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Spin Ladder Compounds

Mikio Takano, Zenji Hiroi and Masaki Azuma

Three kinds of cupric spin ladder compounds, SrCu₂O₃(2-leg), Sr₃Cu₃O₅(3-leg), and LaCu₂O₂(2-leg), have been discovered in the course of studies of high pressure chemistry carried out at 6 GPa and 1200 K, typically. Structures, electrical and magnetic properties of these intriguing compounds, which exemplify the initial stage of the transition from one to two dimensionality, will be summarized.

Keywords: High pressure synthesis / Spin ladder / High $T_c$ superconductivity / Spin liquid

High pressure synthesis at 1−10 GPa is a rather classical but still promising way to discover new compounds. Using a cubic anvil type apparatus mainly, we have carried out a systematic research on cupric oxides at 6 GPa and 1200 K, typically, for about eight years, and it has been shown that new phases crystallizing in various low dimensional structures can be obtained by quenching. Here we will describe structural and physical properties of three $\beta$ spin ladder compounds discovered very recently.

In 1991 we reported the synthesis of a homologous series of high pressure phases Sr$_{n-1}$Cu$_n$O$_{2n}$ [1], in which 2D Cu$_{n+1}$O$_{2n}$ sheets are stacked sandwiching Sr$^{2+}$ ions in-between. As can be seen in Fig. 1 where the Cu$_2$O$_3$ ($n=3$) and Cu$_3$O$_5$ ($n=5$) sheets are illustrated, the Cu$_{n+1}$O$_{2n}$ sheets are made of ladders with a $n$ dependent width: The longitudinal Cu-O-Cu chains are compared to the legs of a ladder and the lateral Cu-O-Cu bonds to the rungs. The leg number is equal to $(n+1)/2$. It is noteworthy that neighboring ladders are phase-shifted from each other and that the phase shift causes spin frustration between the neighboring ladders. The Cu$_{n+1}$O$_{2n}$ sheets can thus be considered as being made of tightly bound but magnetically separated $(n+1)/2$-leg ladders. For these compounds a dramatic change of electronic properties with leg number was predicted by Rice et al. in 1993 [2]: Ladders with an even number of legs have purely short range magnetic correlation and a finite energy

Figure 1. Schematic drawings of the Cu$_2$O$_3$ sheet of SrCu$_2$O$_3$ (left) and the Cu$_5$O$_7$ sheet of Sr$_3$Cu$_3$O$_5$ (right). The filled circles are Cu$^{2+}$ ions, and O$^{2-}$ ions exist at the corners of the gray squares. Cu ions interact antiferromagnetically with each other within each ladder as shown with dashed lines.

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. Particularly the search for spin ladder materials is intensively conducted by means of a high pressure synthesis at 3-8 GPa, where materials of high density unavailable under ambient pressure can be obtained.

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gap to all magnetic excitations, while odd-leg ladders are gapless as a single chain is. The magnitude of the gap \( \Delta \) is equal to \( J/2 \) for an isotropic 2-leg ladder. And it has been predicted that holes doped in even-leg ladders will pair and possibly superconduct. For further details the readers are referred to a nice and compact review by Dagotto and Rice [3].

The electronic properties have been studied experimentally by means of SQUID magnetometry [4], NMR [5], \( \mu \)SR [6], and also inelastic neutron scattering [7]. All these showed quite consistently that the 2-leg ladder system assumes the so-called singlet spin liquid state, in which a Cu ion is coupled with the counter Cu ion on the same rung mainly. The magnitude of the spin gap was estimated to be 420 K from the temperature dependence of magnetic susceptibility [4], and the more recent direct determination using inelastic neutron scattering indicated a value of 410 K [7]. In marked contrast with the 2-leg ladder system that retains the unique coherent singlet ground state down to at least 20 mK, the 3-leg ladder compound becomes magnetically ordered at rather high temperatures [6]. Thus, \( \text{SrCu}_2\text{O}_3 \) and \( \text{Sr}_2\text{Cu}_3\text{O}_6 \), which crystallize in essentially the same structures except for the leg number, have proved to show quite different magnetic properties. However, it has not been possible to test the possibility of high-\( T_c \) superconductivity in the 2-leg ladder compound, because the solubilities at the Sr site of aliovalent cations like \( \text{Na}^+ \) for hole-doping and \( \text{La}^{3+} \) for electron-doping proved to be low.

More recently, another 2-leg ladder compound \( \text{LaCuO}_2\text{.5} \) was found in the La-Cu-O system treated at 6 GPa and 1173 K [8]. There are, however, important differences between this compound and \( \text{SrCu}_2\text{O}_3 \) concerning the anion coordination and the arrangement of ladders. In \( \text{LaCuO}_2\text{.5} \) the Cu ions are all five-fold coordinated, not four-fold coordinated as in \( \text{SrCu}_2\text{O}_3 \). The Cu-O distances in the inter-ladder Cu-O-Cu bond are 1.941 Å and 2.285 Å and the bond angle is 152.2°. Weak inter-ladder interactions would be mediated by this bond. The investigation of the electronic properties is in a preliminary stage. For example, susceptibility data seem to be inconsistent with NMR measurements. Theoretical fitting to the susceptibility data goes very well down to 5 K, from which the spin gap \( \Delta \) was estimated to be 474 K [8]. This value is comparable with that for \( \text{SrCu}_2\text{O}_3 \), 420 K. However, as will be reported soon, the temperature dependences of \( T_1 \) and the NMR spectral intensity have revealed a rapid growth of spin-spin correlations which suggests the occurrence of a magnetic ordering at \( \sim 120 \) K [9]. The ordering was confirmed by a more recent magnetic measurement. This is quite inconsistent with the spin liquid picture suggested from the susceptibility data, in contrast to the case of \( \text{SrCu}_2\text{O}_3 \) where the picture was supported by all the measurements quite consistently. Various additional measurements including elastic and inelastic neutron scatterings are in progress. In contrast to the case of \( \text{SrCu}_2\text{O}_3 \) again, chemical substitution for the purpose of hole-doping can fortunately be done up to \( x = 0.2 \) for \( \text{La}_{1-x}\text{Sr}_x\text{Cu}_2\text{O}_5 \). Resistivity at 300 K drops quickly from \( -10^4 \) cm for \( x = 0 \) to \( -10^2 \) cm for \( x = 0.15 \) and \( -10^3 \) cm for \( x = 0.2 \). There is, unfortunately, no sign of superconductivity down to 1.5 K anyway. The interpretation of these results might be complex in nature because of the effects of inter-ladder interactions [10] and random potentials caused by the aliovalent \( \text{Sr}^{2+} \)-for-\( \text{La}^{3+} \) substitution.

The final conclusion to be drawn here is quite simple. Both physics and chemistry of spin ladder compounds are quite new. The researches summarized here are nothing but the first steps on the ladder [11]. We believe that there would be various interesting findings in the future in this new research field.

References

Figure 2. Crystal structure of \( \text{LaCuO}_2\text{.5} \). Small circles: \( \text{Cu}^{2+} \) ions, middle circle: \( \text{O}^{2-} \) ion and large circles: \( \text{La}^{3+} \) ions.