

## Relationship between degree of order and magnetic moments in candidate of spin-gapless semiconductor CoFeCrAl studied by XMCD

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Half-metals exhibit fully spin-polarized band structures and therefore are suitable for spintronic applications. The half-metallicity is seen in different classes of materials, such as magnetic oxides, diluted magnetic semiconductors, and Heusler alloys. Cobalt-based Heusler alloys are very interesting due to their theoretically predicted half-metallic electronic structures and experimentally observed high spin polarization with high Curie temperatures [1]. Spin-gapless semiconductors (SGS) are recognized as a candidate of ideal room-temperature ferromagnetic semiconductors. Bainsla *et al.* have investigated the growth and characterization of SGS in the quaternary Heusler alloy CoFeMnSi [2]. Other SGS candidates are also required. Here, we focus on the quaternary CoFeCrAl (CFCA) films.

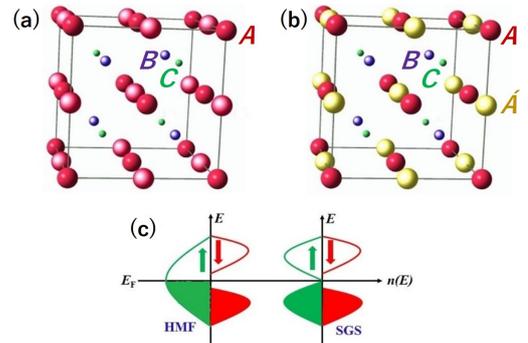
Original and stoichiometric full-Heusler alloys have  $A_2BC$  in their chemical formulas, where  $A$  and  $B$  are transition-metal elements and  $C$  is a main group element and those alloys have a cubic  $L2_1$  crystal structure [Fig. 1(a)]. A quaternary Heusler alloy with a different structural symmetry is obtained when  $A$  in  $A_2BC$  partially is replaced by another element  $\tilde{A}$ , i.e.,  $A\tilde{A}BC$ , as shown in Fig. 1(b). The crystal structure is defined as a LiMgPdSn prototype or  $Y$  structure. Depending on the occupation of various lattice sites, different types of  $Y$  structure are possible for CFCA. One is defined as  $A\tilde{A}$  consists of Fe, Co ( $BC$  is Cr, Al). The other is defined as  $A\tilde{A}$  consists of Co, Cr ( $BC$  is Fe, Al) by swapping between  $A\tilde{A}$  and  $BC$  layers. The SGS is defined as a presence of a pseudo energy band gap in the majority spin channel at the Fermi level. The density of states for half-metals and SGS are given in Fig. 1(c) for comparison. Due to their unique band structures, SGS have been predicted to possess interesting properties, such as (i) spin-polarized current resulting from the electrons as well as holes; (ii) high spin polarization; and (iii) tunable spin polarization by voltage varying the Fermi level [3].

In this report, we focus on the structural and magnetic properties for CFCA films. We deduce the element-specific magnetic moments of Fe and Co using x-ray magnetic circular dichroism (XMCD) and dis-

cuss the ordering types of CFCA by comparing with the first-principles band structure calculations.

The samples of 30-nm-thick CFCA were grown on MgO (001) substrates with Cr buffer. Sample surfaces were capped by MgO layer. The MgO(001) substrate was flushed thermally at 700°C in the UHV chamber prior to the deposition process. All of the layers were deposited at room temperature. The Cr layer was *in situ* annealed at 700°C before the CFCA deposition. One of the samples was *in situ* annealed at temperature of 700°C after the CFCA deposition [4].

XMCD was performed at BL-7A in the Photon Factory (KEK). Photon helicity was fixed, and a magnetic-field switching between  $\pm 1$  T was applied along the incident polarized soft x-ray. A total-electron-yield mode was adopted. The measurements were carried out in a grazing incidence setup to the sample surface normal in order to detect the in-plane spin and orbital magnetic moments. All the measurements were performed at room temperature.



**Fig. 1** — The schematic of the crystal structures for (a) the  $L2_1$  structure for  $A_2BC$  Heusler alloys and (b) the  $Y$  structure for  $A\tilde{A}BC$  Heusler alloys. (c) The schematic density of states near the Fermi level for the half-metals and spin-gapless semiconductors [2].

