , it leads to chemical formulae of three known phases [1-4] of the given family:  $A_{10}Cu_{17}O_{29}$ ,  $A_{14}Cu_{24}O_{41}$ , and  $A_{18}Cu_{31}O_{53}$ , respectively.

In  $Sr_{14}Cu_{24}O_{41}$  a dimerized singlet state has been reported [5, 6] with an energy gap between the ground and excited states. The mechanism of dimerization in such case has not been still clarified. The concentration of holes and their distribution over various sites influences significantly the magnetic properties of investigated compounds.

Because the ladders in the investigated compounds are similar to those in  $SrCu_2O_3$  (with an energy gap of 400-600 K [7]), their contribution to magnetic properties below room temperature can be neglected. Therefore, the magnetism

in our compounds originates mainly from Cu in chains and from rare-earth ions (if any present) in A-site.

The aim of this work was to study the influence of substitution of rare-earth ions ( $\text{Nd}^{3+}$  or  $\text{Pr}^{3+}$ ) in place of  $\text{Sr}^{2+}$  on magnetic properties of the studied crystals.

The investigated crystals of  $(\text{A}_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$  family ( $\text{A} = \text{Sr}, \text{Ca}, \text{Y}, \text{Nd}, \text{Pr}$ , and some small admixtures) were grown using a flux method with a decantation at  $900^\circ\text{C}$  [8]. The X-ray powder diffraction confirmed that the obtained single crystals were single phase samples of an incommensurate phase.

Three kinds of crystals were the subject of studies:

(i) Crystals of the composition  $(\text{Sr}_{6.2}\text{Y}_{0.4}\text{Ca}_{3.4})(\text{Cu}_{16.7}\text{Bi}_{0.1}\text{Pb}_{0.1})\text{O}_{29}$  whose magnetism originates from copper ions only (S1). The single-crystalline X-ray structural analysis of these crystals and a refinement of the parameters of two structural modules showed that they should be assigned to the  $\text{A}_{10}\text{Cu}_{17}\text{O}_{29}$  compounds (with the space group  $F_{222}$  in the commensurate approximation). Their lattice parameters  $a, b, c$  are as follows:  $a = 11.346(3) \text{ \AA}$ ,  $b = 12.996(3) \text{ \AA}$ ,  $c = 19.586(9) \text{ \AA}$ .

(ii) Crystals of the composition  $(\text{Y}_{1.3}\text{Nd}_{3.7}\text{Sr}_{2.5}\text{Ca}_{6.5})(\text{Cu}_{23.2}\text{Ca}_{0.4}\text{Sr}_{0.4})\text{O}_{41}$  (S2). According to the X-ray analysis they should be assigned to the  $\text{A}_{14}\text{Cu}_{24}\text{O}_{41}$  compounds (with the space group  $Abmm$  in the commensurate approximation). The lattice constants  $a, b, c$  are as follows:  $a = 11.294(6) \text{ \AA}$ ,  $b = 12.515(2) \text{ \AA}$ ,  $c = 27.544(8) \text{ \AA}$ .

(iii) Crystals of the composition  $(\text{Y}_{2.2}\text{Pr}_{5.2}\text{Sr}_{10}\text{Ba}_{0.6})\text{Cu}_{30.7}\text{O}_{53}$  (S3). According to the X-ray analysis they should be assigned to the  $\text{A}_{18}\text{Cu}_{31}\text{O}_{53}$  compounds. Their lattice parameters  $a, b, c$  are as follows:  $a = 11.3176(1) \text{ \AA}$ ,  $b = 12.967(2) \text{ \AA}$ ,  $c = 35.60(5) \text{ \AA}$ .

The dc magnetization measurements were performed with a SQUID magnetometer (MPMS-5, Quantum Design) in magnetic fields up to 50 kOe and in the temperature range of 2–300 K.

The experimental  $\chi(T)$  data for samples S1 can be well described assuming the contribution to the magnetic susceptibility from Curie–Weiss paramagnetism  $\chi_{\text{cw}}$  as well as from the dimerized chains  $\chi_{\text{ch}}$  (see Fig. 1a in [9]) similarly as for the  $(\text{Sr}, \text{Ca})_{14}\text{Cu}_{24}\text{O}_{41}$  system (e.g. [10, 11]). At low temperatures ( $T < 15 \text{ K}$ ) there is only a dominant contribution from Curie–Weiss paramagnetism. This well coincides with a nonlinearity in  $M(H)$  relation at  $T \leq 5 \text{ K}$ , which appears in a sufficiently high magnetic field for the field directed along all main crystallographic axes.

