Electronic structures of magnetic semiconductors FeCr$_2$Se$_4$ and Fe$_{0.5}$Cu$_{0.5}$Cr$_2$Se$_4$

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Abstract. Electronic structures of Cr-based chalcogenide magnetic semiconductors FeCr$_2$Se$_4$ and Fe$_{0.5}$Cu$_{0.5}$Cr$_2$Se$_4$ are investigated by using the full-potential augmented plane wave (FLAPW) band method in both the generalized gradient approximation (GGA) and the GGA + $U$ (GGA incorporating the on-site Coulomb interaction). The GGA band calculation for the Jahn–Teller distorted FeCr$_2$Se$_4$ with monoclinic structure yields an antiferromagnetic (AF) metallic electronic structure. The GGA + $U$ band calculation yields an insulating electronic structure for AF FeCr$_2$Se$_4$ in agreement with experiments. The orbital ordering in FeCr$_2$Se$_4$ driven by the Jahn–Teller and on-site Coulomb interactions is demonstrated based on the GGA + $U$ electronic structures. For ferrimagnetic Fe$_{0.5}$Cu$_{0.5}$Cr$_2$Se$_4$ with a cubic spinel structure, the GGA and the GGA + $U$ yield nearly insulating and insulating electronic structures, respectively. We have also studied the experimental electronic structure of FeCr$_2$Se$_4$ by employing soft x-ray absorption spectroscopy, soft x-ray magnetic circular dichroism and valence-band photoemission spectroscopy. Both calculational and experimental electronic structure studies indicate that the valence states of Fe and Cr ions in FeCr$_2$Se$_4$ are nearly divalent (Fe$^{2+}$) and trivalent (Cr$^{3+}$), respectively.
The observation of large negative magneto-resistance (MR) and metal–insulator (MI) transition in the spinel sulfide Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$ has invoked renewed interest in Cr-based chalcogenide magnetic semiconductors FeCr$_2$X$_4$ (X = S, Se) [1, 2]. FeCr$_2$S$_4$ is a ferrimagnetic semiconductor with $T_C \sim 172$ K, while isoelectronic FeCr$_2$Se$_4$ is an antiferromagnetic (AF) insulator with $T_N \approx 218$ K [3]–[9]. Upon cooling, the resistivity $\rho(T)$ of FeCr$_2$S$_4$ shows a crossover transition from insulator to metal near the magnetic transition temperature $T_C$, and then shows an insulating feature again below $T \sim 140$ K [2, 10]. Thus, in the finite temperature range below $T_C$, the metallic feature ($\frac{d\rho}{dT} > 0$) is observed. On the other hand, the resistivity behavior of FeCr$_2$Se$_4$ is insulating ($\frac{d\rho}{dT} < 0$) all over the temperature range. At low temperatures below 75 K, FeCr$_2$Se$_4$ appears to become ferrimagnetic with a small magnetic moment of 0.007 $\mu_B$ [7]. Note that FeCr$_2$Se$_4$ crystallizes in the Cr$_3$S$_4$-type monoclinic structure ($I2/m$) in contrast to the cubic spinel structure of FeCr$_2$S$_4$.

Cu-doped FeCr$_2$S$_4$, Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$, has a higher ferrimagnetic transition temperature and a larger magnetic moment with increasing $x$ [11]. Regardless of $x$, Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$ retains the ferrimagnetic phase and the cubic spinel structure. Similarly as in FeCr$_2$S$_4$, the resistivity in Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$ also manifests semiconducting behavior for $T > T_C$ ($\approx 340$ K) and $T \ll T_C$, while, in the infinite temperature range below $T_C$, the metallic feature is observed. The temperature range of the metallic feature is wider for $x = 0.5$ than for $x = 0$. In contrast, Cu-doped FeCr$_2$Se$_4$, Fe$_{1-x}$Cu$_x$Cr$_2$Se$_4$, has a different crystal structure and magnetic phase, depending on $x$. Fe$_{1-x}$Cu$_x$Cr$_2$Se$_4$ crystallizes in a monoclinic structure for 0.0 $\leq x \leq$ 0.1 as FeCr$_2$Se$_4$, whereas, for 0.4 $\leq x \leq$ 1.0, it crystallizes in a cubic spinel structure. In between 0.1 $< x < 0.4$, the two phases coexist with a tendency to form the spinel structure with increasing annealing time [6]. Hence, Fe$_{0.5}$Cu$_{0.5}$Cr$_2$Se$_4$ ($x = 0.5$) has a cubic spinel structure with the ferrimagnetic phase. Transport properties are not available for Fe$_{0.5}$Cu$_{0.5}$Cr$_2$Se$_4$, but it is expected that Fe$_{0.5}$Cu$_{0.5}$Cr$_2$Se$_4$ is more conductive than FeCr$_2$Se$_4$, as Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$ is than FeCr$_2$S$_4$.

