Valence-band photoemission spectroscopy of the giant magnetoresistive spinel compound Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$

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Electronic structures of the giant magnetoresistive Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$ (FCCS) spinel compound have been investigated using photoemission spectroscopy (PES). Resonant PES measurements around the Cu, Fe, Cr 3$p$→3$d$ absorption edges exhibit negligible resonant interference behavior for the Cu 3$d$ valence electrons, indicating the monovalent valence state of the Cu ion in FCCS. The top of the valence band is found to be predominantly of the Cr 3$d$ and the nearly filled Cu 3$d$ electron character, whereas the Fe 3$d$ electron character is distributed over the whole valence band. The measured valence-band PES spectra of FCCS yield better agreement with the LSDA+U calculation than with the local spin-density approximation (LSDA) calculation, suggesting the importance of the large Coulomb interactions $U$ between $d$ electrons. On the other hand, the low spectral intensity near $E_F$ in the measured valence-band spectrum suggests an extra localization in FCCS, not explained by the large $U$ alone.

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I. INTRODUCTION

The discovery of the colossal magnetoresistance phenomenon in the perovskite Mn oxides of $R_{1-x}A_x$MnO$_3$ (RAMO; $R$= rare earth, $A$= divalent or tetravalent cation) has generated wide attention due to a variety of interesting physical properties and their potential for technological applications. Very large magnetoresistance (MR) has also been observed in the Cr-based chalcogenide spinel compounds Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$ ($x=0.05$), both of which are ferrimagnetic semiconductors at $T=0$ K. In the spinel structure, the Fe and Cu ions occupy the tetrahedral sites and the Cr ions occupy the octahedral sites, surrounded by four and six sulfur ions, respectively. The observed MR of Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$ (FCCS) was $\sim 7\%$ at $T_C\sim 340$ K ($T_C$= the magnetic transition temperature) under the external magnetic field of 6 T. This size of MR is as large as in giant magnetoresistance (GMR) metallic multilayers. Similarly as in the perovskite manganites, a metal-insulator ($M$-$I$) transition occurs simultaneously with the magnetic transition in the spinel compounds. The temperature dependence of the resistivity $\rho$ ($T$) shows the semiconducting behavior for $T>T_C$ and then the metallic feature below $T_C$ down to $\sim 150$ K. Upon further cooling below $\sim 150$ K, the semiconducting behavior is observed again.

It has been pointed out that the mechanisms of the $M$-$I$ transition and the magnetic transition in the spinel compounds are different from those in the perovskite manganites. In a divalent ion-doped RAMO system, Mn ions exist in the formally trivalent and tetravalent states. Then the Zener-type double exchange (DE) between spin-aligned Mn$^{3+}$ ($t_{2g}^2e_{g}^1$) and Mn$^{4+}$ ($t_{2g}^3$) ions through oxygen ions yields the metallic conductivity and ferromagnetism. In the DE model, there should exist mixed-valent ions to maintain the correlation between magnetism and conductivity. Further, the strong electron-phonon interaction due to the Jahn-Teller effect at the Mn$^{3+}$ ion is invoked to elucidate the $M$-$I$ transition in RAMO systems. In contrast, there seems to be no evidence for the DE mechanism in FeCr$_2$S$_4$ (Ref. 5) and no Jahn-Teller active ions.

One of the important issues in the chalcogenide spinel compounds is the valence states of constituent elements. Indeed, the question on the valency of Cu in CuM$_2$X$_4$ ($M$= transition metal element; $X=S$, Se, Te) has been a longstanding problem. Goodenough claimed the Cu ion to be divalent, while Lotgering et al. claimed it to be monovalent. If the Cu ion is monovalent in spinels, the valence configurations of the Cr ion in CuCr$_2$S$_4$ are expected to be Cu$^+$($Cr^{3+}$Cr$^{4+}$)S$_2$$^2_4$-, yielding a formal mixed valence of +3.5. Then the ferromagnetic ground state of CuCr$_2$S$_4$ can be explained in terms of the DE interaction.

Various experiments give different results on the valence state of the Cu ion in spinels. Core-level x-ray photoemission spectroscopy (XPS), x-ray emission spectroscopy, and the Cu $K$-edge x-ray absorption spectroscopy (XAS) measurements on the spinel compounds of CuM$_2$X$_4$ ($M$= V, Cr, Rh, Ir; $X=S$, Se, Te) suggested that the Cu ions in the spinels are monovalent. However, NMR, neutron diffraction, and magnetic studies suggest that experimental results could be interpreted with the divalent Cu ions. Therefore it is essential to determine the valence states of the Cu and Cr ions in spinel compounds to understand the underlying physics properly. The core-level XPS study on FeCr$_2$S$_4$ and FCCS (Ref. 16) shows that the Cr ions are in the trivalent states ($3d^3$) in both compounds, whereas the Cu ion in FCCS is likely to be in the monovalent state ($3d^10$). Note that core-level XPS is rather an indirect probe for the valence electronic structures because the XPS spectra are determined by the final state effects which reflect the response of the valence electrons to the core hole created in the photoionization process. On the other hand, valence-band