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EPL, **78** (2007) 27004

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## Valence values of the cations in selenospinel $\text{Cu}(\text{Cr}, \text{Ti})_2\text{Se}_4$

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received 18 January 2007; accepted in final form 4 March 2007  
published online 29 March 2007

PACS 71.20.Be – Transition metals and alloys  
PACS 78.70.Dm – X-ray absorption spectra

**Abstract** – A long-standing issue about the Cu valency in selenospinel  $\text{CuCr}_2\text{Se}_4$  was investigated by soft X-ray absorption spectroscopy (XAS) and magnetic circular dichroism (XMCD). Using the sensitivity of XAS and XMCD to the valence value of transition metal ion and its local symmetry, we checked the valence value of each cation in selenospinel  $\text{CuCr}_x\text{Ti}_{2-x}\text{Se}_4$  ( $x = 1.0, 1.1, 1.5,$  and  $2.0$ ) and obtained spectroscopic evidence that a small amount of the Cu cation changes the valency from Cu(I) to Cu(II) as the Cr concentration increases from 1.0 to 2.0. Dependence of the Cu(II) concentration and the mean field magnetic exchange energy on the Cr concentration suggests the Cu  $d$ -hole could play a crucial role in the intriguing magnetic/electrical properties of  $\text{CuCr}_2\text{Se}_4$ .

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The magnetic and electrical properties of the spinel  $\text{CuCr}_2\text{X}_4$  ( $X = \text{S}, \text{Se},$  and  $\text{Te}$ ) have been one of the long-standing issues in solid state physics. Experimentally it is well established that  $\text{ACr}_2\text{X}_4$  ( $A = \text{Zn}, \text{Cd},$  and  $\text{Hg},$  and  $X = \text{S}, \text{Se},$  and  $\text{Te}$ ) is a ferro- or antiferro-magnetic semiconductor while  $\text{CuCr}_2\text{X}_4$  is a ferromagnetic metal with a relatively high Curie temperature [1]. An easily noticed difference between them is that all of the A-site cations are definitely divalent in the semiconducting spinels, whereas it is not clear whether the Cu ion is divalent or monovalent in the metallic spinels. This ambiguity of the Cu valency in  $\text{CuCr}_2\text{X}_4$  has given rise to a scientific debate about its origin of the peculiar magnetic and electrical properties. Two models, one by Lotgering and van Stapele [2] that monovalent Cu induces one hole in a ligand  $p$  orbital, thereby making the system metallic, and the other by Goodenough [3] that a  $d$  hole of divalent Cu forms a metallic band, have been proposed so far, but have not been clearly resolved yet.

The apparently simple issue, however, turns out to be difficult to definitively determine because various experiments have given open conclusions on this issue. Studies with various spectroscopic tools have suggested

monovalency in the Cu ion [4–9] while the magnetic study does not exclude the possibility that divalent Cu ions exist [10–12]. As the spectroscopic data has accumulated, consensus on the monovalency of the Cu ion seems to have been reached, though the issue has not been finally settled. Since the essence of this issue is what the main character of the conduction carriers is and why they have a high Curie temperature, not all the studies supporting the monovalency of the Cu ion agree to the model by Lotgering and van Stapele.

To check the valence value and magnetic moment of each transition metal cation, soft X-ray absorption spectroscopy (XAS) and magnetic circular dichroism (XMCD) are the most appropriate tools. Their sensitivity to the valency of  $3d$  transition metal ions has been thoroughly tested both theoretically and experimentally [13]. So far, several studies with these tools have been reported for the compounds in which A-site Cu ions are substituted by Fe or Cd, but no systematic study for B-site substitution has been reported [6,7]. In this paper, we have used polycrystalline  $\text{CuCr}_x\text{Ti}_{2-x}\text{Se}_4$  ( $x = 1.0, 1.1, 1.5$  and  $2.0$ ) compounds as sample systems and investigated all of the valence values of the cation constituents by XAS and XMCD in order to obtain a clue for understanding physics of the electrical/magnetic properties. Our experimental

