Inorg. Chem. **2009**, *48*, 3499−3501

Inorganic Chemistry
Communication

Orbital Hybridization and Magnetic Coupling of the A-Site Cu Spins in $CaCu_3B_4O_{12}$ (B = Ti, Ge, and Sn) Perovskites

M. Mizumaki,*,† T. Saito,‡ H. Shiraki,‡ and Y. Shimakawa‡

Japan Synchrotron Radiation Research Institute (JASRI), Sayo-cho Sayo-gun, Hyogo 679-5198, Japan, and Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Received November 12, 2008

X-ray absorption spectroscopy (XAS) spectra near the O K-edge of A-site-ordered perovskite with A-site Cu^{2+} ($S = ^1/_2$) spins were measured. The spectra of ferromagnetic $CaCu_3Ge_4O_{12}$ and $CaCu_3Sn_4O_{12}$ showed hybridization between Cu 3d and O 2p orbitals, but magnetic circular dichroism measurement revealed that the O 2p orbital played a less important role in magnetic interaction. The XAS spectra of antiferromagnetic $CaCu_3Ti_4O_{12}$, on the other hand, showed strong hybridization of the Cu 3d, Ti 3d, and O 2p orbitals. These results demonstrated that direct exchange interaction of the Cu^{2+} spins primarily determined the ferromagnetic ordering of $CaCu_3Ge_4O_{12}$ and $CaCu_3Sn_4O_{12}$, whereas the involvement of Ti 3d orbitals induced the antiferromagnetic property in $CaCu_3Ti_4O_{12}$.

A-site-ordered perovskites with the general formula $AA'_3B_4O_{12}$ show diverse and intriguing physical properties.[1,2] Figure 1 shows the crystal structure of these compounds. Distinctive features of these compounds are not only that they have a very unusual ordered arrangement of A-site ions but also that they contain magnetic Jahn−Teller ions such as Cu^{2+} and Mn^{3+} at the originally 12-fold-coordinated A′ site. A compound thus could be a rare A-site magnetic material due to interaction between the magnetic ions at the A site.

$CaCu_3Ge_4O_{12}$, $CaCu_3Ti_4O_{12}$, and $CaCu_3Sn_4O_{12}$ are examples of such A-site magnetic materials; all of them contain magnetic Cu^{2+} ions at the A′ site and nonmagnetic ions at the B site. Only Cu^{2+} ($S = ^1/_2$) spins at the A′ site thus contribute to the magnetic properties of the oxides. Interestingly, $CaCu_3Ge_4O_{12}$ and $CaCu_3Sn_4O_{12}$ show ferromagnetic properties with Curie temperatures of 13 and 10 K, respectively, in contrast to an antiferromagnetic one for $CaCu_3Ti_4O_{12}$ ($T_N = 25$ K).[3,4] Therefore, the A-site Cu^{2+} spins can align either ferromagnetically or antiferromagnetically within the same structural framework, depending on the nonmagnetic B-site ion.

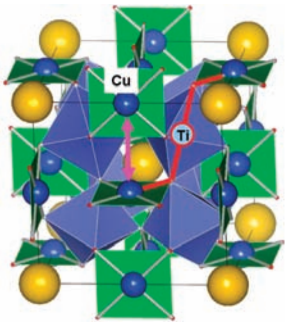

Figure 1. Crystal structure of $ACu_3B_4O_{12}$ (B = Ti, Ge, and Sn). A (large sphere) and Cu (middle sphere) ions are ordered, and the B-site ions form BO_6 octahedra. The two-headed arrow shows direct interaction between Cu^{2+} spins, and the thick lines show the Cu−O−Ti−O−Cu path.

