

# Induced half-metallicity in Cr-based ferromagnetic chalcospinels with anion substitutions: $\text{CuCr}_2\text{S}(\text{Se})_{4-x}\text{E}_x$ ( $\text{E}=\text{F}, \text{Cl}, \text{Br}$ ), $\text{Cu}(\text{Cd})\text{Cr}_2\text{S}(\text{Se})_{4-x}$ , and $\text{CdCr}_2\text{S}(\text{Se})_{4-x}\text{D}_x$ ( $\text{D}=\text{N}, \text{P}, \text{As}$ )

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First-principles calculations of the electronic structures of chalcogenide spinels with anion vacancy and substitutions are presented. Our calculations predict that  $\text{Cu}(\text{Cd})\text{Cr}_2\text{S}(\text{Se})_{4-x}$ ,  $\text{CuCr}_2\text{S}(\text{Se})_{4-x}\text{E}_x$  ( $\text{E}=\text{F}, \text{Cl}, \text{Br}$ ), and  $\text{CdCr}_2\text{S}(\text{Se})_{4-x}\text{D}_x$  ( $\text{D}=\text{N}, \text{P}, \text{As}$ ) can be half-metallic over a range of concentrations. The magnetic moment is found to scale approximately linearly on adding or withdrawing electrons and varies between 5.0 and 6.0  $\mu_B/\text{f.u.}$  © 2009 American Institute of Physics. [DOI: 10.1063/1.3080210]

Magnetic materials with diverse electronic transport properties (metallic, semiconducting, insulating) and sufficiently high Curie temperature ( $T_C$ ) are needed for room temperature operation of spin-based electronic (spintronic) devices. In view of the high  $T_C$  requirement, the chromium based chalcospinels (chalcogenide-based spinel)  $\text{ACr}_2\text{X}_4$  ( $\text{A}=\text{Cu}, \text{Cd}$ , etc. and  $\text{X}=\text{S}, \text{Se}, \text{Te}$ ) are potentially attractive candidates. The compounds  $\text{CuCr}_2\text{S}_4$ ,  $\text{CuCr}_2\text{Se}_4$  and  $\text{CuCr}_2\text{Te}_4$  are metallic with Curie temperatures of 377, 430, and 360 K, respectively.<sup>1–5</sup> Furthermore, a number of the Cr-based chalcospinels have generated renewed interest in recent years because of their unique magnetotransport and magnetodielectric properties. For example, the Cu-chromium chalcogenides exhibit unusual transport properties characterized by a large, temperature-dependent magnetoresistance.<sup>6</sup> Similarly,  $\text{CdCr}_2\text{S}_4$  and  $\text{HgCr}_2\text{S}_4$  display unusual time-dependent ferroelectric and colossal magnetocapacitance properties.<sup>7</sup> A dissipationless anomalous Hall current has also recently been observed in the ferromagnetic spinel  $\text{CuCr}_2\text{Se}_{4-x}\text{Br}_x$ .<sup>8</sup> These observations have provoked strong interest in these materials for possible spintronic applications.

From the view point of electronic structure, a number of chalcospinels are predicted to be highly spin-polarized based on band structure calculations.<sup>9–11</sup> *Ab initio* band structure calculations of  $\text{CdCr}_2\text{S}_4$  and  $\text{CdCr}_2\text{Se}_4$  show that while  $\text{CdCr}_2\text{S}_4$  is a ferromagnetic insulator,  $\text{CdCr}_2\text{Se}_4$  has a ferromagnetic semimetallic ground state with very low density of states (DOS) at the Fermi energy.<sup>10</sup> Additionally, strong exchange splitting exists in both compounds, suggesting that with suitable substitution the Cr-based chalcospinels can likely be induced to be half-metallic—materials that can simultaneously be an excellent metal for one spin channel and an excellent insulator for the other spin channel. Indeed, our recent results on  $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{S}_4$  and  $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$  predict that their properties can be tuned from ferromagnetic metal/semiconductor to half-metal by changing the concentration

of cadmium.<sup>12</sup> In earlier studies, the  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$  system was also predicted to be half-metallic.<sup>9</sup>

In this letter, we report the prediction of half-metallicity in  $\text{CuCr}_2\text{S}(\text{Se})_{4-x}\text{E}_x$  ( $\text{E}=\text{F}, \text{Cl}, \text{Br}$ ),  $\text{Cu}(\text{Cd})\text{Cr}_2\text{S}(\text{Se})_{4-x}$ , and  $\text{CdCr}_2\text{S}(\text{Se})_{4-x}\text{D}_x$  ( $\text{D}=\text{N}, \text{P}, \text{As}$ ) by performing systematic spin-polarized electronic structure calculations. We show that their properties can be tuned to be half-metallic both by small amounts of  $\text{D}$  and  $\text{E}$  anion substituting and also by creating S or Se anion vacancies. While  $\text{CuCr}_2\text{S}(\text{Se})_{4-x}$  has been synthesized,<sup>13</sup> its detailed properties have not yet been reported. We also are not aware of any experimental work on nitrogen, phosphorus or arsenic anion substitution in the ferromagnetic chalcospinels  $\text{CdCr}_2\text{S}(\text{Se})_4$ .