The theoretical electronic structure of FeCr$_2$Se$_4$ has not been reported yet. In order to understand the differences in transport and magnetic properties between FeCr$_2$S$_4$ and FeCr$_2$Se$_4$, we have investigated the electronic structures of the Cr-based magnetic semiconductors FeCr$_2$Se$_4$ and Fe$_{0.5}$Cu$_{0.5}$Cr$_2$Se$_4$. We have used both the generalized gradient approximation (GGA) [12] and the GGA+$U$ scheme [13] (GGA+$U$: GGA incorporating the on-site Coulomb interaction $U$) on the basis of the full-potential augmented plane wave (FLAPW) band
method [14]. In our earlier work [15], we have found that the band calculation for FeCr$_2$S$_4$ in the local spin density approximation (LSDA) yields the half-metallic electronic structure [15]. Note that Fe$^{2+}$ ions at the tetrahedral sites of FeCr$_2$S$_4$ are Jahn–Teller active. Hence, the metallic nature of FeCr$_2$S$_4$, obtained in the LSDA, implies that the Jahn–Teller effect is not large enough to induce the insulating ground state for FeCr$_2$S$_4$. In order to have the insulating ground state with orbital ordering, the effect of the Coulomb correlation between d-electrons of Fe and Cr should also be incorporated. In fact, the insulating nature of FeCr$_2$S$_4$ and Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$ is described well by the LSDA + U method [15].

We have also investigated the experimental electronic structure by carrying out soft x-ray absorption spectroscopy (XAS), x-ray magnetic circular dichroism (XMCD) and valence-band photoemission spectroscopy (PES) measurements for a polycrystalline sample of FeCr$_2$Se$_4$. For comparison, we have carried out the same XAS, XMCD and PES experiments for Fe$_{0.9}$Cu$_{0.1}$Cr$_2$S$_4$, the electronic structure of which is considered to be close to FeCr$_2$S$_4$. Polycrystalline samples were prepared by the standard solid-state reaction method [10]. XAS and XMCD are good experimental tools for studying the valence states of transition metal ions in solids [16]–[18] and the element-specific local magnetic moments [19, 20], respectively. XAS and XMCD experiments were performed at the 2A beamline and the PES experiment at the 8A1 beamline of the Pohang Accelerator Laboratory (PAL). XAS and XMCD data were obtained at a liquid nitrogen temperature $T \approx 80$ K, and the total instrumental resolution was $\approx 120$ meV for XMCD at a photon energy, $h\nu \sim 600$ eV. XMCD spectra were obtained with the applied magnetic field of $\sim 0.7$ Tesla and the degree of circular polarization $> 90\%$. The details of the experimental conditions will be described elsewhere [21].

2. Electronic structure of FeCr$_2$Se$_4$

We have performed both the GGA and GGA + U band calculations for a monoclinic FeCr$_2$Se$_4$ of a layered-type structure (see figure 1). We employed the structural data from the literature [9]. Both Fe and Cr ions are located at the centers of face-shared distorted octahedra. This feature of the octahedral environment of Fe ions in FeCr$_2$Se$_4$ is different from that of the tetrahedral environment of Fe ions in FeCr$_2$S$_4$. As shown in figure 1(b), FeCr$_2$Se$_4$ is known to have a rather complicated AF structure. Fe and Cr spins are antiferromagnetically aligned along the $a$- and $b$-directions, while they are aligned ferromagnetically along the $c$-direction [5]. Hence, to describe the AF structure, one needs to consider a $(2 \times 2 \times 1)$ supercell of eight formula units of FeCr$_2$Se$_4$.

