Electronic structure of Cu in ferromagnetic CaCu$_3$Sn$_4$O$_{12}$

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Abstract. We have investigated the electronic structure of Cu ions in ferromagnetic compound CaCu$_3$Sn$_4$O$_{12}$ by using X-ray absorption and magnetic circular dichroism (MCD) measurements around the Cu $L_{3,2}$- and O $K$-edges. In both edges, the signal of MCD were clearly observed. By using sum rules, we could obtained $M_{\text{spin}} = 0.87 \pm 0.01 \mu_B$, $M_{\text{orb}} = 0.07 \pm 0.01 \mu_B$, and $M_{\text{total}} = 0.93 \pm 0.02 \mu_B$, per Cu ion. The orbital magnetic moments of Cu ions are significant and are originated from the spin-orbit interactions.

1. Introduction
A-site-ordered perovskites $AA’B_4O_{12}$ show diverse and intriguing physical properties. For example, CaCu$_3$Ti$_4$O$_{12}$, exhibits a colloidal dielectric constant over a wide temperature range [1]. CaCu$_3$Mn$_4$O$_{12}$ is a ferrimagnetic semiconductor with a Curie temperature above room temperature [2]. CaCu$_3$Ru$_4$O$_{12}$ is a Pauli-paramagnetic metal and its magneto-transport properties are reported to show a heavy-fermion like behavior [3, 4].

It is very difficult to understand the origin of these compounds magnetic properties due to the balance among the strength of interaction between $A’$-$A’$, $A’$-$B$, and $B$-$B$ sites. Especially, it was widely known that magnetic Jahn-Teller ions of Cu at the square-planar coordinated $A’$-site
play a crucial role in all properties of these perovskites. Therefore, we have tried to extract $A'\cdot A'$ interaction by introduced non-magnetic ions to the $B$-site. CaCu$_3$B$_4$O$_{12}$ ($B$ = Ge, Sn, and Ti) and their solid solutions show unusual transitions from ferromagnetic CaCu$_3$Ge$_4$O$_{12}$ to antiferromagnetic CaCu$_3$Ti$_4$O$_{12}$ to ferromagnetic CaCu$_3$Sn$_4$O$_{12}$. The ferro- to antiferromagnetic transition mechanism in these materials is not based on the superexchange interaction [5]. While the Sn-ions in the B-sites of the CaCu$_3$Sn$_4$O$_{12}$ (CCSO) are non-magnetic, the materials show the ferromagnetic ordering below 10 K [6]. There is no study of electronic and magnetic states of Cu ions from the microscopic point of view. Therefore, we carried out the X-ray absorption (XAS) and magnetic circular dichroism (MCD) measurements in order to elucidate the electronic and magnetic states of Cu ions and O ions in CCSO.

2. Experimental

The XAS and MCD for Cu $L_{3,2}$ and O $K$-edges for the disproportionated CCSO were measured at 9 K by a total electron yield method at BL25SU of SPring-8 in Japan. The energy resolution $E/\Delta E$ at the Cu $L_{3,2}$- and O $K$-edges was greater than 5000. The incident photon energy was calibrated by measuring the energies of the Ti $L_{3,2}$-edges of TiO$_2$ and the Ni $L_{3,2}$-edges of NiO. Powder sample was pasted uniformly on a sample holder by using carbon tape. The spectra were obtained using parallel (I$_+$) and antiparallel (I$_-$) photon spins along the magnetization direction of the sample, to which a static magnetic field of 1.9 Tesla was applied. The MCD intensity was defined by the difference between the two absorption spectra ($I_{MCD} = I_- - I_+$).

3. Results and Discussion

Figure 1 shows the I$_+$ and I$_-$ XAS spectra at the Cu $L_{3,2}$-edges. This spectral shape is similar to that of BiCu$_3$Mn$_4$O$_{12}$ containing typical divalent Cu ions. [7, 8] The MCD intensities at the Cu $L_3$-edge ($\sim$931.5 eV) are negative while those at the Cu $L_2$-edge ($\sim$951.3 eV) are positive.

![XAS and MCD spectra at Cu $L_{3,2}$-edges for CaCu$_3$Sn$_4$O$_{12}$ at $T = 9$ K. Red (I$_+$) and green (I$_-$) circles show the XAS spectra measured with external field 1.9 T applied parallel and antiparallel to the light propagation axis. The bottom line represents the MCD intensity $I_{MCD}$. The arbitrary unit of intensity in XAS spectrum was set to unity at 965 eV.](image)

Figure 2 shows the XAS spectrum ($(I_- + I_+)/2$) at the O $K$-edge, which originates from an excitation of electrons from the O 1s state to the unoccupied O 2p states in the conduction band. Since the empty O 2p states hybridize with the 3d and 4sp states of cations in oxides, the observed O-XAS spectrum reflects the features of the electronic structures of the constituent transition-metal ions [9]. The spectrum from 529 to 532 eV mainly represents the nature of the Cu 3d bands (the upper Hubbard band).