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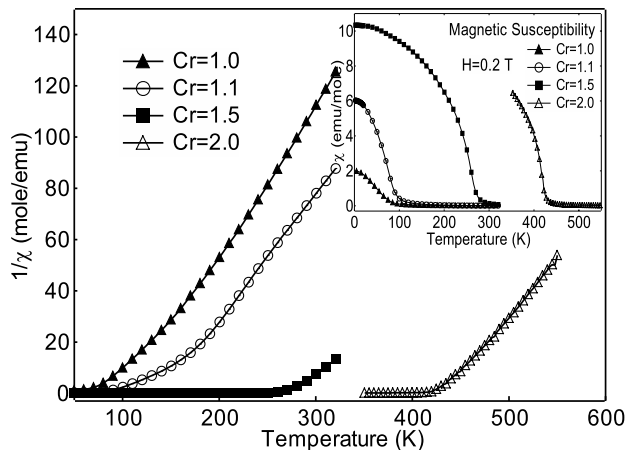


Fig. 1: Inverse magnetic susceptibility *vs.* temperature. Inset: magnetic susceptibility *vs.* temperature.

data and the analysis reveal that the Cr valence states and the magnetic interaction between Cr ions do not change even if the Cr concentration is decreased, and there exists a small amount of divalent Cu ions in  $\text{CuCr}_2\text{Se}_4$ , implying the Cu *d*-holes play a role in the magnetic/electrical properties.

Polycrystalline  $\text{CuCr}_x\text{Ti}_{2-x}\text{Se}_4$  ( $x = 1.0, 1.1, 1.5,$  and  $2.0$ ) samples were synthesized by the standard solid state reaction method. Stoichiometric amounts of high purity ( $\geq 99.99\%$ ) Cu, Cr, Ti, and Se powders were weighed and mixed with a pestle and mortar. The mixtures were fired three times in evacuated quartz ampoules at temperature of  $900^\circ\text{C}$  for four days. Grinding of the materials was repeated after each firing. All the samples were confirmed to be a single phase by powder X-ray diffraction. Magnetization measurement shows that the Curie temperatures are 105, 150, 275, and 440 K for  $x = 1.0, 1.1, 1.5,$  and  $2.0$ , respectively (see figs. 1 and 6(a)). Resistivity measurement by the standard four-probe method reveals that  $\text{CuCrTiSe}_4$  is a semiconductor, and the others are metals, which is consistent with the previous report about thiospinels [14]. The XAS and XMCD measurements were performed at beamline 2A1 of Pohang Accelerator Laboratory (PAL) in Pohang, Korea. The chamber pressure and sample temperature were kept at  $\sim 10^{-9}$  torr and 100 K, respectively. The photon polarization was controlled by the elliptically polarized undulator, and the resolving power ( $E/\Delta E$ ) was set to  $\sim 3000$  through the whole measurement. The samples were scraped *in situ* to obtain clean surfaces. The spectra were recorded in the total electron yield mode and normalized by the photon flux. A 0.6 T magnetic field was applied to the samples during XMCD recording, and the field was reversed at each data point to obtain dichroism signal.

The Cr  $L_{2,3}$  XAS and XMCD spectra of  $\text{CuCr}_x\text{Ti}_{2-x}\text{Se}_4$  are displayed in figs. 2(a) and (b), respectively. All the spectra are split into  $L_3$  and  $L_2$  regions due to the spin-orbit splitting energy of the  $2p$  core hole. In the  $L_3$

