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$_4$ are very similar to that of Fe metal, indicating that Fe 3$d$ states are strongly hybridized to S 3$p$ states. The XMCD measurements for Fe, Cr, and Cu 2$p$ 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 3$d$ states are located at $\sim -1.5$ eV, while Fe 3$d$ states are very broad, in agreement with the calculated DOS. This study indicates that the minority-spin $e_g$ states of Fe 3$d$ electrons are located very close to $E_F$, suggesting that the hybridized Fe $e_g$-S 3$p$ 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—FeCr$_2$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$_4$ ($x = 0, 0.5, 0.75$) exhibit the large negative magnetoresistance (MR) effect [1], [2]. Upon cooling, the resistivity $\rho (T)$ shows a crossover transition from an 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 both the Fe and Cr sublattices order ferromagnetically, while the two sublattices are coupled antiferromagnetically to each other, resulting in the ferrimagnetic 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$_4$, Lottgering and van Stapele [9] developed a model considering the monovalent Cu$^+$ ions. If the Cu ion is monovalent in CuCr$_2$S$_4$, the valence configuration of Cu$^+$[Cr$^{3+}$Cr$^{4+}$]S$_2^-$ is expected, implying the formally mixed-valent Cr ions. The ferromagnetic metallic ground state of Cu$_x$Cr$_2$S$_4$ was attributed to the double exchange (DE) interaction between Cr$^{3+} (3t^2)$ and Cr$^{4+} (3t^2)$ 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 3$d$ electron configurations, the crystal field, and the hybridization of 3$d$ electrons to other valence electrons. Hence, the peak positions and the line shape of the T 3$p$ 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$_4$ ($0.1 \leq x \leq 0.5$) and Cr$_2$S$_4$ ($x = 0.1$). 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$_{0.9}$Cu$_{0.1}$Cr$_2$S$_4$, obtained with the photon energy ($h\nu$) being set at the Fe 2$\gamma_{3/2}$...
absorption peak ($\hbar\nu \approx 706.5$ eV) [see Fig. 2(b)]. Therefore, the brightness of the SPEM image in Fig. 1 is proportional to the concentration distribution of Fe ions [17]. However, the observed irregular SPEM image for Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$ in Fig. 1 is interpreted to reflect the irregular surface morphology and surface roughness, caused by scraping, but not to arise from the inhomogeneous Fe concentration distribution. This argument is supported by the observation that the survey PES spectra, obtained at the bright spot (B) and the dark spot (D), respectively, are essentially the same. If the bright and dark spots in the SPEM image correspond to the Fe-rich and Fe-poor regions, respectively, then their survey PES spectra are expected to be very different, because the Fe-rich spots should reveal much larger Fe-derived peaks. In particular, the resonantly enhanced Fe Auger peaks should be observed for the Fe-rich region [17]. Therefore, Fig. 1 provides evidence that Cu ions are substituted for Fe ions homogeneously at least in the $\mu$m scale.

Fig. 2 shows the Cr 2p XMCD spectra of Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$. The top panel of Fig. 2(a) shows the XAS spectra of Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$, obtained with the photon helicity parallel ($\rho_+$) to and antiparallel ($\rho_-$) to the magnetization, respectively. The Cr 2p XMCD ($\rho_+ - \rho_-$) spectrum (blue) was obtained by taking the difference between $\rho_+$ and $\rho_-$. The red line represents the integrated value of the XMCD spectrum ($\int (\rho_+ - \rho_-) \, dE$), which can be used to estimate $m_8$ and $m_7$ by applying the sum rule [15].

The Cr 2p XAS spectrum of Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$ is qualitatively similar to that of Cr$_2$O$_3$ [18], indicating that Cr ions are in the formally trivalent (3+) states with the $3d^5$ configuration for $0.1 \leq x \leq 0.5$. Both the Fe 2p XAS and XMCD spectra of Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$ in Fig. 2(b) are very similar to those of Fe metal [15], indicating that the bonding nature of Fe 3$d$ electrons in Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$ is metallic-like, and that there are the large spin magnetic moments ($m_8$) on the Fe sites in Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$. In addition, neither the Fe 2$p_{3/2}$ nor 2$p_{1/2}$ peaks in the XAS and XMCD spectra of Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$ exhibit multiplet features, which again supports that the Fe 3$d$ − S 3$p$ bonding is very far from the ionic bonding, but rather close to the metallic-like bonding. This finding makes a contrast to those for Cr 2$p$ and Cu 2$p$ XAS spectra that indicate the covalent and/or ionic bonding for Cr and Cu 3$d$ electrons. This point will be discussed further in Fig. 3. The Cu 2$p$ XAS spectrum of Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$ in Fig. 2(c) is very similar to that of formally monovalent (Cu$^+$) Cu$_2$Fe$_4$ [19], but quite different from that of CuO [20], providing evidence that Cu ions are formally monovalent ($3p^0$). These findings of trivalent Cr$^{3+}$ ions and monovalent Cu$^+$ ions in Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$ seem to support the model by Lotgering and van Stapele [9] rather than that by Goodenough [10]. Note, however, that we are looking at the sample of Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$ for $x \leq 0.5$, but the controversy between two groups is for $x > 0.5$.