The absorption spectrum at approximately 534 - 540 eV reflects the characters of the Sn 5sp and Ca 3d bands. [9, 10, 11] In the MCD spectrum also shown in Fig. 2, it is notable that
negative signals are clearly observed around the Cu 3d region. As seen in La$_{1-x}$Sr$_x$MnO$_{3+\delta}$, [12] the negative MCD signal at the O K-edge with intensity of a few percent of the XAS suggests the contribution of a direct transfer from the 3d orbital magnetic moment of a transition metal to the O 2p states. Thus, the result of the O K-edge MCD indicates that Cu 3d orbital magnetic moments contributed to the magnetic properties of the ferromagnetic CCSO.

We quantitatively analyze the orbital magnetic moment of Cu ions in CCSO by using the magneto-optical sum rules. [13, 14] Total magnetic moment ($M_{\text{total}}$) consists of orbital ($M_{\text{orb}}$) and spin ($M_{\text{spin}}$) parts and they are expressed as

$$M_{\text{orb}} = -\frac{4\pi n_h}{3} \left( \frac{I_{e_3} + I_{L_2}}{W_{e_3} + W_{L_2}} \right),$$

$$M_{\text{spin}} = -n_h \left( \frac{I_{e_3} - 2I_{L_2}}{W_{e_3} + W_{L_2}} \right),$$

where I and W represent the spectral weights of the MCD and XAS intensities, respectively, and $n_h$ is the number of holes in the 3d state. The boundaries between the $L_3$ and $L_2$ edges of the Cu spectra are set to 946.5 eV. Because the sample is a poly-crystal and the Cu ions in CCSO are located at the high symmetry D$_{4h}$ sites, respectively, the magnetic dipole matrix operator is zero and thus the $M_{\text{spin}}$ is simplified as in equation (2). From an ab-initio band calculation with the local spin density approximation, $n_h$ for Cu-3d were estimated to be 0.97. [15] With these values, we can obtain $M_{\text{spin}} = 0.87 \pm 0.01 \mu_B$, $M_{\text{orb}} = 0.07 \pm 0.01 \mu_B$, and $M_{\text{total}} = 0.93 \pm 0.02 \mu_B$, per Cu ion. The orbital part of the magnetic moment for Cu is significant, consistent with the observation of the O K-edge MCD spectrum.

First, we discuss the origin of the orbital magnetic moments. Within the crystal field theory, the 3d electrons of transition metal ions in $e_g$ orbitals under a cubic crystal field have no orbital magnetic moments [16] because the $3z^2-r^2$ and $x^2-y^2$ orbitals cannot be transformed into each other by rotation about any axis. The presence of orbital magnetic moments requires the spin-orbit interaction. That is to say, orbital magnetic moment is produced in the $e_g$ state by the spin-orbit interaction between the unoccupied $|x^2-y^2;\uparrow\rangle$ and the occupied $|xy,yz,zx;\downarrow\rangle$ states and between the unoccupied $|3z^2-r^2;\downarrow\rangle$ and the occupied $|yz,zx;\uparrow\rangle$ ones. According to the perturbation theory [12, 17], orbital magnetic moments of 3d electrons are proportional to $\xi_{3d}/10Dq$ ($\xi_{3d}$ is the spin-orbit interaction of 3d electrons). It is determined that $M_{\text{orb}}$ of Cu ions is 0.068 $\mu_B$ using the value of $\xi_{3d} = 102$ meV and $10Dq = 1.5$ eV for Cu ions. This value is acceptably close to our estimation value of 0.07 $\mu_B$ by using sum rules. This result indicates that the orbital magnetic moments of Cu ions are originated from the spin-orbit interaction.
4. Summary
We have investigated the electronic structure of Cu ions in ferromagnetic compound CCSO by using XAS and MCD measurements around the Cu $L_{3,2}$- and O $K$-edges. In both edges, the signal of MCD were clearly observed. By using sum rules, we could obtained $M_{\text{spin}}= 0.87 \pm 0.01 \mu_B$, $M_{\text{orb}}= 0.07 \pm 0.01 \mu_B$, and $M_{\text{total}}= 0.93 \pm 0.02 \mu_B$, per Cu ion. The orbital magnetic moments of Cu ions are significant and are originated from the spin-orbit interactions.

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