In the special alignment of the CuO_4 units in the ordered structure, normal superexchange interaction through O ions is not induced. Thus, the observed ferromagnetic and antiferromagetic behaviors are completely different from a bond-angle switching in the $SeCuO_3$−$TeCuO_3$ perovskites from ferromagnetic to antiferromagetic regions according to the Kanamori-Goodenough rules.[5] Instead, direct exchange interaction between Cu^{2+} ions at the A′ site in $CaCu_3B_4O_{12}$ appears to primarily determine the magnetic properties, which explains the ferromagnetic behavior in $CaCu_3Ge_4O_{12}$ and $CaCu_3Sn_4O_{12}$. In $CaCu_3Ti_4O_{12}$, on the other hand, antiferromagnetic superexchange interaction should overcome ferromagnetic direct interaction. Because the empty Ti 3d band can hybridize with the O 2p and Cu 3d orbitals near the Fermi energy (E_F), the contribution of the Ti 3d band should play an important role in the magnetic property.

In this study, we investigated the electronic structures of $CaCu_3Ge_4O_{12}$, $CaCu_3Ti_4O_{12}$, and $CaCu_3Sn_4O_{12}$ by using X-ray absorption spectroscopy (XAS). We can clearly see the difference in O K-edge spectra between the ferromagnetic ($CaCu_3Ge_4O_{12}$ and $CaCu_3Sn_4O_{12}$) and the antiferromagnetic

---

* To whom correspondence should be addressed. E-mail: mizumaki@spring8.or.jp.

† JASRI.

‡ Kyoto University.

(1) Shimakawa, Y. *Inorg. Chem.* **2008**, *47*, 8562.

(2) Vasil'ev, A. N.; Volkova, O. S. *Low Temp. Phys.* **2007**, *33*, 895.

(3) Shiraki, H.; Saito, T.; Yamada, T.; Azuma, M.; Kurata, H.; Isoda, S.; Takano, M.; Shimakawa, Y. *Phys. Rev. B* **2007**, *76*, 140403.

(4) Shimakawa, Y.; Shiraki, H.; Saito, T. *J. Phys. Soc. Jpn.* **2008**, *77*, 113702.

(5) Kohn, K.; Inoue, K.; Horie, O.; Akimoto, S. *J. Solid State Chem.* **1976**, *18*, 27.

10.1021/ic802166b CCC: $40.75

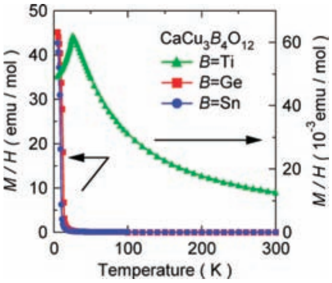

Figure 2. Temperature dependence of the magnetic susceptibility of $CaCu_3B_4O_{12}$ (B = Ti, Ge, and Sn). These data are from ref 3.

($CaCu_3Ti_4O_{12}$) compounds. The observed spectral weight in $CaCu_3Ti_4O_{12}$ is the result of strong hybridization between Ti 3d and O 2p orbitals, and we believe this is clear evidence of the involvement of Ti 3d orbitals in the antiferromagnetic property.

Powder samples of $CaCu_3Ge_4O_{12}$, $CaCu_3Ti_4O_{12}$, and $CaCu_3Sn_4O_{12}$ were prepared by solid-state reaction processes in the same manner as that described in refs 3 and 6. $CaCu_3Ge_4O_{12}$ and $CaCu_3Sn_4O_{12}$ were synthesized under high-pressure and high-temperature conditions. All of the samples obtained were confirmed to be single phases by X-ray diffraction. As shown in Figure 2 (data from ref 3), magnetic measurements confirm the ferromagnetic behavior for $CaCu_3Ge_4O_{12}$ and $CaCu_3Sn_4O_{12}$ and the antiferromagnetic one for $CaCu_3Ti_4O_{12}$. Effective magnetic moments calculated from the Curie constants in the Curie−Weiss susceptibility also confirm the Cu^{2+} ($S = {}^1/_2$; $\mu_{eff} = 1.73$) localized spins.

The O K-edge XAS spectra of the samples were measured at 9 and 300 K by a total electron yield method for the synthesized samples at BL25SU and BL27SU of SPring-8 in Japan. The energy resolution $E/\Delta E$ at the O K-edge was greater than 5000. The incident photon energy was calibrated by measuring the energies of the Ti $L_{2,3}$-edges of TiO_2 and the Ni $L_{2,3}$-edges of NiO. Powder samples were pasted uniformly on a sample holder by using carbon tape. In order to investigate magnetic interaction, the O K-edges magnetic circular dichroism (MCD) spectra of $CaCu_3Ge_4O_{12}$ and $CaCu_3Sn_4O_{12}$ were also measured at BL25SU at temperatures below the Curie temperatures. The MCD intensity was defined as the difference between two absorption spectra, which are obtained using parallel and antiparallel photon spins along the magnetization direction.

