Observation of polarization-dependent x-ray absorption spectra arising from Cu 3*d*-F 2*p* hybridization in the two-dimensional ferromagnets A_2CuF_4 (A=K, Cs)

H. Manaka,* T. Koide, and T. Shidara
Photon Factory, IMSS, High Energy Accelerator Research Organization, Tsukuba, Ibaraki 305-0801, Japan

I. Yamada
Department of Physics, Faculty of Science, Chiba University, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan
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We report on a study of the polarization dependence of the x-ray absorption spectra (XAS) at the Cu $L_{2,3}$ edges and the F K edge in single crystals of two-dimensional ferromagnets A_2CuF_4 (A=K, Cs). We successfully observed polarization-dependent XAS at the Cu $L_{2,3}$ edges. This provides experimental support of the antiferrodistortive orbital ordering (AFDOO) model proposed by Khomskii and Kugel [D. I. Khomskii and K. I. Kugel, Solid State Commun. **13**, 763 (1973)]. We also observed polarization dependence of the XAS at the F K-edge peak at ~681 eV, which reveals the F $2p_\sigma$-hole orbitals arising from Cu 3*d*-F 2*p* hybridization. We argue its implication in relation to the realization of AFDOO.

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Magnetism in a number of magnetic compounds is governed mainly by several types of superexchange interactions, i.e., mechanisms of spin hopping between two magnetic ions mediated by a ligand ion.[1] About thirty years ago, Khomskii and Kugel proposed an antiferrodistortive orbital ordering (AFDOO) model[2] in order to theoretically explain the origin of the ferromagnetic superexchange interaction in an optically transparent ferromagnet K_2CuF_4.[3] Several magnetic oxides with AFDOO have attracted renewed interest in relation to clarifying the orbital degrees of freedom. Extensive studies on such compounds were performed using hard x-ray diffraction and neutron diffraction techniques.[4–7] However, these previous studies neglected hybridization between the wave functions of magnetic ions and those of ligand ions, which were assumed to form a closed shell. Even though such a hybridization is weak, it could play a key role in producing magnetism associated with AFDOO. To experimentally elucidate the relation between AFDOO and magnetism, hybridized-orbital states between a magnetic ion and a ligand ion should be investigated. However, our understanding of such hybridization is still poor, because it is difficult to directly observe orbital states in a ligand ion by conventional techniques, such as hard x-ray diffraction and neutron diffraction. In contrast, a study of the polarization dependence of the x-ray absorption spectra (XAS) in the soft x-ray region gives element-specific information about the spatial anisotropy of the wave functions of unoccupied states, not only in a magnetic ion, but also in a ligand ion, if a cleaved clean surface of single crystals is obtained. In this paper, the polarization dependence of the Cu $L_{2,3}$-edge and the F K-edge XAS is studied to elucidate what role Cu 3*d*-F 2*p* hybridization could play in producing the correlation between magnetism and AFDOO in single crystals of A_2CuF_4 (A =K, Cs).

The compound K_2CuF_4 has essentially a K_2NiF_4-type crystal structure, as schematically shown in Fig. 1(a). The cooperative Jahn-Teller distorted CuF_6 octahedra take an antiferrodistortive arrangement, i.e., the elongated axes of the octahedra lie in the c plane and are completely orthogonal to those in adjacent octahedra.[8] This leads to an expectation for formation of Cu 3*d*-hole orbitals with $d_{x^2-z^2}$ and $d_{y^2-z^2}$ symmetries, as shown in Fig. 1(b).[2] Many experimental studies of K_2CuF_4 have supported the formation of such AFDOO, which could be the origin of the intralayer ferromagnetic superexchange interaction.[9–11] Because the AFDOO in K_2CuF_4 is closely related to the cooperative Jahn-Teller effect, it disappears above ~900 K at which temperature the cooperative Jahn-Teller distortion collapses, as confirmed by a differential thermal analysis.[12]

The magnetic parameters of K_2CuF_4 relevant to the present study are summarized as follows. The values of the