Density functional theory implemented in the Vienna *ab initio* simulation package was used in our calculations. For the exchange-correlation potential, we used the generalized gradient approximation. The pseudopotentials we used are based on projector augmented wave.<sup>12</sup> A 14 atom cell was used for the calculations in which the anion sites (S or Se) were substituted by F, Cl, Br, N, P and As. We present results for substituting 1/8 and 1/4 of the anion sites for the entire series of A-site Cu and Cd-based chalcospinels. The results presented here do not depend on arbitrary changes in the choice of the anion site(s) for making the substitution(s).

As a first step, we completely relaxed the structures both in shape and volume to determine the lowest energy configuration. Calculation results for both end compounds [ $\text{CuCr}_2\text{S}(\text{Se})_4$  and  $\text{CdCr}_2\text{S}(\text{Se})_4$ ], including the relaxed deviations of S/Se away from the ideal  $u$  value of 3/8, are in very good agreement with the experimentally determined values (Table I). To investigate the band structure of  $\text{CuCr}_2\text{S}(\text{Se})_{4-x}\text{E}_x$  ( $\text{E}=\text{F}, \text{Cl}, \text{Br}$ ),  $\text{Cu}(\text{Cd})\text{Cr}_2\text{S}(\text{Se})_{4-x}$ , and  $\text{CdCr}_2\text{S}(\text{Se})_{4-x}\text{D}_x$  ( $\text{D}=\text{N}, \text{P}, \text{As}$ ), we have assumed a normal spinel structure over the entire composition range and used 14-atom supercells as mentioned earlier.

Here we predict that the electronic properties at the Fermi level are strongly dependent on the amount of anionic substitution. We find that the sulfide compounds, except for the  $\text{CdCr}_2\text{S}_{3.5}\text{As}_{0.5}$  and  $\text{CdCr}_2\text{S}_{3.5}$ , are half-metallic (shown underlined in Table I) for  $x=0.5$  composition. As an ex-

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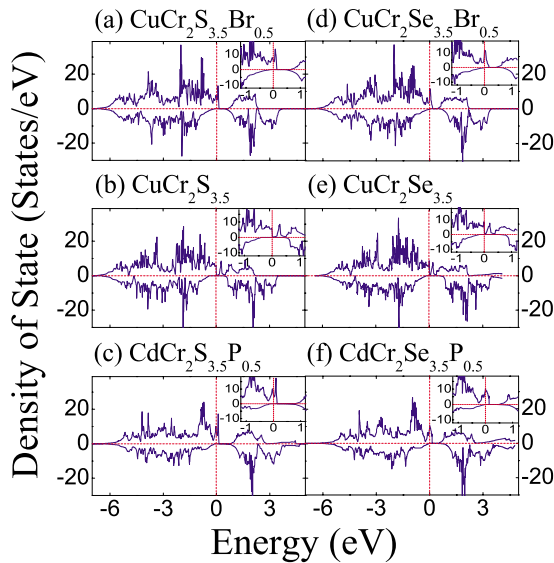


FIG. 1. (Color online) Calculated total density of electronic states of the  $\text{CuCr}_2\text{S}(\text{Se})_{3.5}\text{Br}_{0.5}$ ,  $\text{CuCr}_2\text{S}(\text{Se})_{3.5}$ , and  $\text{CdCr}_2\text{S}(\text{Se})_{3.5}\text{P}_{0.5}$  systems for both the majority and minority spin bands.

ample, DOS are shown in Figs. 1(a)–1(c) for  $\text{CuCr}_2\text{S}_{3.5}\text{Br}_{0.5}$ ,  $\text{CuCr}_2\text{S}_{3.5}$ , and  $\text{CdCr}_2\text{S}_{3.5}\text{P}_{0.5}$ , respectively. There is a clear gap appearing around  $E_F$  for all cases. In addition, for the composition with  $x=1$ , namely  $\text{CuCr}_2\text{S}_3\text{F}$ ,  $\text{CdCr}_2\text{S}_3\text{N}$ , and  $\text{CdCr}_2\text{S}_3$  also show a half-metal state. At the same time,  $\text{CuCr}_2\text{S}_3\text{Cl}$  and  $\text{CuCr}_2\text{S}_3\text{Br}$  are semiconductors (shown dotted underlined in Table I), while  $\text{CdCr}_2\text{S}_3\text{P}$  and  $\text{CdCr}_2\text{S}_3\text{As}$  are metals.