In the GGA calculation, FeCr$_2$Se$_4$ with the above AF supercell structure is found to be more stable than ferrimagnetic FeCr$_2$Se$_4$ and the simple AF FeCr$_2$Se$_4$ of layered type. This finding is in agreement with experiment. But, as shown in figure 2, the GGA calculation for the AF supercell FeCr$_2$Se$_4$ yields the metallic phase with high Fe-d density of states (DOS) at the Fermi energy ($E_F$), in disagreement with experiment. Due to Jahn–Teller active Fe$^{2+}$ ions, the FeS$_6$ octahedra in the monoclinic FeCr$_2$Se$_4$ are distorted. Hence, the resulting metallic phase in the GGA calculation reflects that the Jahn–Teller interaction is not large enough to

$^4$ We do not have data for FeCr$_2$S$_4$. However, we have measured PES, XAS and XMCD spectra for Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$ ($x = 0.1, 0.2, 0.5$) and obtained very similar spectra regardless of $x$. This observation suggests that the electronic structure of Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$ ($x = 0.1$) is very similar to that of FeCr$_2$S$_4$ ($x = 0$).
induce the insulating phase in FeCr$_2$Se$_4$. Thus, to describe the insulating phase of FeCr$_2$Se$_4$, we have performed the GGA + $U$ calculation for the AF supercell of FeCr$_2$Se$_4$.

Figure 3 provides the DOS of the AF supercell of FeCr$_2$Se$_4$ in the GGA + $U$ scheme. We have employed the following parameters: $U = 2.45$ eV and $J = 0.95$ eV ($J$ is the intra-atomic exchange interaction) for Fe d-electrons; $U = 1.50$ eV and $J = 0.82$ eV for Cr d-electrons. The energy gap feature is clearly seen near $E_F$, which takes place due to the splitting of Fe-d DOS by the on-site Coulomb interaction $U$. Fe-d DOS in figure 3(b) indicates that the Fe-t$_{2g}$ minority spin states are split into the lower and upper Hubbard bands to have a valence state close to Fe$^{2+}$. Cr-d DOS in figure 3(c) shows that Cr-t$_{2g}$ majority spin states are filled to have $\approx$Cr$^{3+}$ valence states. Se-p DOS in figure 3(d), however, shows that many of the Se-p states are unoccupied. This implies that the covalent bonding nature also exists in FeCr$_2$Se$_4$, and so the ionic valence states of Fe$^{2+}$ and Cr$^{3+}$ ions should be considered as just nominal.

In figure 4(a) is plotted the charge density on the $xy$-plane of the monoclinic FeCr$_2$Se$_4$ at $z = 1/2$ of figure 1(a). Here, the charge density is obtained by integrating the density of the specific spin over the finite energy interval up to $E_F$, as indicated in figure 3(b). Thus the local charge density of Fe corresponds to the minority spin part, while the local charge density of Cr to the majority spin part. The zigzag bonding nature along Se, Cr, Se, Fe, Se, Cr and Se ions is shown along the $b$-direction. To examine the bonding nature between Fe and neighboring Se ions, we have plotted in figure 4(b) the local charge density for the Fe-d minority spin states on the FeS$_6$ layer of the FeS$_6$ octahedron (the layer represented by the red line in figure 4(a)). The local charge density of Fe in figure 4(b) shows a typical Fe-t$_{2g}$ ($\approx$d$_{yz}$-type) state. The lobe axes are not on the FeS$_6$ layer plane, but tilted towards the $xz$-plane, as shown in figure 4(a). This is
Figure 2. Total and partial DOSs of the AF FeCr$_2$Se$_4$ supercell in the GGA.

expected considering the compressed FeS$_6$ octahedron along the $b$-direction in FeCr$_2$Se$_4$. This feature is consistent with the existence of Jahn–Teller active Fe$^{2+}$ ions in FeCr$_2$Se$_4$, which would give rise to the collective Jahn–Teller orbital ordering.

3. Electronic structure of Fe$_{0.5}$Cu$_{0.5}$Cr$_2$Se$_4$

Now let us study the electronic structure of ferrimagnetic Fe$_{0.5}$Cu$_{0.5}$Cr$_2$Se$_4$ with a cubic spinel structure. For Fe$_{0.5}$Cu$_{0.5}$Cr$_2$Se$_4$, one Fe is replaced by Cu in the face-centered cubic (fcc) unit cell with two formula units of FeCr$_2$Se$_4$. As in Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$ [15], the GGA band calculation for Fe$_{0.5}$Cu$_{0.5}$Cr$_2$Se$_4$ at the optimized lattice constant of $a \approx 10.3\text{Å}$ produces the nearly insulating DOS with an energy gap feature near $E_F$ (see figure 5).