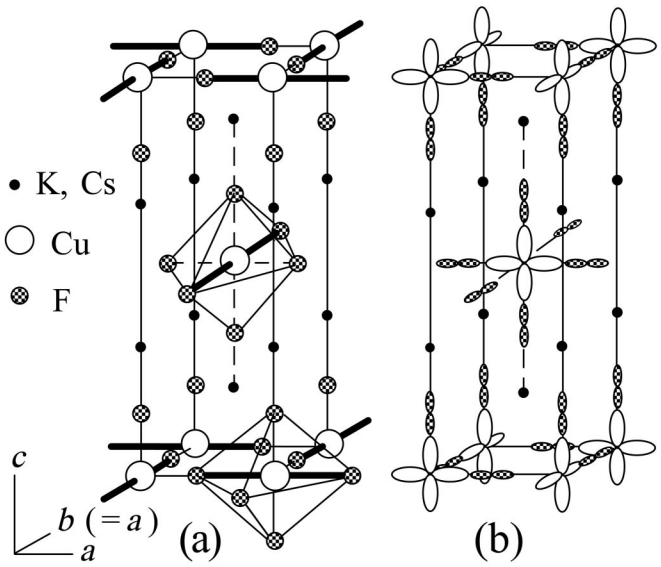

FIG. 1. (a) Crystal structure of A_2CuF_4 (A=K, Cs). The bold lines represent the elongated axes of the cooperative Jahn-Teller distorted CuF_6 octahedra. (b) Schematic drawing of the hole orbital models. The Cu 3*d* holes and the F $2p_\sigma$ holes arise from Cu 3*d*-F 2*p* hybridization. The *a*, *b*, and *c* axes are taken to be the *x*, *y*, and *z* axes, respectively.

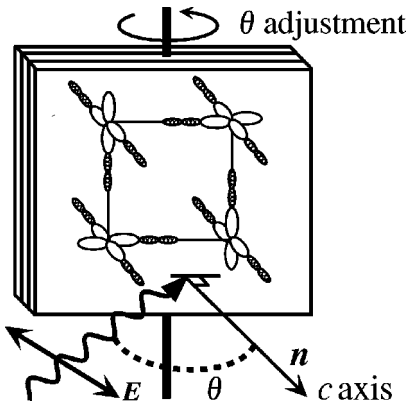

FIG. 2. Arrangement for polarization-dependent XAS measurements. The anisotropic Cu $3d$- and F $2p_\sigma$-hole orbitals are exaggeratedly shown for a comparison with the direction of $\boldsymbol{E}$.

intralayer ferromagnetic superexchange interaction ($J>0$) and of the interlayer one ($J'>0$) are $J/k_B \simeq 11$ K and $J'/J \simeq 1\times10^{-3}$, with k_B being the Boltzmann constant.[3,13,14] Thus, K_2CuF_4 is well regarded as an ideal two-dimensional magnet. The nonnegligible J', whose origin is different from that of J,[15] is thought to cause a ferromagnetic phase transition at $T_C=6.25$ K.[3] The magnetic properties of Cs_2CuF_4 are very similar to those of K_2CuF_4, i.e., $J/k_B \simeq 8$ K and $T_C=4.45$ K in Cs_2CuF_4. Single crystals of these compounds allow obtaining a high-quality cleavage surface perpendicular to the c axis. Hence, measurements of polarization-dependent XAS could provide new information about the hole orbitals on both Cu and F ions associated with the expected AFDOO shown in Fig. 1(b).

Incident angle-dependent XAS measurements were made using linearly polarized synchrotron radiation from the bending-magnet beamline (BL-11A) at the Photon Factory. The degree of linear polarization is almost perfect, $S_1/S_0 \simeq 1$, with S_0 and S_1 being the Stokes parameters. XAS data were taken using the total electron-yield method at the Cu $L_{2,3}$ edges and the F K edge at 295 K in single crystals of A_2CuF_4 (A=K, Cs). Since the two compounds exhibit insulatorlike behavior, both good electrical insulation of the sample holder and avoiding the charging effects are decisive for a successful measurement. The sample was cleaved *in situ* just before each measurement at pressures of $2\times10^{-9} \sim 8\times10^{-10}$ Torr. Each cleaved surface is parallel to the c plane. As shown in Fig. 2, angle θ is defined as the angle between the c axis and the wave vector of incident light ($\boldsymbol{k}$). The angle θ was changed by rotation of the sample about the vertical axis in order to determine the relation between θ and the electric field vector of the light ($\boldsymbol{E}$); $\theta=0°$ corresponds to $\boldsymbol{E}\perp c$ axis and $\theta=90°$ to $\boldsymbol{E}\parallel c$ axis. Thus, the θ dependence of XAS is equivalent to the polarization dependence of XAS, providing direct information about the difference between the hole orbital states in the c plane and those along the c axis. However, no polarization dependence in XAS is expected to appear in the c plane because of the identity $a=b$[8] and the absence of any magnetic anisotropy in the c plane.[16–18]