Figure 3 shows the O K-edge XAS spectra of $CaCu_3Ge_4O_{12}$, $CaCu_3Ti_4O_{12}$, and $CaCu_3Sn_4O_{12}$. The arbitrary unit of intensity in each spectrum was set to unity at $E = 550$ eV. The observed spectrum is the result of an excitation of electrons from the O 1s states to unoccupied O 2p states in the conduction band. Because the empty O 2p states hybridize with states of cations coordinated by O ions, the observed spectra show mostly the transition-metal character.[7] The spectral weight from 530 to 532 eV corresponds to the Cu 3d and Ti 3d bands, and that around 535 eV corresponds to the Ca 3d, Ge s, and Sn s bands. The absorption spectra around 540−545 eV reflect the character of the Cu 4sp and Ti 4sp bands. These assignments are consistent with previously analyzed $CaMnO_3$ and germanium oxides.[7−9]

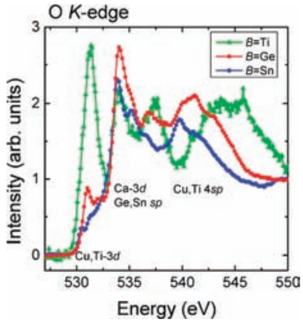

Figure 3. O K-edge XAS spectra for $CaCu_3Ge_4O_{12}$ (solid squares), $CaCu_3Ti_4O_{12}$ (solid triangles), and $CaCu_3Sn_4O_{12}$ (solid circles).

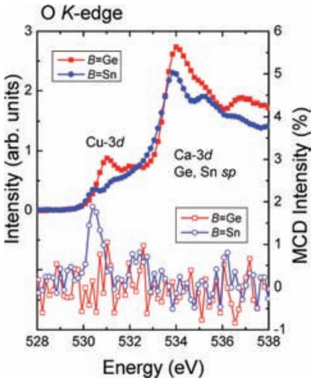

Figure 4. O K-edge XAS (closed symbols) and MCD (open symbols) spectra at $T = 9$ K for $CaCu_3Ge_4O_{12}$ (squares) and $CaCu_3Sn_4O_{12}$ (circles).

Figure 4 shows magnified XAS spectra near the Cu 3d−O 2p hybridized region and the XAS−MCD spectra at the O K-edge for the ferromagnetic $CaCu_3Ge_4O_{12}$ and $CaCu_3Sn_4O_{12}$. The MCD signal for $CaCu_3Ge_4O_{12}$ is not evident, and that for $CaCu_3Sn_4O_{12}$ is very weak, less than 2% around the Cu 3d band region. Compared with the O K-edge MCD intensities reported for other ferromagnetic transition-metal oxides, such as 5% for $La_{1-x}Sr_xMnO_3$,[10] 5% for $CaCu_3Fe_4O_{12}$,[11] and 4% for $BiCu_3Mn_4O_{12}$,[11] the observed MCD intensities of the present compounds are apparently weak. Thus, the results clearly show that the magnetic polarization of O 2p electrons in $CaCu_3Ge_4O_{12}$ and $CaCu_3Sn_4O_{12}$ is very low, suggesting that the Cu−O−Cu path plays a less important role in magnetic interaction. This implies that superexchange interaction is not induced between the Cu spins in the A-site-ordered perovskite compounds and also gives evidence that ferromagnetic direct exchange interaction primarily determines the magnetic properties. This is also consistent with the experimental results on magnetism and our discussion from a structural point of view.[3]

---

(6) Ozaki, Y.; Ghedira, M.; Chenavas, J.; Joubert, J. C.; Marezio, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 3615.