We find the behavior of the selenides significantly different from the sulfides in being more difficult to tune into half-metal. For the composition with  $x=0.5$ ,  $\text{CuCr}_2\text{Se}_{3.5}$  [Fig. 1(e)],  $\text{CdCr}_2\text{Se}_{3.5}\text{N}_{0.5}$ , and  $\text{CdCr}_2\text{Se}_{3.5}\text{P}_{0.5}$  [Fig. 1(f)] show half-metallic behavior while the others are metals ( $\text{CdCr}_2\text{Se}_{3.5}$  is a semiconductor). In Fig. 1(d), we show the

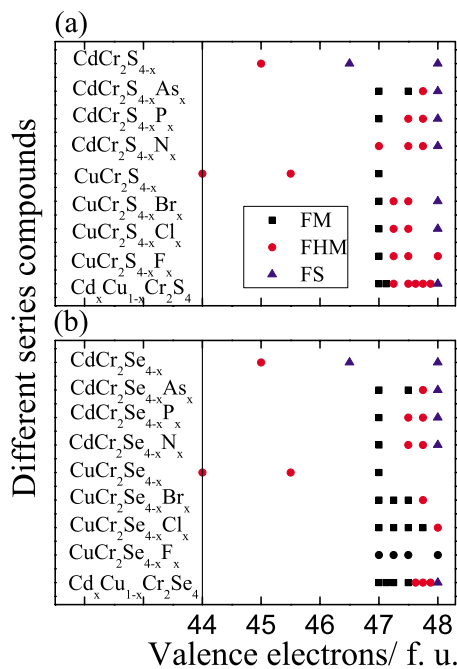


FIG. 2. (Color online) The calculated range of ferromagnetic metal (FM), ferromagnetic half-metal (FHM) and ferromagnetic semiconductor (FS) as a function of total valence electrons per formula unit for the different anion substituted systems.

