Valence States of Transition-Metal Ions and Electronic Structures of Spinel $Fe_{1-x}Cu_xCr_2S_4$

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The valence states and electronic structures of transition-metal ions in spinel $Fe_{1-x}Cu_xCr_2S_4$ $(0.1 \leq x \leq 0.5)$ have been investigated by using scanning photoelectron microscopy (SPEM), 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 $2p$ XAS spectra of $Fe_{1-x}Cu_xCr_2S_4$ 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 at ~ -1.5 eV, while Fe $3d$ states are very broad, in agreement with the calculated DOS. This study indicates that the minority-spin e_g states of Fe $3d$ electrons 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 $Fe_{1-x}Cu_xCr_2S_4$ for $x \leq 0.5$.

Index Terms—**$FeCr_2S_4$, $Fe_{0.5}Cu_{0.5}Cr_2S_4$, photoemission spectroscopy (PES), scanning photoelectron microscopy (SPEM), spinel, X-ray absorption spectroscopy (XAS), X-ray magnetic circular dichroism (XMCD).**