(7) Abatte, M.; Pen, H.; Czyzyk, M. T.; de Groot, F. M. F.; Fuggle, J. C.; Ma, Y. J.; Chen, C. T.; Sette, F.; Fujimori, A.; Ueda, Y.; Kosuge, K. *J. Electron Spectrosc. Relat. Phenom.* **1993**, *62*, 185.

(8) Zampieri, G.; Prado, F.; Caneiro, A.; Briatico, J.; Causa, M. T.; Tovar, M.; Alascio, B.; Abatte, M.; Morikawa, E. *Phys. Rev. B* **1998**, *58*, 3755.

(9) Cabaret, D.; Mauri, F.; Henderson, G. S. *Phys. Rev. B* **2007**, *75*, 184205.

(10) Koide, T.; Miyauchi, H.; Okamoto, J.; Shidara, T.; Sekine, T.; Saitoh, T.; Fujimori, A.; Fukutani, M.; Takano, H.; Takeda, Y. *Phys. Rev. Lett.* **2001**, *87*, 246404.

(11) Mizumaki, M., private communication.

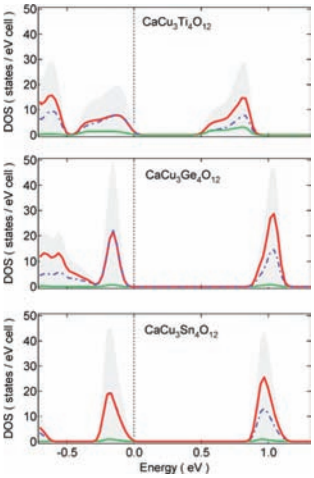

Figure 5. Calculated DOS for CaCu$_3$Ti$_4$O$_{12}$ (upper panel), CaCu$_3$Ge$_4$O$_{12}$ (middle panel), and CaCu$_3$Sn$_4$O$_{12}$ (lower panel). The total DOS (shaded region) and partial DOS of Cu (thick lines), B (thin lines), and O (dashed lines) ions are shown in each panel.

For antiferromagnetic CaCu$_3$Ti$_4$O$_{12}$, as shown in Figure 3, it is noted that the XAS intensity at 530−532 eV shows a significant difference from those of ferromagnetic CaCu$_3$Ge$_4$O$_{12}$ and CaCu$_3$Sn$_4$O$_{12}$. Because the absorption spectra in the region mainly reflect the hybridization of orbitals between Cu 3d, Ti 3d, and O 2p, this result strongly indicates the contribution of Ti 3d orbitals in the hybridized states in antiferromagnetic CaCu$_3$Ti$_4$O$_{12}$. Thus, hybridization of Ti 3d orbitals should induce antiferromagnetic interaction between the Cu^{2+} spins.

In order to investigate oxygen−metal hybridization in detail, the density of states (DOS) near E_F for CaCu$_3$Ge$_4$O$_{12}$, CaCu$_3$Ti$_4$O$_{12}$, and CaCu$_3$Sn$_4$O$_{12}$ were calculated by full potential linearized augmented plane-wave (FLAPW) first-principle calculations within the generalized gradient approximation exchange-correlation function. The antiferromagnetic state for CaCu$_3$Ti$_4$O$_{12}$ was calculated with a $Pm\bar{3}$ structure model, in which the Cu^{2+} spins are ordered along the [111] direction in an antiparallel manner, whereas ferromagnetic states were investigated for CaCu$_3$Ge$_4$O$_{12}$ and CaCu$_3$Sn$_4$O$_{12}$. The FLAPW sphere radii used for the calculations were 2.0, 2.0, 1.9, 1.9, 2.2, and 1.6 au for Ca, Cu, Ge, Ti, Sn, and O, respectively. Self-consistent calculation was carried out on 45 *k*-point meshes in the irreducible Brillouin zone (1000 *k* points in the whole Brillouin zone).