Figures 3(a) and 3(b) show the θ dependence of the Cu $L_{2,3}$-edge and F K-edge XAS observed in K_2CuF_4 and in Cs_2CuF_4, respectively. Since a correction for the saturation effect in the total electron yield[19] has not been made, a slight ambiguity remains concerning the absolute absorption intensities; the absorption intensities are generally underestimated as θ increases from 0° to 90°. As far as a qualitative discussion about A_2CuF_4 (A=K, Cs) is concerned, the saturation effect is insignificant, as explained later. The effect of charging of the sample on the absorption intensities is also serious when the total electron yield is used for insulatorlike samples. But the charging effect in A_2CuF_4 (A=K, Cs) is shown to be negligible at 295 K by the following observations. When the XAS were measured at ~6 K, the photocurrent from the sample rapidly decreased immediately after the sample was exposed to the incident light and then it decreased slowly for a long time. This is attributable to the charging effect. At 295 K, in contrast, the sample photocurrent was confirmed to be almost constant at a fixed photon energy within an accuracy of this experiment, thus excluding an artifact due to the charging effect. Both the Cu L_2- and L_3-edge XAS exhibit a single peak, irrespective of θ (Fig. 3). Since A_2CuF_4 (A=K, Cs) are strongly ionic and charge-transfer-type insulators, the ground state is dominantly of the $p^6d^9(\equiv Cu^{2+})$ configuration with only the ^2D multiplet term in the configuration picture. In the Russell-Saunders coupling scheme, the L_3 and L_2 edges, which correspond to $^2D \rightarrow {}^2P_{3/2}$ and $^2P_{1/2}$ (p^5d^{10}) transitions, respectively, do not produce any satellites. From the energy separation between the L_2- and L_3-edge peak positions, the value of the spin-orbit interaction in the $2p$-core hole is estimated to be about 20 eV, which is almost the same as those obtained for other copper fluorides.[20] Most importantly, the absorption intensity increases when θ changes from 0° to 60°. Since the present θ dependence is *opposite* to the θ dependence arising from the saturation effect in the total electron yield, the observed θ dependence is an intrinsic one. If the saturation effect is corrected for in Figs. 3(a) and 3(b), the difference of the peak intensities between $\theta=0°$ and 60° should be larger, with the tendency of the θ dependence being kept. We can state that the saturation effect gives rise to no artifact, at least qualitatively, in the present case. Thus, we qualitatively discuss the increase of the peak intensities with increasing θ from 0° to 60°. If we assume the AFDOO model [Fig. 1(b)] based on a simple atomic model, we can calculate the ratio of the absorption intensity at $\theta=0°$ to that at $\theta=90°$ to be 1:2.[21] This is intuitively understood by noting that the lobes directed toward the c axis of the $d_{x^2-z^2}$ and $d_{y^2-z^2}$ hole orbitals are two times as many as their lobes directed toward the $a(b)$ axis. The observation of the polarization dependence of the XAS at the Cu $L_{2,3}$ edges agrees qualitatively well with the prediction of the AFDOO model.