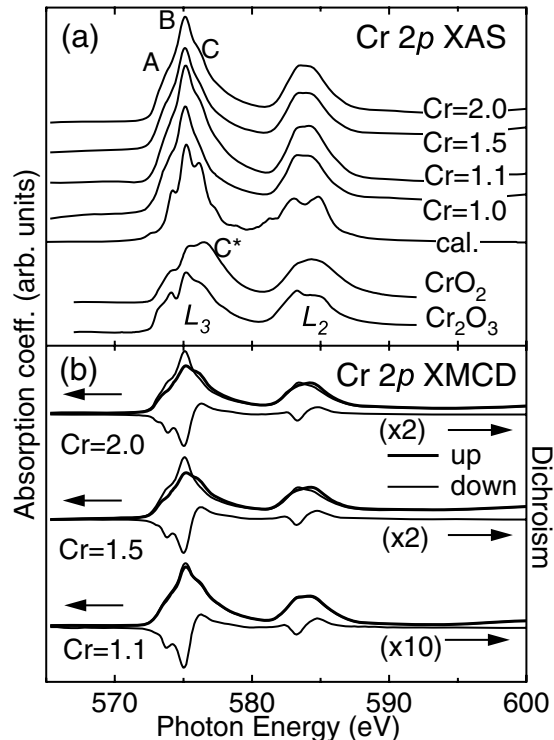


Fig. 2: (a) Cr  $L_{2,3}$ -edge XAS spectra of  $\text{CuCr}_x\text{Ti}_{2-x}\text{Se}_4$  ( $x = 1.0, 1.1, 1.5$  and  $2.0$ ). The fifth spectrum from top was calculated by the configuration interaction cluster model with full ionic multiplet structure. The last two spectra are taken from the literature [16]. They were shifted by 3.0 eV toward the low photon energy side for comparison. (b) Cr  $L_{2,3}$ -edge XMCD spectra. All the dichroism spectra essentially look the same, which means there is no change in local magnetic state of Cr  $3d$  orbitals in spite of the Cr concentration change.

region of the XAS spectra we can identify three dominant peaks, denoted as **A**, **B**, and **C**, showing very small changes in their position and intensity. To determine the valency of the Cr ion we applied the configuration interaction cluster model calculation with full ionic multiplet structure to simulate our Cr  $L_{2,3}$ -edge spectra [15]. The calculated spectrum is also shown in fig. 2(a). All the features in the experimental spectra are well reproduced by this model calculation with the hybridization parameter ( $V_{pd\sigma}$ ) of 1.3 eV, the charge transfer energy ( $\Delta$ ) of 2.0 eV from the ligand *p* orbital to the Cr  $3d$  orbital, on-site Coulomb energy ( $U$ ) of 5.5 eV, and the crystal field strength ( $10Dq$ ) of 0.7 eV under  $d^3$  configuration and  $O_h$  symmetry, showing that the valencies of the Cr ions are all (+3). The other parameters follow the method given in ref. [15].

The XAS spectra for  $\text{CrO}_2$  and  $\text{Cr}_2\text{O}_3$  taken from the literature [16] are presented to show the prototypical shapes for  $\text{Cr}^{4+}$  and  $\text{Cr}^{3+}$  ions. If these spectra are compared with those for  $\text{Cu}(\text{Cr},\text{Ti})_2\text{Se}_4$  peak **C** in selenospinel may be suspected to be the same structure to **C\*** in  $\text{CrO}_2$ , indicating the mixture of  $\text{Cr}^{3+}$  and  $\text{Cr}^{4+}$  ions. However, the XMCD measurement shows peak **C\***

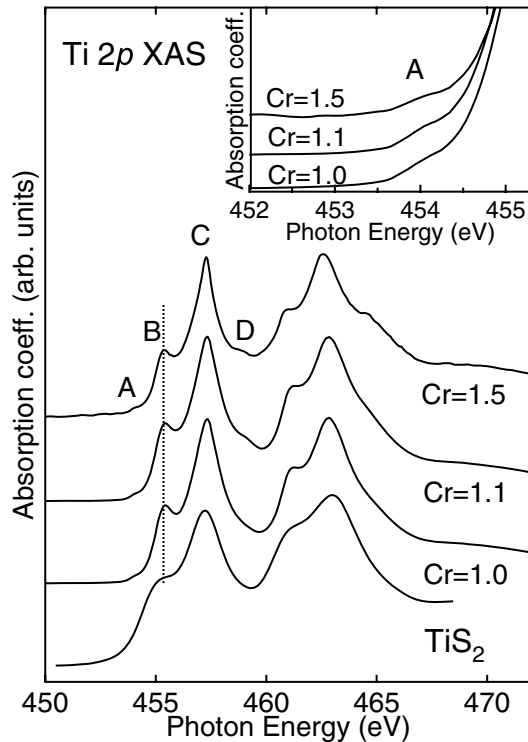


Fig. 3: Ti  $L_{2,3}$ -edge XAS spectra of  $\text{CuCr}_x\text{Ti}_{2-x}\text{Se}_4$ . The electron energy loss spectrum for  $\text{TiS}_2$  is taken from the literature [20]. It was shifted toward the low photon energy side by 0.4 eV for comparison. The existence of peak **A** and no energy position change of peak **B** are used as the indications of Ti tetravalency. The inset shows peak **A** at length.