Figure 2 shows the x-ray absorption spectra (XAS) of Cr, Fe, and Co  $L_{2,3}$  edges, respectively, for the sample annealed at 700°C. XAS are normalized by the photon fluxes. Clear metallic peaks are observed, which confirms that there is no mixing of oxygen atoms into CFCA. Shoulder structures appear in the higher photon energy region of Co  $L_{3,2}$  XAS peaks,

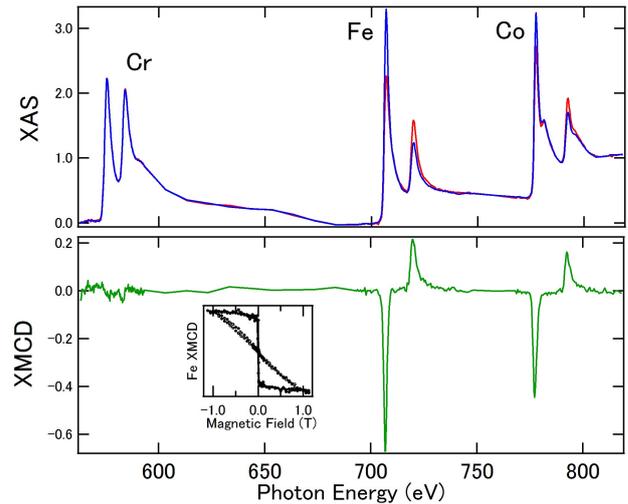
which correspond to the formation of Heusler alloys due to the Co-Co bonding states within the molecular orbital calculations [5]. Finite XMCD signals at the Cr  $L$ -edges are not detected. The spin and orbital magnetic moments are estimated by applying the magneto-optical sum rules. The magnetic moment summing both spin and orbital components of each element is estimated to be 1.14 and 0.52  $\mu_B$  for Fe and Co, respectively. Total magnetic moment is 1.66  $\mu_B$  and 1.29  $\mu_B$  in the samples of 700°C annealing and no annealing, respectively, which is similar to the value estimated from the magnetization measurements. The hysteresis loops taken at Fe  $L_3$ -edge XMCD is also consistent with that by magnetization measurements. We deduced the magnetic moments depending on the annealing temperature. The results clearly indicates the increase of magnetic moments with annealing temperature, suggesting the improvement of the crystallinity by post annealing procedure.

In the case of highly ordered  $Y$ -type CFCA, the SGS characteristics are anticipated in the first-principles calculation. The highly ordered  $Y$  structure consists of  $AA$  in Fe and Co,  $BC$  in Cr and Al. The Fe and Co atoms are coupled antiferromagnetically. By introducing the disorder within the layer between Fe-Co, the magnetic moment values remain unchanged. In the case of Cr-Al disorder within the layer, the largest moments are estimated in Cr sites and antiparallel coupling between Fe and Co is kept. Furthermore, in the case of including Fe-Cr swapped disorder between layers, the calculation results in the parallel coupling between Fe and Co and both positive and negative values of Cr magnetic moments which is canceled out each other. Quite small magnetic moments are also induced at the Al sites. We found that the disordered state can clearly explain the XMCD results and the SGS states are broken. Previous report in the calculation of CFCA also suggests the collapse of SGS by introducing Coulomb interaction  $U$  within the scheme of GGA+ $U$  methods [6].

Considering these results, we discuss how the SGS materials are designed. In order to achieve the SGS possessing the advantages of ferromagnetic semiconductors, not only high ordering but also lattice strain controlling which modulates the electron orbital hybridization is essential to obtain the ideal SGS states. Further, antiparallel coupling between Fe and Co esti-

mated from the calculations might be originated from the exchange coupling with antiferromagnetic Cr sites in Cr-Al layer. These behaviors are analogous to the interfacial exchange coupling between transition metals and antiferromagnetic or ferrimagnetic MnGa [7]. Further studies of ordered CFCA alloys are needed to develop the SGS materials.

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**Fig. 2** — The x-ray absorption spectra with different magnetic fields for the CFCA sample annealed at 700°C measured at the Cr, Fe, and Co  $L_{3,2}$  edges. The XMCD spectra for the corresponding elements are also shown. Inset shows the XMCD hysteresis curves taken at Fe  $L_3$ -edge. Solid and dot lines show in-plane (easy) and out-of-plane (hard) directions, respectively, to the film [4].

## References

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