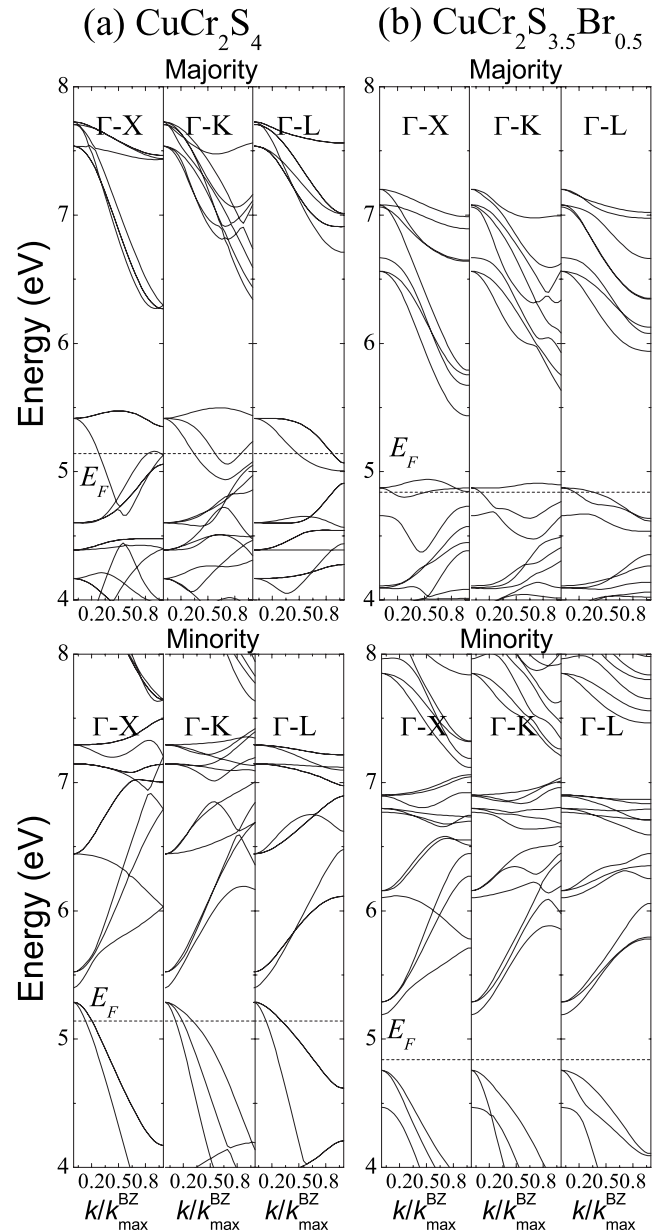


FIG. 3. Majority and minority energy bands near the Fermi energy (dashed line) along  $\Gamma$ -X,  $\Gamma$ -K, and  $\Gamma$ -L directions for (a)  $\text{CuCr}_2\text{S}_4$  and (b)  $\text{CuCr}_2\text{S}_{3.5}\text{Br}_{0.5}$ .

DOS for  $\text{CuCr}_2\text{Se}_{3.5}\text{Br}_{0.5}$ . It has a nonvanishing DOS in the minority band at the Fermi level so it is predicted to be a metal instead of a half-metal. For the composition with  $x=1$ , only  $\text{CuCr}_2\text{Se}_3\text{Cl}$ ,  $\text{CuCr}_2\text{Se}_3\text{Br}$ , and  $\text{CdCr}_2\text{Se}_3$  are predicted to be half-metals. In addition, we explored the composition with  $x=0.25$  (one anion substituted) and  $0.75$  (three anions substituted). For these calculations a 28 atom supercell was used. In the case of  $x=0.25$ , fourteen compounds were investigated. Out of these, eleven compositions still showed half-metallic character while  $\text{CuCr}_2\text{Se}_{3.75}\text{E}_{0.25}$ , ( $\text{E}=\text{F}, \text{Cl}, \text{Br}$ ) did not. Compared to the case of  $x=0.25$ , the case with composition  $x=0.75$  show a more complicated behavior. For example,  $\text{CdCr}_2\text{S}_{3.25}\text{P}_{0.75}$  has lower energy and displays metallic behavior when three phosphorus atoms are placed in the same layer. However, configurations with different placement of phosphorus atoms are about  $0.25$  eV higher in energy and predicted to be half-metallic. On the contrary,  $\text{CuCr}_2\text{S}_{3.25}\text{Cl}_{0.75}$  results in the lowest energy when

TABLE I. Calculated structural and magnetic properties of relaxed  $\text{CuCr}_2\text{S}(\text{Se})_{4-x}E_x$  ( $E=\text{F}, \text{Cl}, \text{Br}$ ),  $\text{Cu}(\text{Cd})\text{Cr}_2\text{S}(\text{Se})_{4-x}$ , and  $\text{CdCr}_2\text{S}(\text{Se})_{4-x}D_x$  ( $D=\text{N}, \text{P}, \text{As}$ ) supercells, along with comparison with the experimental data: lattice parameters,  $u$  parameters, and low temperature magnetic moment.