is not relevant to peak **C** in selenospinel. The dichroism spectra look the same for the samples of  $x = 1.1, 1.5,$  and  $2.0$ , which means there is no change in local magnetic states of Cr  $3d$  orbitals between  $\text{CuCrTiSe}_4$  and  $\text{CuCr}_2\text{Se}_4$ . In the  $x = 1.0$  case, a meaningful XMCD spectrum was not obtained due to the temperature limit of the experimental facilities. All these results reveal that the dominant Cr ions are trivalent and the tetravalent Cr ions are of very small, if any, amount.

In Lotgering and van Stapele's original model, they proposed mixed valent Cr ions, *i.e.* Cr(III) and Cr(IV), and attributed the strong ferromagnetic metallic property to the double exchange mechanism. However, the original model was modified after many experimental observations supporting the pure trivalent Cr ion [9,17]. In their modified model, Cr ion is all trivalent, Cu ion is still monovalent, and one hole resides on the top part of the chalcogen  $p$  orbital valence band. Therefore, confirming the trivalent Cr ion in  $\text{CuCr}_2\text{Se}_4$  does not mean resolving this debate. Definitely our XMCD result also shows that the double exchange is not relevant to the magnetism of  $\text{CuCr}_2\text{Se}_4$ .

The valency of Ti ions is also checked in the XAS spectra as shown in fig. 3. In interpreting the Ti  $L_{2,3}$ -edge spectra, previous studies about titanium oxides [18] and other  $d^0$  compounds [19] are good references. Though

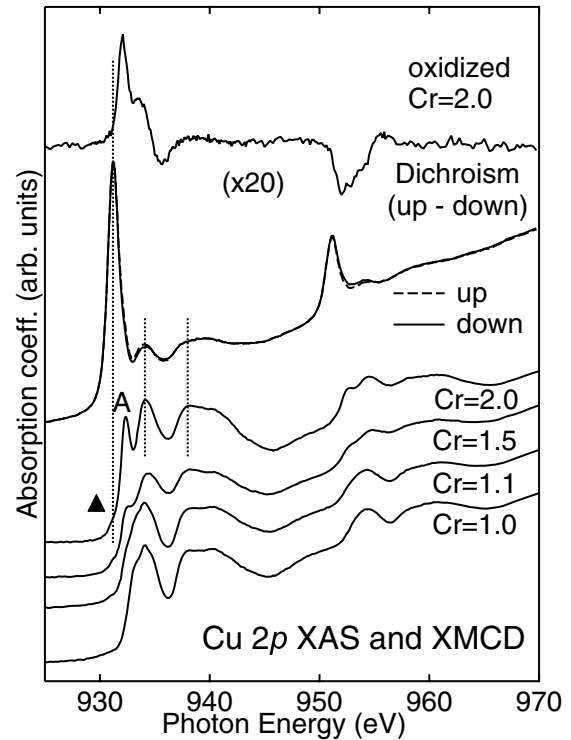


Fig. 4: Cu  $L_{2,3}$ -edge XAS and XMCD spectra. Peak **A** grows as the Cr concentration increases. The solid triangle ( $\blacktriangle$ ) indicates divalent copper impurity peak. The oxidized Cr = 2.0 spectrum shows the origin of peak **A** is not the  $\text{CuO}$  impurity. The XMCD spectrum definitely excludes the possibility that peak **A** is related to the  $\text{CuO}$  impurities.

