Valence States of Transition-Metal Ions and Electronic Structures of Spinel Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$


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The valence states and electronic structures of transition-metal ions in spinel Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$($0.1 \leq x \leq 0.5$) have been investigated by using scanning photodetection microscopy (SPM), photoemission spectroscopy (PES), soft-X-ray absorption spectroscopy (XAS), and soft X-ray magnetic circular dichroism (XMCD). The experimental data have been compared to the calculated density of states (DOS). It is found that the valence states of Cr and Cu ions are nearly trivalent (Cr$^{3+}$) and monovalent (Cu$^+$), respectively. The Fe 2$p$ XAS spectra of Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$ are very similar to that of Fe metal, indicating that Fe $3d$ states are strongly hybridized to S $3p$ states. The XMCD measurements for Fe, Cr, and Cu $2p$ states show evidence that the magnetic moments of Cr ions are antiparallel to those of Fe ions and that Cu ions are weakly polarized parallel to Fe ions. Valence-band PES reveals that Cr $3d$ states are located very close to E$_F$, suggesting that the hybridized Fe $e_g$-S $3p$ states near E$_F$ play an important role in determining the transport properties of Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$ for $x \leq 0.5$.

**Index Terms—**Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$, Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$, photoemission spectroscopy (PES), scanning photoelectron microscopy (SPM), spinel, X-ray absorption spectroscopy (XAS), X-ray magnetic circular dichroism (XMCD).

SPINEL compounds of Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$($x = 0, 0.5$) exhibit the large negative magnetoresistance (MR) effect [1], [2]. Upon cooling, the resistivity $\rho(T)$ shows a crossover transition from insulator to metal near the magnetic transition temperature $T_C$, and then again the insulating feature far below $T_C$ [2], [3]. With increasing $x$ in Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$, $T_C$ increases monotonically, whereas the room temperature resistivity and the MR decrease first and then increase to exhibit local minima near $x = 0.2$ and local maxima at $x = 0.5$ [4]–[7]. It is considered that each of the Fe and Cr sublattices orders ferromagnetically, while the two sublattices are coupled antiferromagnetically to each other, resulting in the ferromagnetic ground states [8]. In order to explain the physical properties of Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$($x > 0.5$), two competing models have been proposed, with different valence states of the constituent elements. For CuCr$_2$S$_4$, Lotgering and van Stapele [9] developed a model considering the monovalent Cu$^+$ ions. If the Cu ion is monovalent in Cu$_2$Cr$_2$S$_4$, the valence configuration of Cu$^+$[$\text{Cr}^{3+}$Cr$^{4+}$]$\text{S}^{2-}_2$ is expected, implying the formally mixed-valent Cr ions. The ferromagnetic metallic ground state of Cu$_2$Cr$_2$S$_4$ was attributed to the double exchange (DE) interaction between Cr$^{3+}$($3d^3$) and Cr$^{4+}$($3d^2$) ions. On the other hand, Goodenough [10] postulated divalent Cu$^{2+}$ ions and trivalent Cr$^{3+}$ ions for $x > 0.5$.

Despite extensive studies on the valence states of transition-metal elements in spinel systems, this issue has not been settled down yet. Therefore, it is necessary to perform the element-specific experiment that provides the direct information on the electronic and magnetic structure of Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$($0 \leq x \leq 1$). Photoemission spectroscopy (PES), soft X-ray absorption spectroscopy (XAS), and X-ray magnetic circular dichroism (XMCD) are good experimental tools for studying the electronic structures [11], the valence states of transition-metal (T) ions in solids [12], [13], and the element-specific local magnetic moments of both spin ($m_s$) and orbital ($m_l$) components [14], [15], respectively. The line shapes of XAS and XMCD spectra are strongly dependent on the occupied $3d$ electron configurations, the crystal field, and the hybridization of $3d$ electrons to other valence electrons. Hence, the peak positions and the line shape of the $T'_2p$ XAS spectrum depend on the local electronic structure of the T ion, providing the information about the valence state and the ground state symmetry of the T ion. The magnitudes of $m_s$ and $m_l$ can be estimated quantitatively by applying the sum rules to the measured XMCD spectrum [15].

We have carried out PES, soft X-ray XAS, and XMCD experiments for polycrystalline samples of Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$($0.1 \leq x \leq 0.5$). Polycrystalline samples were prepared by the standard solid-state reaction method [3]. Valence-band PES, XAS, and XMCD measurements were performed at the 8A1 and 2A undulator beamlines of the PAL. The experimental conditions are the same as those described in [16]. Scanning photoelectron microscopy (SPM) measurements were performed at the 8A1 beamline of the PAL, with the spatial resolution of $\sim 0.5 \mu m$. Topographic SPM images were constructed by employing the total electron yield method (sample current) so as to represent the bulk features of the measured samples [17]. SPM is known to be a powerful method for studying the chemical distribution of specific elements in the sub-$\mu m$ scale.

Fig. 1 shows the measured SPM image of Fe$_{0.3}$Cu$_{0.7}$Cr$_2$S$_4$, obtained with the photon energy ($h\nu$) being set at the Fe $2p_{3/2}$