A quite different behavior of  $M(H)$  was observed for S2 and S3 samples at the lowest temperature (2–5 K) than for S1 samples. For  $H \parallel a$  and for  $H \parallel c$  linear  $M(H)$  relations were obtained (see Fig. 1). One should interpret the behavior as due to the antiferromagnetic ordering at low temperature. However, for  $H \parallel b$  a nonlinearity in  $M(H)$  suggests an existence of a “weak” ferromagnetic moment lying along a direction close to the  $b$ -axis. The assumption of magnetic order at low temperature correlates with some peculiarities in  $\chi(T)$  at about 20 K and below (see Fig. 2). The weak ferromagnetism seems to appear due to Dzyaloshinskii–Moriya exchange interactions. Although the antiferromagnetic ordering was reported [12] in  $\text{La}_6\text{Ca}_8\text{Cu}_{24}\text{O}_{41}$ , the weak ferromagnetic moment both in 7/10 and 9/13 compounds is observed here for the first time.

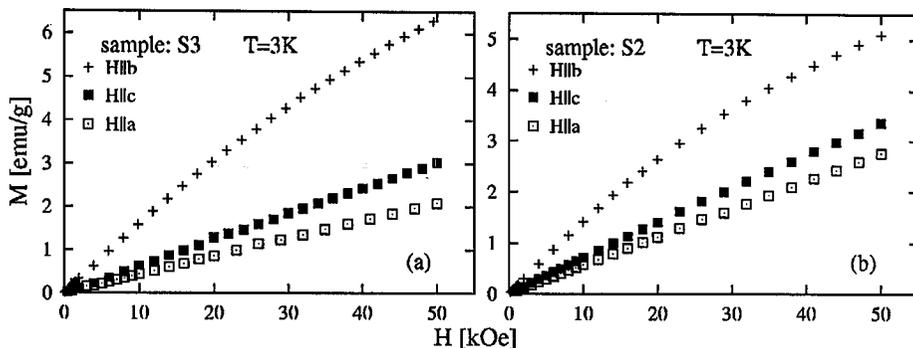


Fig. 1. Magnetization vs. magnetic field at  $T = 3$  K, for samples S3 (a) and S2 (b) for  $H$  along  $a$ -,  $b$ -, and  $c$ -axes.

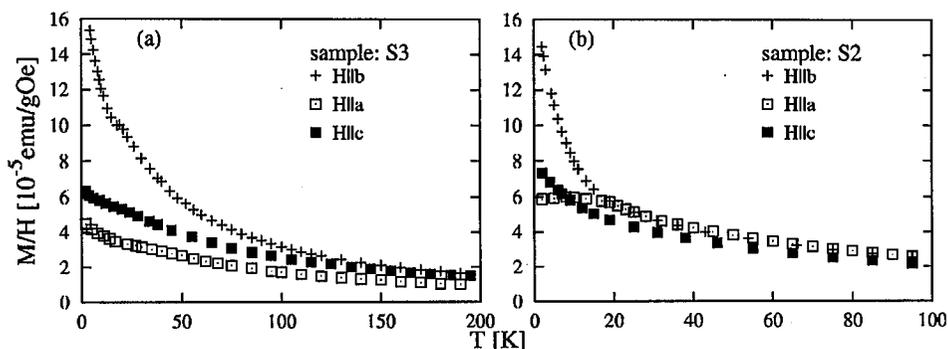


Fig. 2. Susceptibility vs. temperature for samples S3 (a) and S2 (b) for  $H$  along  $a$ -,  $b$ - and  $c$ -axes. The temperature ranges are limited to show better all peculiarities at low temperatures.

In the case of S1 samples both  $M(H)$  and  $\chi(T)$  are anisotropic — a relation  $\chi(H \parallel b) > \chi(H \parallel a) \approx \chi(H \parallel c)$  is fulfilled in the whole temperature range. The anisotropy of the susceptibility observed in these samples (especially in a higher temperature range for  $T > 100$  K) is typical of all compounds of the studied family in which only Cu is characterized by the magnetic moment. The character of anisotropy does not depend on nonmagnetic substitutions in A-sites, even for such which can lead to magnetic order at low temperature [12] or to a significant change of transport properties (even to superconductivity [13–15]).

An inserting of large rare-earth ions ( $\text{Nd}^{3+}$  or  $\text{Pr}^{3+}$ ) to A-sites of S2 and S3 samples (besides the contribution to magnetization of their magnetic moments) enlarges the distance between chains and ladders influencing the holes distribution and their localization. The anisotropy of the susceptibility observed in S2 and S3 samples in a higher temperature range ( $T > 70$  K) is quite different than that for S1 samples. It seems reasonable to attribute this anisotropy change to the influence of the crystal field on rare-earth ions. From a rough estimation of various possible contributions to the susceptibility at higher temperatures ( $T = 70 \div 300$  K), the assumption that a contribution from Cu in ladders is neg-

ligible seems to be reasonable. Besides rare-earth ions, only Cu ions from chains contribute distinctly to the total susceptibility. However, because of the magnetic order at low temperatures, it is impossible to separate contributions from free Cu and dimerized Cu in chains.

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