chalcogenides, unlike oxides, do not show sharp multiplet structure due to their strong covalency, two combined features can be used to determine the valency of Ti ion. One is to see the pre-edge peaks in Ti(IV) spectra, denoted as **A** in fig. 3, which are enlarged in the inset. Because this peak is apart from the main peak group, it is easily separated even in blurred spectra as in the chalcogenide case. The other is to check the change of the energy position of peak **B**. Because the peak position shifts to the lower binding energy side as the oxidation number decreases from (+4) to (+3), it can be used as an indication of the valency change. From these two criteria, it is clear that all of the Ti ions in our  $\text{CuCr}_x\text{Ti}_{2-x}\text{Se}_4$  compounds are tetravalent. For comparison, the electron energy loss spectrum taken from the literature [20] for  $\text{TiS}_2$  is also presented, showing a very similar shape to those of the selenospinel. In the spectrum of  $x = 1.5$ , though peak **D** and a portion of peak **C** originate from  $\text{TiO}_2$  impurities, they do not have any effect on this conclusion.

Now we are in a position to scrutinize the Cu valency problem. The XAS spectra of the Cu  $L_{2,3}$ -edge, unlike the cases of Cr and Ti ions, show a dramatic change as displayed in fig. 4. Peak **A** in the  $\text{CuCr}_2\text{Se}_4$  spectrum vanishes as the Cr concentration decreases. The spectrum of  $\text{CuCrTiSe}_4$  ( $x = 1.0$ ) is that of typical monovalent copper chalcogenides [21]. However, growing peak **A** with

the increase of the Cr concentration raises the question of whether the copper ion in  $\text{CuCr}_2\text{Se}_4$  ( $x = 2.0$ ) should be interpreted as purely monovalent. According to the previous studies of the Cu  $L$ -edge XAS spectra, the divalent Cu peak and the monovalent Cu peak should be separately interpreted [22]. The highly intense divalent Cu peak, which comes from the excitonic state between Cu  $2p$  core hole and localised Cu  $3d$  orbital, is located at a lower photon energy ( $\sim 931.3$  eV) than the binding energy determined by X-ray photoelectron spectroscopy (XPS) due to the core hole effect, while the monovalent Cu peaks reflect the partial density of states (pDOS) projected on the Cu site. Thus, one can blame peak **A** on unavoidable divalent copper impurities as in the case of various copper minerals [23], but the impurity peak (931.3 eV), denoted as ( $\blacktriangle$ ) in fig. 4, is also identified at  $\sim 1.0$  eV lower photon energy than the position of peak **A** (932.3 eV) in the spectrum.

To experimentally exclude the CuO impurity scenario we exposed the  $\text{CuCr}_2\text{Se}_4$  sample to the air for a day and obtained the Cu  $2p$  XAS and XMCD spectra as shown in fig. 4. The large Cu(II) peak position exactly coincides with the impurity peak ( $\blacktriangle$ ) in  $\text{CuCr}_2\text{Se}_4$ . The XMCD spectrum also supports our argument. Because CuO is anti-ferromagnetic, no dichroism signal should be measured at the divalent Cu peak position in XMCD measurement. The small but meaningful dichroism signal (at most  $\sim 0.1 \mu_B$ ) with the opposite direction to that of Cr ions at the photon energy not of the impurity peak ( $\blacktriangle$ ) but of peak **A** in our Cu  $L$ -edge spectrum shows peak **A** is not related with the CuO impurities. The previous studies also observed the same structure in  $\text{CuCr}_2\text{Se}_4$  [6] and single crystalline  $\text{Fe}_{0.5}\text{Cu}_{0.5}\text{Cr}_2\text{S}_4$  [7], but the origin was not analysed in detail. The LDA calculation for  $\text{CuCr}_2\text{Se}_4$  also supports peak **A** is an intrinsic structure [24]. Their results predict that  $\text{CuCr}_2\text{Se}_4$  has a small amount of Cu  $d$  holes and their spin moments are anti-ferromagnetically coupled with those of Cr ions, which is consistent with our XAS and XMCD results.