The DOS in the GGA + $U$ band calculation in figure 6 provides the insulating ground state more clearly. In the GGA + $U$ band calculations, the parameters used are $U = 2.45$ eV and $J = 0.95$ eV for Fe and $U = 1.50$ eV and $J = 0.95$ eV for Cr, respectively. By Cu doping, there occurs a charge transfer from Fe to Cu, and so the valence states of Fe and Cu
become \( \approx \text{Fe}^{3+} \) and \( \approx \text{Cu}^{1+} \), respectively. Thus, distinctly from the case of FeCr\(_2\)Se\(_4\), Fe ions in Fe\(_{0.5}\)Cu\(_{0.5}\)Cr\(_2\)Se\(_4\) are not Jahn–Teller active and so no cooperative Jahn–Teller orbital ordering occurs. Since Fe and Cr spins are antiferromagnetically coupled, the total magnetic moment becomes 7.0 \( \mu_B \) per unit cell.

4. XAS, XMCD and PES experiments

Figure 7(a) compares the Fe 2p XAS spectra of FeCr\(_2\)Se\(_4\) and Fe\(_{0.9}\)Cu\(_{0.1}\)Cr\(_2\)S\(_4\) to that of Fe metal [20]. It is seen that the Fe 2p XAS lineshapes of FeCr\(_2\)Se\(_4\) and Fe\(_{0.9}\)Cu\(_{0.1}\)Cr\(_2\)S\(_4\) are very similar to each other. No multiplet structures are observed in FeCr\(_2\)Se\(_4\) and Fe\(_{0.9}\)Cu\(_{0.1}\)Cr\(_2\)S\(_4\), resulting in lineshapes that are very similar to that of Fe metal. The absence of multiplet structures in FeCr\(_2\)Se\(_4\) and Fe\(_{0.9}\)Cu\(_{0.1}\)Cr\(_2\)S\(_4\) indicates that the Fe 3d-electrons are strongly hybridized to the other valence electrons, mainly to the Se and S p-electrons. Then the strong hybridization will result in metallic-like bonding in Fe 3d–X p-electrons (X = S, Se), which is far from ionic bonding. This finding makes a contrast to that of Cr 2p XAS in figure 7(b), which indicates covalent bonding for Cr 3d-electrons.
The metallic-like bonding nature of Fe 3d-electrons in FeCr$_2$ spectra. Such differences imply the covalent bonding nature of Cr 3d-electrons, in contrast to the simple lineshape of the Fe 2p XMCD. Further, the Cr 2p XAS spectra of FeCr$_2$ Fe$_4$ systems. Further, the Cr 2p XAS spectra of FeCr$_2$ Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$ are qualitatively similar to that of Cr$_2$O$_3$, indicating that Cr ions in FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$ are mainly trivalent (3+) with the $t_{2g}^1$ occupied configuration. On the other hand, the multiplet structures in FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$ are broader than those of Cr$_2$O$_3$. Such differences reflect that the character of the Cr–X bonding (X = S, Se) is not simple ionic bonding but rather close to covalent bonding, as compared to the more ionic Cr–O bonding in Cr$_2$O$_3$. This is probably due to the weaker electronegativity of X ions (X = S, Se) compared with oxygen (O) ions.

Figures 7(c) and (d) show the Fe 2p and Cr 2p XMCD spectra of FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$. This figure reveals the following features. (i) The polarity of the Fe 2p XMCD is opposite to that of the Cr 2p XMCD, indicating the antiparallel alignment of the spin moments between Fe and Cr ions. This finding agrees with those of the neutron diffraction study [23] and the Mössbauer spectroscopy study [24]. (ii) The lineshapes of both the Fe 2p and Cr 2p XMCD spectra of FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$ are nearly identical, which implies very similar electronic spin configurations in FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$. (iii) The magnitudes of the XMCD signals of FeCr$_2$Se$_4$ are much smaller than (about 1/20) those of Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$. (iv) The Fe 2p XMCD spectra of FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$ are very similar to that of ferromagnetic Fe metal, in agreement with the finding in figure 7(a).