We proceed to examine the θ dependence of the F K-edge XAS in Fig. 3. Several peaks were observed above 679 eV in both K_2CuF_4 and Cs_2CuF_4. The observed spectra demonstrate the existence of hybridization-induced holes in the F $2p$ state. Such hole states in ligand ions have been neglected in the experimental investigations of AFDOO until now, although hybridization between the orbitals of the magnetic

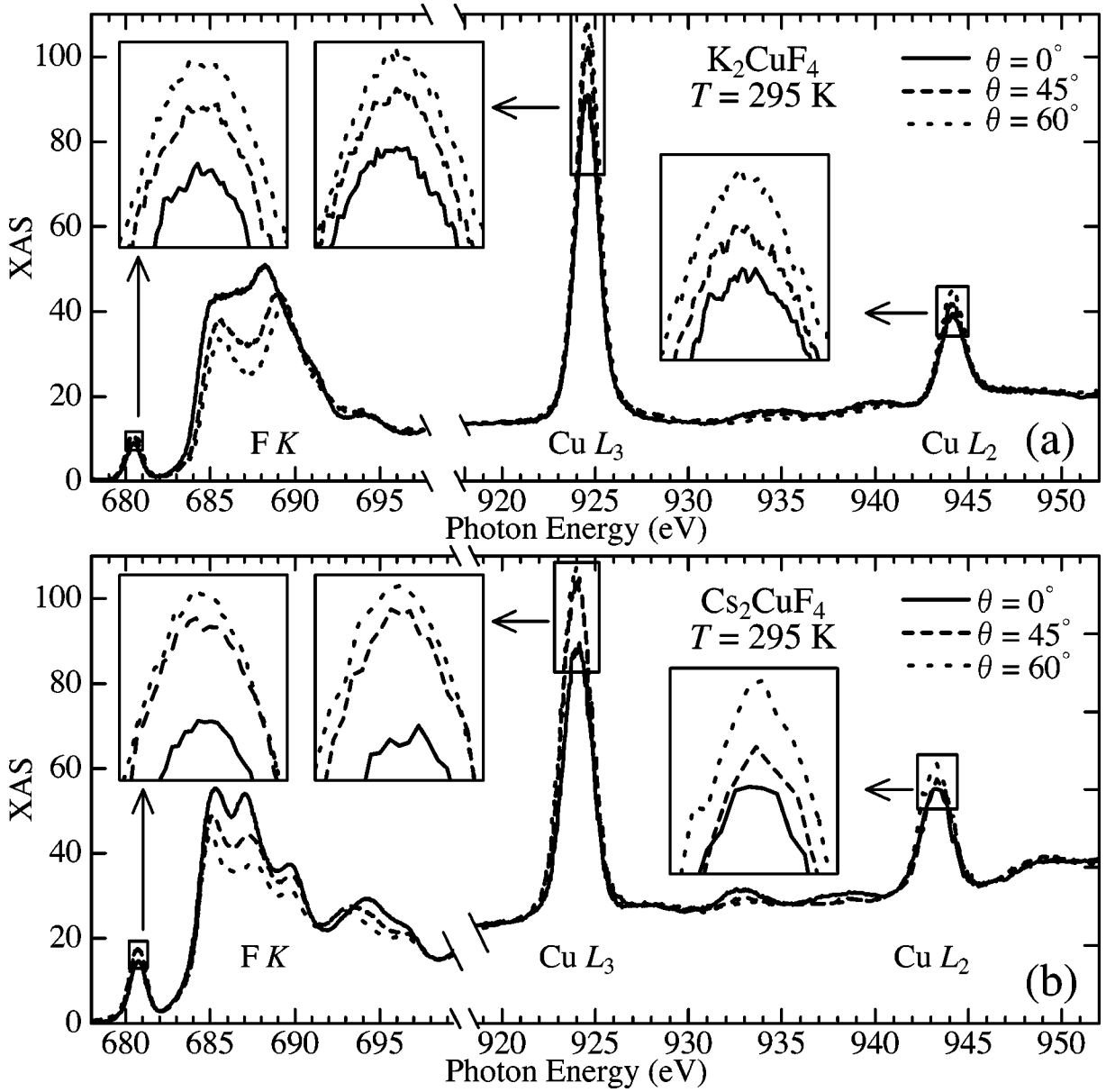

FIG. 3. Variation of XAS with θ at 295 K in (a) K_2CuF_4 and (b) Cs_2CuF_4. A correction for the saturation effect has not been made. The average peak height at the Cu L_3 edge was normalized to be 100.

ion and ligand ion is important and nonnegligible for understanding the mechanism of ferromagnetic superexchange interaction in AFDOO compounds. The single peak at ~681 eV is almost the same in energy and shape for both compounds, whereas broad peaks above 683 eV are significantly different in shape and energy for two compounds. The coincidence of the 681 eV peak in both compounds indicates that this peak arises from Cu $3d$-F $2p$ hybridization, whereas the high-energy broad peaks originate from other types of hybridization, which are predominantly of the K $3d$-F $2p$ and Cs $5d$-F $2p$ characters. From now on, we concentrate our discussion on the single peak.