If peak **A** in fig. 4 represents the intrinsic structure of  $\text{CuCr}_x\text{Ti}_{2-x}\text{Se}_4$ , an interesting correlation between the Cu  $d$ -holes and magnetic properties is inferred from our spectra. To see the correlation more quantitatively, we extract the Cu(II) portion from the Cu  $L$ -edge spectra as follows. After subtracting the arctangent-like background from the raw spectra, the  $L_3$ -edge spectrum is compared with the theoretically determined pDOS projected on the Cu site as shown in fig. 5 [24]<sup>1</sup>. One can see peak **A** has mainly  $d$ -character, peak **B** is mixed with  $s$ - and  $d$ -character, and peak **C** has mainly  $s$ -character. Based on this peak character assignment, we assume only peak **A** comes from the divalent Cu ions for simplicity and estimate the weight of peak **A** by decomposing each  $L_3$ -edge spectrum with four Lorentzian profiles as shown

<sup>1</sup>To simulate the experimental effect, we convoluted the pDOS with a Lorentzian [FWHM = 0.4 eV + 0.1( $E - E_F$ )] and a Gaussian (FWHM = 0.4 eV).

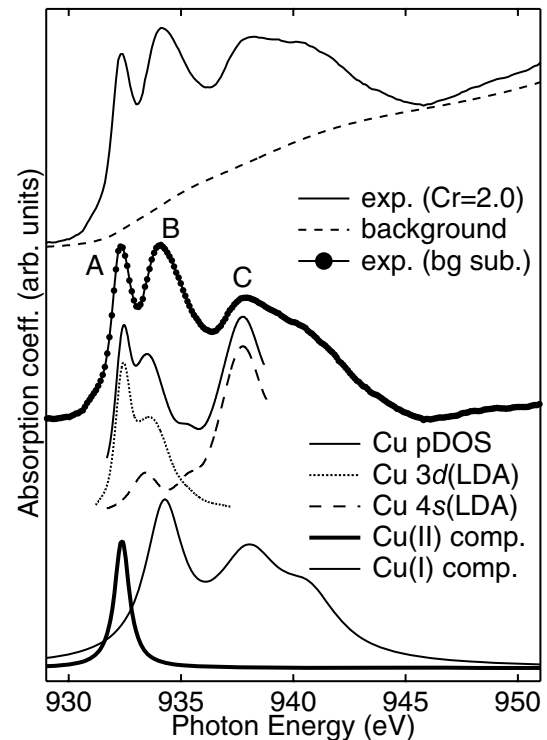


Fig. 5: Decomposition of the Cu  $L_3$ -edge spectrum into Cu(II) and Cu(I) components.

at the bottom of fig. 5. To convert these portions into real concentrations, the transition matrix element effects should be taken into account. Here, the ratio of  $2p \rightarrow 4s$  to  $2p \rightarrow 3d$  transition probability is assumed to be  $\sim 5\%$  according to the theoretical calculation [25].

On the other hand, the effective exchange integral,  $J_{MF}$ , in the mean field theory is described as  $J_{MF} = 3k_B T_C / 2zS(S+1)$ , where  $k_B$ ,  $T_C$ ,  $S$ , and  $z$  are the Boltzmann's constant, absolute temperature, magnetic moment, and number of nearest magnetic neighbors, respectively [26]. Though it is disputable to apply the mean field theory to the metallic system, it can be a good starting point to estimate the magnetic interaction between Cr  $3d$  electrons if we consider the facts that the local magnetic states of the Cr  $3d$  orbitals do not change very much as shown in fig. 2(b), and are similar to those of semiconducting sulphospinels [6,7]. Under the assumption that only Cr ions are magnetic in  $\text{CuCr}_x\text{Ti}_{2-x}\text{Se}_4$  and that the spin is  $3/2$  ( $d^3$  in  $\text{Cr}^{+3}$ ) for all of the samples, which is supported by our XMCD measurement result, the mean field exchange integral for each compound is estimated by using the  $T_C$  values obtained from the magnetization measurements as shown in figs. 6(a) and (b). Here, the average number of nearest magnetic neighbors,  $z$ , is calculated under the assumption that the Cr ions occupy only octahedral sites in spinel structure.

