Spin-hole order in the 1-D chain cuprate $Ca_{0.824}CuO_2$

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Abstract

We have studied the magnetic state from a viewpoint of crystallographic features of the 1-D chain compound $Ca_{0.824}CuO_2$, and determined a possible spin-hole arrangement in the coexisting state by precisely analyzing the local structural distortion in the CuO_2 chain using a modulated-crystal-structure analysis technique. The essential periodic sequence expected is $\cdots\uparrow\bigcirc\downarrow\downarrow\bigcirc\uparrow\cdots$ ($\uparrow$ $\downarrow$: up- and down-spin, $\bigcirc$: hole) along the chain.

Key words: Heisenberg chain; spin singlet; antiferromagnetism; modulated-crystal-structure analysis

1. Introduction

The hole-doped edge-sharing Cu-O chain compound Ca_xCuO_2 (x ~0.83) has a novel quantum electronic state where spatially modulated spin staggered moment coexists in a site with a spin-singlet ground state [1]. It is important to solve the magnetic structure in the coexisting state, because it seems to be related to an electronic state of the under-doped region in high-T_C cuprate superconductors.

The present system has a unique crystal structure, which is incommensurately modulated by mismatch interaction between the CuO_2 and Ca sub-lattices [2]. Each atomic position is displaced from the average one in the fundamental structure. The magnetic state, i.e., magnetic structure, should be strongly affected by the local structural distortion through ionic potential. Therefore, if we obtain precise crystal structure data, in particular, Cu–O distances and Cu–O–Cu bond-angles in the chain, we can estimate a localized-hole distribution and spin-spin magnetic interactions by utilizing bond-valence calculation [3] and relation between magnetic interaction and the bond-angles [4].

In this short paper, we report the crystal-structure data of the chain system precisely refined by a modulated-crystal-structure analysis technique. We discuss the magnetic state with a possible spin-hole arrangement model obtained by the structural data.

2. Structure analysis

The x-ray diffraction data of a pure polycrystalline sample of Ca_xCuO_2 (T_N=11.8 K) were analyzed with a Rietveld-refinement program, PREMOS [5], assuming the superspace-group, F2/m(1+α 0 γ)0s, for the composite crystal. Detail of the analysis is reported in our previous paper [6]. The reliability factor obtained was R_{WP}=0.0289. The actual Ca ratio x in the sample was determined to be 0.8240(1) as a mismatch parameter between the sub-lattices, and then the average hole concentration was estimated to be 0.352 ($= 2(1-x)$) per formula unit.

3. Results and discussion

Figure 1(a) shows the bond-valence sum (BVS) of the Cu atoms plotted in order of the Cu-site number i from 0 to 40 along a chain. The each value was calculated using Cu–O inter-atomic distances around the Cu(i) site. The BVS can be regarded as a probability of hole occupancy at the each Cu site. The horizontal

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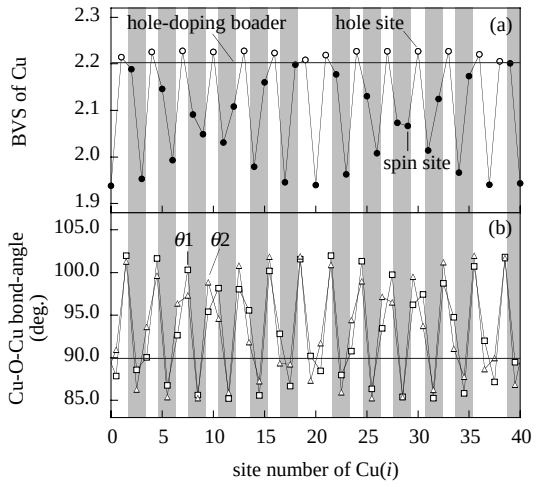

Fig. 1. Bond-valence sum of the Cu(i) atoms (a), and Cu(i)–O–Cu(i+1) bond-angles (b) plotted in order of the Cu-site number i from 0 to 40 along a chain. The open circles indicate hole-occupied sites, while the closed circles indicate hole-unoccupied sites (≡ spin sites). The shaded area indicates adjoining two spin sites, which gives the nearest-neighbor spin-spin interaction J_1.

line in the graph indicates a border of the BVS value which divides hole-occupied sites from hole-unoccupied ones. This border was determined by the average hole concentration. In the graph, the open circles denote hole-occupied sites, while the closed circles indicate hole-unoccupied sites (≡ spin sites). The hole occupation occurs at every third Cu site in most parts of the chain, and the hole occupied sites are never placed in succession. It is probably due to large Coulomb repulsion between holes in the edge-sharing chain. The sites that two spins adjoin along the chain are shaded in the graph. The main periodic sequence of the hole and spin is ... hole–spin–spin–hole–spin–spin ... along the chain.

Figure 1(b) shows the Cu(i)–O–Cu(i+1) bond-angles θ. It can be seen that the bond-angle is largely modulated and varies over a wide range of 85–102 deg. However, note that the Cu–O–Cu bond-angles between adjoining two spin sites, which gives the nearest-neighbor magnetic interaction J_1, are always smaller than 90 deg. According to the theoretical calculation by Mizuno et al. [4], an edge-sharing Cu-O chain system with θ <95 deg. has a ferromagnetic J_1. Therefore, in the present system, the J_1 is expected to be ferromagnetic. In contrast, the next nearest-neighbor magnetic interaction J_2 is always antiferromagnetic on regardless of Cu–O–Cu bond-angles in edge-sharing Cu-O chain systems [4]. By comparing the obtained bond-angles and the theoretical results, the magnitude of J_1 and J_2 were roughly estimated to be about -300 ± 100 K and 100 ± 50 K, respectively. Therefore, the $|J_1|$ value is expected to be comparable to or even larger than J_2.

Based on the hole distribution and the signs of the magnetic interactions, we constructed a possible spin-hole arrangement model as illustrated in Fig. 2. It is noteworthy that all the spins are arranged without magnetic frustration regarding the nearest-neighbor and next nearest-neighbor couplings. The most parts in the arrangement consists of a sequence, $\cdots\uparrow\bigcirc\downarrow\downarrow\bigcirc\uparrow\cdots$, which can be regarded as a kind of chain having alternate ferromagnetic and antiferromagnetic couplings.

The antiferromagnetic interaction acts between two spins via a hole in the $\uparrow\bigcirc\downarrow$ configuration. This configuration seems to be an origin of the dimerized spin-singlet ground state realized in the present system [1]. The ferromagnetic interaction will act as inter-dimer interaction. If staggered magnetic moment is induced on a site with the spin singlet in accordance with the arrangement, long-range spin order without magnetic frustration can coexist with the spin-singlet state. The proposed spin-hole arrangement is most likely realized in the coexisting state.

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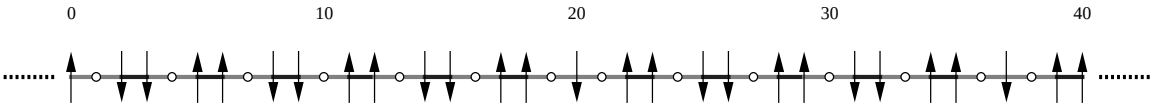

Fig. 2. Possible spin-hole arrangement on Cu(i) sites with i=0–40 in a chain.