As shown in figure 7(d), the Cr 2p XMCD spectra of FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$ show the multiplet structures clearly, in contrast to the simple lineshape of the Fe 2p XMCD spectra. Such differences imply the covalent bonding nature of Cr 3d-electrons, in contrast to the metallic-like bonding nature of Fe 3d-electrons in FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$. That is, the Fe 3d states in FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$ are strongly hybridized with the X p states (X = S, Se). The multiplet structures originate from the localized atomic-like local electronic

Figure 4. (a) The charge density plotted on the xy-plane of the monoclinic FeCr$_2$Se$_4$ at z = 1/2 of figure 1(a). Here, the charge density is obtained by integrating the charge density of a specific spin over the finite energy interval up to $E_F$, as shown in figure 3(b): the minority spin part for Fe and the majority spin part for Cr. Blue and red lines represent the FeS$_6$ octahedron geometry. (b) The local charge density for the Fe-d minority spin states plotted on the FeS$_4$ layer of the FeS$_6$ octahedron (the layer represented by the red line in figure 4(a)).

Figure 7(b) compares the Cr 2p XAS spectra of FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$ to that of Cr$_2$O$_3$ (Cr$^{3+}$) [22]. This figure shows that the Cr 2p XAS spectra of FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$ are essentially identical, indicating the same valence states of Cr ions in both systems. Further, the Cr 2p XAS spectra of FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$ are qualitatively similar to that of Cr$_2$O$_3$, indicating that Cr ions in FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$ are mainly trivalent (3+) with the $t_{2g}^1$ occupied configuration. On the other hand, the multiplet structures in FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$ are broader than those of Cr$_2$O$_3$. Such differences reflect that the character of the Cr–X bonding (X = S, Se) is not simple ionic bonding but rather close to covalent bonding, as compared to the more ionic Cr–O bonding in Cr$_2$O$_3$. This is probably due to the weaker electronegativity of X ions (X = S, Se) compared with oxygen (O) ions.

Figures 7(c) and (d) show the Fe 2p and Cr 2p XMCD spectra of FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$. This figure reveals the following features. (i) The polarity of the Fe 2p XMCD is opposite to that of the Cr 2p XMCD, indicating the antiparallel alignment of the spin moments between Fe and Cr ions. This finding agrees with those of the neutron diffraction study [23] and the Mössbauer spectroscopy study [24]. (ii) The lineshapes of both the Fe 2p and Cr 2p XMCD spectra of FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$ are nearly identical, which implies very similar electronic spin configurations in FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$. (iii) The magnitudes of the XMCD signals of FeCr$_2$Se$_4$ are much smaller than (about 1/20) those of Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$. (iv) The Fe 2p XMCD spectra of FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$ are very similar to that of ferromagnetic Fe metal, in agreement with the finding in figure 7(a).

As shown in figure 7(d), the Cr 2p XMCD spectra of FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$ show the multiplet structures clearly, in contrast to the simple lineshape of the Fe 2p XMCD spectra. Such differences imply the covalent bonding nature of Cr 3d-electrons, in contrast to the metallic-like bonding nature of Fe 3d-electrons in FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$. That is, the Fe 3d states in FeCr$_2$Se$_4$ and Fe$_4$Cu$_{0.1}$Cr$_2$S$_4$ are strongly hybridized with the X p states (X = S, Se). The multiplet structures originate from the localized atomic-like local electronic
Figure 5. Total and partial DOSs of the ferrimagnetic Fe\textsubscript{0.5}Cu\textsubscript{0.5}Cr\textsubscript{2}Se\textsubscript{4} in the GGA.