Figure 5 shows the calculated DOS for the three compounds. In order to compare the results with the experimentally observed XAS spectra, we especially pay attention to the unoccupied region above E_F. In Figure 6, the unoccupied O 2p partial DOS of each compound is plotted in such a manner that the energy position with the maximum partial DOS is shifted to the origin. The widths of the unoccupied O 2p bands are narrow (∼0.3 eV) for the ferromagnetic CaCu$_3$Ge$_4$O$_{12}$ and CaCu$_3$Sn$_4$O$_{12}$. These bands mainly hybridize with the Cu 3d orbitals. For antiferromagnetic CaCu$_3$Ti$_4$O$_{12}$, on the other hand, the corresponding band is apparently broad (∼0.5 eV) and much of the spectral weight is seen at a lower energy region than the O 2p top position. This band hybridizes with not only Cu 3d but also Ti 3d orbitals. Although the O K-edge XAS intensity is not proportional to the O 2p partial DOS, the observed strong XAS intensity at 530−532 eV in antiferromagnetic CaCu$_3$Ti$_4$O$_{12}$ should be the result of strong hybridization of Ti 3d orbitals with O 2p.

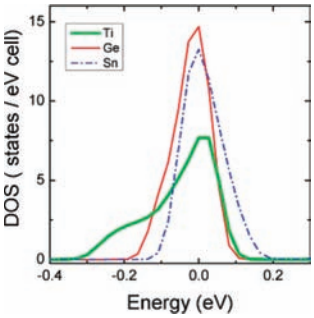

Figure 6. O 2p DOS for CaCu$_3$Ti$_4$O$_{12}$ (thick line), CaCu$_3$Ge$_4$O$_{12}$ (thin line), and CaCu$_3$Sn$_4$O$_{12}$ (dashed line). Each energy position with the maximum partial DOS is shifted to the origin.

The present results of our XAS−MCD experiments and the electronic structure calculation demonstrate that the O 2p orbitals in ferromagnetic CaCu$_3$Ge$_4$O$_{12}$ and CaCu$_3$Sn$_4$O$_{12}$ mainly hybridize with Cu 3d but that they do not play an important role in magnetic interaction. On the other hand, the empty Ti 3d orbitals strongly hybridize with O 2p and Cu 3d near E_F. Therefore, we can conclude that direct exchange interaction between the Cu^{2+} spins, as shown in Figure 1, primarily determines the ferromagnetism of CaCu$_3$Ge$_4$O$_{12}$ and CaCu$_3$Sn$_4$O$_{12}$ but that antiferromagnetic superexchange interaction through the Cu−O−Ti−O−Cu path, also as shown in Figure 1, overcomes ferromagnetic direct interaction, leading to antiferromagnetism in CaCu$_3$Ti$_4$O$_{12}$.

In summary, we investigated the electronic structures and magnetic interaction of A-site magnetic perovskites by XAS and MCD measurements. The O K-edge XAS spectra of ferromagnetic CaCu$_3$Ge$_4$O$_{12}$ and CaCu$_3$Sn$_4$O$_{12}$ showed hybridization between Cu 3d and O 2p orbitals, but the MCD spectra showed that magnetic polarization of O 2p electrons was very low. The results implied that ferromagnetic direct exchange interaction primarily determined the magnetic ordering of CaCu$_3$Ge$_4$O$_{12}$ and CaCu$_3$Sn$_4$O$_{12}$. For antiferromagnetic CaCu$_3$Ti$_4$O$_{12}$, on the other hand, the spectrum showed strong hybridization of Cu 3d, Ti 3d, and O 2p orbitals, suggesting the involvement of Ti 3d orbitals with the antiferromagnetic property. We thus concluded that the antiferromagnetism of CaCu$_3$Ti$_4$O$_{12}$ originated from superexchange interaction through the Cu−O−Ti−O−Cu path, which overcame ferromagnetic direct exchange interaction.

Acknowledgment. We thank M. Azuma for fruitful discussions of sample preparation and magnetic measurements and N. Kawamura for his experimental assistance in the XAS−MCD measurements. The XAS−MCD measurements at BL25SU (Proposal No. 2008A-1001) and BL27SU (Proposal No. 2008A-1276) in SPring-8 were performed with the approval of the JASRI. This work was partly supported by a Grant-in-Aid for Scientific Research (Grant 19GS0207) and by the Global COE Program "Integrated Materials Science" (No. B-09) from the Ministry of Education, Science and Technology of Japan.

IC802166B