Figure 6(b) implies there could be a correlation between the divalent Cu ions and the exchange energy in  $\text{CuCr}_2\text{Se}_4$ . This interesting correlation gives a clue to the reason why only  $\text{CuCr}_2\text{X}_4$  ( $X = \text{S}, \text{Se}, \text{and Te}$ ) is a metallic

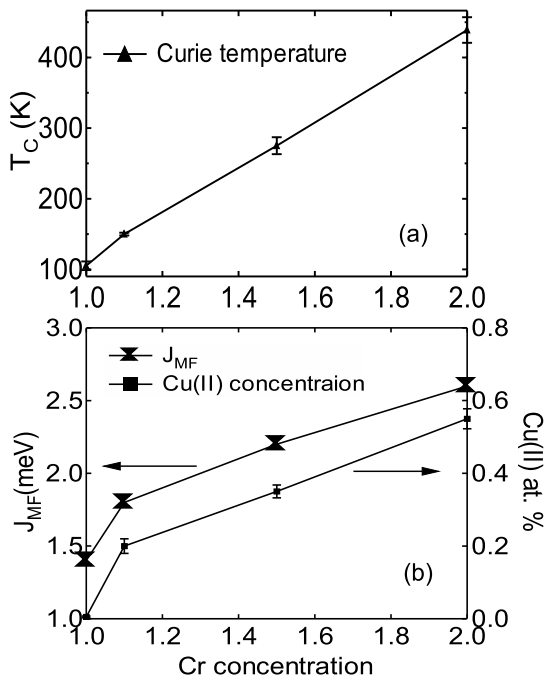


Fig. 6: (a) Curie temperature vs. Cr concentration. (b) (Left ordinate) Mean field effective exchange energy vs. Cr concentration. (Right ordinate) Divalent Cu ion vs. Cr concentration.

ferromagnet with a relatively high Curie temperature ( $T_C$ ) compared with other sulpho-spinel compounds. First, the metallic conductivity can be explained by the itinerant Cu 3d hole as is proposed by Goodenough. However, the small amount of the divalent Cu concentration suggests the other cations and anions also play a role in the transport property. Second, the relatively high Curie temperature of  $\text{CuCr}_2\text{X}_4$  is likely to be connected with the antiferromagnetic coupling of the itinerant Cu  $d$ -hole to the localized spin moment of  $\text{Cr}^{3+}$ . In a spin system like this, two extra spin interactions can arise aside from the interaction between the  $\text{Cr}^{3+}$  ions. One is the indirect interaction between the Cr ions arising from the RKKY interaction. The other is the interaction between Cr ions and the itinerant Cu  $d$ -holes. Considering that the small magnetic moment and the anti-ferromagnetic coupling of  $\text{Cu}^{2+}$  to  $\text{Cr}^{3+}$ , the RKKY-assisted indirect interaction seems to mainly contribute to the enhancement of the Curie temperature.

In summary, we have investigated the valencies of all the cation constituents of  $\text{CuCr}_x\text{Ti}_{2-x}\text{Se}_4$  ( $x = 1.0, 1.1, 1.5, \text{ and } 2.0$ ) using transition metal  $L_{2,3}$ -edge XAS and XMCD to clarify the long-standing Cu valency problem in  $\text{CuCr}_2\text{Se}_4$ . The Cr  $L_{2,3}$ -edge XAS and XMCD spectra show the Cr ions are all trivalent and the system has no change in local magnetic states of Cr 3d orbitals in spite of the variation of the Cr concentration. The Ti  $L_{2,3}$ -edge XAS spectra show the Ti ions are all tetravalent. The Cu  $L_{2,3}$ -edge XAS spectra show dramatic change with the increase of the Cr concentration, which implies small amounts of the Cu ions change the valency from

monovalency to divalency. The dependence of the divalent Cu concentration and the mean field magnetic exchange energy on the Cr concentration implies the itinerant Cu  $d$ -holes play a role in the peculiar magnetic/electrical properties of  $\text{CuCr}_2\text{Se}_4$ .

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This work was supported by the KOSEF through the CSCMR at Seoul National University. The work at Rutgers was supported by NSF-DMR-0405682. The PAL is supported by the MOST and POSCO in Korea.

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