It is surprising that finite XMCD signals are observed in both the Fe 2p and Cr 2p XMCD spectra of FeCr\textsubscript{2}Se\textsubscript{4}. Normally, an AF system does not show the XMCD effect. So the existence of the finite XMCD effect in FeCr\textsubscript{2}Se\textsubscript{4} implies that it has a ferromagnetic component at $T \approx 80$ K, where the XMCD data were obtained. The existence of nonzero XMCD signals in FeCr\textsubscript{2}Se\textsubscript{4} seems to be consistent with its ferrimagnetic behavior below 75 K [7]. Further, the much smaller intensity of the XMCD spectrum of FeCr\textsubscript{2}Se\textsubscript{4}, as compared to FeCr\textsubscript{2}S\textsubscript{4}, is qualitatively consistent with the much smaller bulk magnetic moment of FeCr\textsubscript{2}Se\textsubscript{4} than that of Fe\textsubscript{0.9}Cu\textsubscript{0.1}Cr\textsubscript{2}S\textsubscript{4}. The nearly identical XMCD lineshapes for Fe\textsubscript{0.9}Cu\textsubscript{0.1}Cr\textsubscript{2}S\textsubscript{4} and FeCr\textsubscript{2}Se\textsubscript{4} imply similar local electronic structures between $X = S$ and $X = Se$, as explained below.

Figure 8 compares the valence-band PES spectra of FeCr\textsubscript{2}Se\textsubscript{4} and Fe\textsubscript{0.9}Cu\textsubscript{0.1}Cr\textsubscript{2}S\textsubscript{4}. The labels in figure 8, such as Cr 3d, Fe 3d and Se/S p + Fe/Cr 3d, represent roughly the PSW...
Figure 6. Total and partial DOSs of the ferrimagnetic Fe$_{0.5}$Cu$_{0.5}$Cr$_2$Se$_4$ in the GGA+U.

distributions of the corresponding photoelectrons. These PSWs were determined by employing resonant PES (RPES) [18, 25] near the Cr 2p and Fe 2p absorption edges. The details of the extraction procedure for each PSW are explained in [18]. The overall features are very similar to each other. The Cr 3d PES spectra exhibit rather sharp peaks, corresponding to the occupied t^3$_{2g}$-electrons, while the Fe 3d PES spectra are much broader. These differences again indicate that the Fe 3d-electrons are strongly hybridized with the other valence electrons. Then the strong hybridization will result in metallic-like bonding in Fe 3d–X p-electrons (X = S, Se).

In this work, we have found that the electronic structures of Fe 3d and Cr 3d states of FeCr$_2$Se$_4$ and FeCr$_2$S$_4$ are very similar to each other. In view of the different crystal structures for FeCr$_2$Se$_4$ (monoclinic) and FeCr$_2$S$_4$ (spinel), this finding is unexpected. Note that the local environments of Fe ions are different: octahedral (O$_h$) for FeCr$_2$Se$_4$ and tetrahedral (T$_d$) for FeCr$_2$S$_4$. Therefore, the similarity in electronic structures of Fe 3d states of FeCr$_2$Se$_4$ and FeCr$_2$S$_4$ might be due to the metallic-like bonding between Fe 3d states and S 3p or Se 4p states.

5 In this figure, we have neglected the contribution from the Cu 3d PSW.
Figure 7. (a) Comparison of the Fe 2p XAS spectra of FeCr$_2$Se$_4$ and Fe$_{0.9}$Cu$_{0.1}$Cr$_2$S$_4$ to that of Fe metal [20]. (b) Comparison of the Cr 2p XAS spectra of FeCr$_2$Se$_4$ and Fe$_{0.9}$Cu$_{0.1}$Cr$_2$S$_4$ to that of Cr$_2$O$_3$ (Cr$^{3+}$) [22]. (c) Comparison of the Fe 2p XMCD spectrum of FeCr$_2$Se$_4$ to that of Fe$_{0.9}$Cu$_{0.1}$Cr$_2$S$_4$. (d) Comparison of the Cr 2p XMCD spectrum of FeCr$_2$Se$_4$ to that of Fe$_{0.9}$Cu$_{0.1}$Cr$_2$S$_4$.

in FeCr$_2$X$_4$ (X = S, Se); thereby the effect of the local atomic-like environments is weakened. As to the similarity in the Cr 3d electronic structures, it can be understood based on the same local $O_h$ environment of Cr ions in both FeCr$_2$Se$_4$ and FeCr$_2$S$_4$.