The polarity of the Fe 2$p$ XMCD signals is opposite to that of the Cr 2$p$ XMCD signals, indicating the antiparallel alignment of the spin moments between Fe and Cr ions. In addition,
the Cu 2p XMCD spectrum also shows the very weak polarization, which is parallel to that of Fe ions. The very weak Cu 2p XMCD signals, however, suggest that the magnetic moments at the Cu sites should be very small. As to the integrated XMCD, \( \int_{E_1 \rightarrow E_2} \). The contrast, the integrated XMCD of Fe over the whole range \( \int_{E_1 \rightarrow E_2} \) with respect to that over the \( L_3 \) edge alone, \( \int_{L_2} \), is larger than that of Cr, indicating that the orbital moment on the Fe site is not completely quenched [15].

The left panel of Fig. 3 compares the valence-band PES spectra for Fe\(_{1-x}\)Cu\(_x\)Cr\(_2\)S\(_4\), obtained at \( \hbar \nu = 634 \) eV, where the Fe 3d and S 3p electron emissions are much stronger than Fe 3d and Cr 3d emissions, and the extracted partial spectral weight (PSW) distributions of Fe and Cr 3d states (bottom). The extraction procedure for the Fe and Cr 3d states is described in [16]. The sharp Cr 3d states are located at \( \sim 1.5 \) eV below \( E_F \), while the Fe 3d states are broad with the center at \( \sim -4 \) eV, suggesting that the Fe 3d electrons have the metallic-like bonding character. The intensity of the peak at \( \sim -2.5 \) eV (peak A) increases with increasing Cu concentration \( x \), reflecting that this peak has mainly the Cu 3d character. The measured PES spectra reveal that all the Cr 3d, Fe 3d, Cu 3d PSW’s in Fe\(_{1-x}\)Cu\(_x\)Cr\(_2\)S\(_4\)(\( x > 0 \)) have the very small spectral intensity near \( E_F \). The expected metallic Fermi edge is not observed for \( x = 0.5 \), which is probably due to the very small DOS near \( E_F \). Nevertheless, the findings of the metallic-like bonding of the Fe 3d states with the S 3p states and the broad Fe 3d PSW reveal that the top-most valence-band states closest to \( E_F \) have mainly the Fe 3d – S 3p hybridized character. This conclusion is supported by the calculated Fe 3d PDOS and S 3p PDOS, shown in the right panel of Fig. 3. This finding implies that the S 3p band is not fully occupied, and that the charge transfer may occur from S to other sites in Fe\(_{1-x}\)Cu\(_x\)Cr\(_2\)S\(_4\).

Differently from the case of oxide spinels, such charge transfer might be possible because of the smaller electron negativity of a S ion than an O ion. This study suggests that the narrow hybridized Fe 3d – S 3p states near \( E_F \) play an important role in determining the transport properties in Fe\(_{1-x}\)Cu\(_x\)Cr\(_2\)S\(_4\). The right panel of Fig. 3 provides the calculated total density of states (DOS) and partial DOS (PDOS) of Fe\(_{0.5}\)Cu\(_{0.5}\)Cr\(_2\)S\(_4\) [8]. The ferrimagnetic and insulating ground state is revealed with a small gap at \( E_F \) in the total DOS. The valence band extends from \( E_F \) to approximately 7 eV below \( E_F \), and the Cu d bands are nearly occupied, in agreement with the measured PES spectra. The Cr d peaks below \( E_F \) correspond to the spin-up \( t_{2g} \) band, while the unoccupied peaks above \( E_F \) correspond to the spin-up \( e_g \) and spin-down \( t_{2g} \) and \( e_g \) bands. In contrast, the widely spread Fe d states below \( E_F \) correspond to the majority spin-down \( e_g \) and \( t_{2g} \) bands, and the unoccupied peaks above \( E_F \) correspond to the minority spin-up \( e_g \) and \( t_{2g} \) bands. Fe ions are located in the tetrahedral sites, so that the energy levels of \( e_g \) are lower than the energy levels of \( t_{2g} \). Since Cr ions are located in the octahedral sites, the situation is reversed from the case of Fe. Most of the S p states are located well below \( E_F \), and they overlap mainly with the Fe d states, but not with the Cu d states, indicating the large hybridization to the Fe d states, but a weak hybridization to the Cu d states. These findings in the calculated electronic structures are consistent with those in the measured PES spectra, as well as with those of Fig. 2(b).

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