The absorption intensity at ~681 eV increases as θ changes from 0° to 60° (insets in Fig. 3), which is the same tendency as that of the Cu $L_{2,3}$ edges. This polarization dependence is again an intrinsic one for the same reasons as that for the Cu $L_{2,3}$ edges, and for a small saturation effect due to the weak absorption intensity. If we assume a picture of the F $2p_\sigma$ holes arising from hybridization between the Cu $3d_{x^2-z^2}/3d_{y^2-z^2}$ and F $2p_x/2p_y/2p_z$ orbitals (Fig. 2), the absorption intensity is expected to increase when θ goes from 0° to 90°. In fact, the single peak at ~681 eV exhibits such an expected tendency, supporting our assumed picture. It is emphasized that this polarization-dependent XAS at the F K edge directly reflects the nature of the Cu $3d$-F $2p$ hybridization. If the lobes of the wave functions of the Cu $3d_{x^2-z^2}$ and $3d_{y^2-z^2}$ holes and those of the F $2p_x$, $2p_y$ and $2p_z$ holes are aligned in the same direction, as shown in Figs. 1(b) and 2, the resultant Cu $3d$-F $2p$ hybridization will lower the energy of AFDOO effectively. Therefore, the present observation of the polarization-dependent XAS at the F K edge indicates that the Cu $3d$-F $2p$ hybridization could play an

important role in stably realizing the AFDOO structure shown in Fig. 1(b). It is hoped that future sophisticated theories seriously take into account this aspect.

We briefly mention the origin of J' in K_2CuF_4 and Cs_2CuF_4. Recent experimental results under high pressure have shown different responses of J' to pressure; $J>0$ and $J'>0$ persist up to 9 GPa in K_2CuF_4,[22] while a pressure-induced magnetic phase transition from $J>0$ and $J'>0$ to $J>0$ and $J'<0$ occurs around 2 GPa in Cs_2CuF_4.[23] As can be seen from Fig. 1, a K^+ or Cs^+ ion with an appreciably different ionic radius is located between two Cu^{2+} ions in adjacent *c* planes along the predominant interlayer bonding path. This fact leads us to speculate that the difference in the nature between Cu $3d$-F $2p$-K $3d+4sp$ and Cu $3d$-F $2p$-Cs $5d+6sp$ hybridization may play a role in giving rise to such a different pressure dependence of J'. Feldkemper *et al.* theoretically pointed out that not only the Cu-F-F-Cu path but also the Cu-F-K-Cu path between the nearest-neighbor layers in K_2CuF_4 plays an important role in the mechanism of $J'>0$.[15] In fact, the several peaks above 683 eV observed in the F *K*-edge XAS (Fig. 3) show a clear difference for two compounds, as briefly mentioned in the above discussion. It is highly possible that the F $2p$-K $3d+4sp$ (or Cs $5d+6sp$) hybridization could make an essential contribution to the optical transitions associated with the several peaks above 683 eV. Even though their assignment is not easy to make, a detailed XAS study at very low temperatures ($T \approx J'/k_B \sim 10^{-2}$ K) may provide information about the origin of J' in these compounds.

In conclusion, we successfully observed the polarization-dependent XAS at the Cu $L_{2,3}$ edges and F *K* edge in A_2CuF_4 (A=K, Cs). The polarization dependence of the XAS at the Cu $L_{2,3}$ edges gives experimental support of the AFDOO model in these compounds [Fig. 1(b)]. The polarization dependence of the XAS of the F *K*-edge peak at $\sim$681 eV provides evidence for the F $2p_\sigma$-hole orbitals arising from Cu $3d$-F $2p$ hybridization, which could play a key role in stabilizing AFDOO.

*Present address: Department of Nano-Structure and Advanced Materials, Graduate School of Science and Engineering, Kagoshima University, Korimoto, Kagoshima 890-0065, Japan. E-mail address: manaka@eee.kagoshima-u.ac.jp

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