5. Conclusions

We have studied the electronic structures of the Cr-based chalcogenide magnetic semiconductors FeCr$_2$Se$_4$ and Fe$_{0.5}$Cu$_{0.5}$Cr$_2$Se$_4$ by using the FLAPW band method in both the GGA and GGA + $U$ schemes. Insulating ground states of FeCr$_2$Se$_4$ and Fe$_{0.5}$Cu$_{0.5}$Cr$_2$Se$_4$ are
Figure 8. Comparison of the valence-band PES spectra of FeCr$_2$Se$_4$ and Fe$_{0.9}$Cu$_{0.1}$Cr$_2$S$_4$. These PES spectra represent roughly the partial spectral weight (PSW) distributions of the Cr 3d (top), Fe 3d (middle) and Se/S p + Fe/Cr 3d (bottom) states, respectively.

described well by the GGA + $U$. We have shown that the Jahn–Teller interaction in FeCr$_2$Se$_4$ is not large enough to induce the insulating ground state. The Coulomb correlation effects between d-electrons of Fe and Cr should be incorporated to get the AF insulating ground state with the orbital ordering in FeCr$_2$Se$_4$.

The electronic structure of FeCr$_2$Se$_4$ has also been investigated experimentally by employing XAS, XMCD and PES. It is found that the electronic structure of FeCr$_2$Se$_4$ is very similar to that of FeCr$_2$S$_4$. The valence states of Cr and Fe ions are nearly trivalent (Cr$^{3+}$) and divalent (Fe$^{2+}$), respectively. On the other hand, the Fe 2p XAS spectrum of FeCr$_2$Se$_4$ does not exhibit the multiplet structures, similarly as in Fe metal, indicating the strong hybridization between the Fe 3d and Se p electrons.

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References

[1] Watanabe T and Nakada I 1978 Japan. J. Appl. Phys. 17 1745
[2] Ramireza A P, Cava R J and Krajewski J 1997 Nature 386 156
[3] Morris B L, Russo P and Wold A 1970 J. Phys. Chem. Solids 31 635
[4] Kojima K, Matsui M, Sato K and Adachi K 1970 J. Phys. Soc. Japan 29 1643
[5] Hong S R and Ok H N 1975 Phys. Rev. B 11 4176
[6] Ok H N, Chung Y and Kim J G 1979 Phys. Rev. B 20 4550
[7] Snyder G J, Caillat T and Fleurial J-P 2000 Phys. Rev. B 62 10185
[8] Goya G F and Sagredo V 2003 Solid State Commun. 125 247
[9] Kang J H, Kim S J, Lee B W and Kim C S 2006 J. Appl. Phys. 99 08F714
[10] Kim S J, Son B S, Lee B W and Kim C S 2004 J. Appl. Phys. 95 6837
[11] Ando K, Nishihara Y, Okuda T and Tsushima T 1979 J. Appl. Phys. 50 1917
[12] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[13] Anisimov V I, Zaanen J and Andersen O K 1991 Phys. Rev. B 44 943
[14] Wimmer E, Krakauer H, Weinert M and Freeman A J 1981 Phys. Rev. B 24 864
  Weinert M, Wimmer E and Freeman A J 1982 Phys. Rev. B 26 4571
  Jansen H J F and Freeman A J 1984 Phys. Rev. B 30 561
[15] Park M S, Kwon S K, Youn S J and Min B I 1999 Phys. Rev. B 59 10018
[16] de Groot F M F, Fuggle J C, Thole B T and Sawatzky G A 1990 Phys. Rev. B 42 5459
[17] van der Laan G and Kirkman I W 1992 J. Phys.: Condens. Matter 4 14189
[18] Han S W et al 2006 J. Phys.: Condens. Matter 18 7413
[19] Thole B T, Carra P, Sette F and van der Laan G 1992 Phys. Rev. Lett. 68 1943
[20] Chen C T, Idzerda Y U, Lin H-J, Smith N V, Meigs G, Chaban E, Ho G H, Pellegrin E and Sette F 1995 Phys. Rev. Lett. 75 152
[21] Kang J-S et al 2007 unpublished
[22] Theil C, van Elp J and Folkmann F 1999 Phys. Rev. B 59 7931
[23] Kang J-S, Kim S J, Kim C S, Olson C G and Min B I 2001 Phys. Rev. B 63 144412
[24] Shirane G, Cox D E and Pickart S J 1964 J. Appl. Phys. 35 954
[25] Yagnik C M and Mathur H B 1967 Solid State Commun. 5 841

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