Supercell	Lattice parameter (angstrom)		$u$ parameter		Magnetic moment ( $\mu_B/\text{f.u.}$ )		Total spin electrons	
	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	$N\uparrow$	$N\downarrow$
$\text{CuCr}_2\text{S}_4$	9.814	9.812	0.383	0.383	4.85	5.01	26.00(5)	20.99(5)
$\text{CuCr}_2\text{S}_{3.5}\text{F}_{0.5}$	...	9.862	...	0.387	...	5.50	26.5	21.0
$\text{CuCr}_2\text{S}_3\text{F}$	...	9.917	...	0.382	...	6.00	27.0	21.0
$\text{CuCr}_2\text{S}_{3.5}\text{Cl}_{0.5}$	...	9.923	...	0.387	...	5.50	26.5	21.0
$\text{CuCr}_2\text{S}_3\text{Cl}$	...	10.026	...	0.387	...	6.00	27.0	21.0
$\text{CuCr}_2\text{S}_{3.5}\text{Br}_{0.5}$	...	9.969	...	0.390	...	5.50	26.5	21.0
$\text{CuCr}_2\text{S}_3\text{Br}$	...	10.107	...	0.392	...	6.00	27.0	21.0
$\text{CuCr}_2\text{S}_{3.5}$	...	9.955	...	0.384	...	6.00	25.0	19.0
$\text{CuCr}_2\text{Se}_4$	10.337	10.374	0.382	0.383	5.20	5.10	26.05	20.95
$\text{CuCr}_2\text{Se}_{3.5}\text{F}_{0.5}$	...	10.394	...	0.384	...	5.53	26.51(5)	20.98(5)
$\text{CuCr}_2\text{Se}_3\text{F}$	...	10.476	...	0.380	...	6.01(5)	27.01	20.99(5)
$\text{CuCr}_2\text{Se}_{3.5}\text{Cl}_{0.5}$	...	10.415	...	0.384	...	5.50(3)	26.50(3)	21.0
$\text{CuCr}_2\text{Se}_3\text{Cl}$	...	10.538	...	0.383	...	6.00	27.0	21.0
$\text{CuCr}_2\text{Se}_{3.5}\text{Br}_{0.5}$	...	10.482	...	0.387	...	5.50(7)	26.50(7)	21.0
$\text{CuCr}_2\text{Se}_3\text{Br}$	...	10.579	...	0.387	5.99	6.00	27.0	21.0
$\text{CuCr}_2\text{Se}_{3.5}$	...	10.520	...	0.385	...	6.00	25.0	19.0
$\text{CdCr}_2\text{S}_4$	10.207	10.295	0.390	0.390	6.0	6.00	27.0	21.0
$\text{CdCr}_2\text{S}_{3.5}\text{N}_{0.5}$	...	10.064	...	0.380	...	5.50	26.5	21.0
$\text{CdCr}_2\text{S}_3\text{N}$	...	9.751	...	0.376	...	5.00	26.0	21.0
$\text{CdCr}_2\text{S}_{3.5}\text{P}_{0.5}$	...	10.303	...	0.391	...	5.50	26.5	21.0
$\text{CdCr}_2\text{S}_3\text{P}$	...	10.276	...	0.392	...	5.00	26.0	21.0
$\text{CdCr}_2\text{S}_{3.5}\text{As}_{0.5}$	...	10.346	...	0.392	...	5.50(5)	26.50(5)	21.0
$\text{CdCr}_2\text{S}_3\text{As}$	...	10.385	...	0.395	...	5.02	26.01	20.99
$\text{CdCr}_2\text{S}_3$	...	9.721	...	0.384	...	6.00	24.0	18.0
$\text{CdCr}_2\text{Se}_4$	10.721	10.839	0.390	0.390	5.98	6.00	27.0	21.0
$\text{CdCr}_2\text{Se}_{3.5}\text{N}_{0.5}$	...	10.519	...	0.380	...	5.50	26.5	21.0
$\text{CdCr}_2\text{Se}_3\text{N}$	...	10.098	...	0.381	...	5.02	26.01	20.99
$\text{CdCr}_2\text{Se}_{3.5}\text{P}_{0.5}$	...	10.768	...	0.387	...	5.50	26.5	21.0
$\text{CdCr}_2\text{Se}_3\text{P}$	...	10.670	...	0.387	...	5.06	26.03	20.97
$\text{CdCr}_2\text{Se}_{3.5}\text{As}_{0.5}$	...	10.827	...	0.390	...	5.50(5)	26.50(5)	21.0
$\text{CdCr}_2\text{S}_3\text{As}$	...	10.794	...	0.391	...	5.10	26.05	20.95
$\text{CdCr}_2\text{Se}_3$	...	10.173	...	0.381	...	6.00	24.0	18.0

the three Cl are placed in different layers. In Fig. 2, we summarize results of ferromagnetic metal, ferromagnetic half-metal, and ferromagnetic semiconductor as a function of number of valence electrons per formula unit for all the different anion substitutions. It is clear that the sulfur-based systems can be induced to half-metallic state over a wider range of substitutions as compared to the selenium-based systems.

In addition to total energy and DOS calculations, we have calculated the energy band in the symmetry directions  $\Gamma$ -X,  $\Gamma$ -K, and  $\Gamma$ -L. Figures 3(a) and 3(b) represent the majority and minority energy bands of  $\text{CuCr}_2\text{S}_4$  and  $\text{CuCr}_2\text{S}_{3.5}\text{Br}_{0.5}$ , respectively. Interestingly, the majority energy band at the Fermi level changes from bending down as one leaves the  $\Gamma$  point, to being approximately flat or to have higher energy away from  $\Gamma$  point. Similar behavior is seen in the selenium systems.

We have also calculated the magnetic moment per formula unit for all compounds and have listed the values in Table I. In the case of  $A=\text{Cu}$  the moment is found to increase and scale approximately linearly with increasing  $x$  concentration. While for  $A=\text{Cd}$ , the moment decreases and scales approximately linearly with increasing  $x$  concentration [except  $\text{CdCr}_2\text{S}(\text{Se})_{4-x}$ ].

In conclusion, we have studied the electronic band structure of anion substituted Cr-based chalcospinel with  $A=\text{Cu}$  and  $\text{Cd}$  and predict a wide range of possible half-metal compositions which can be tuned both from ferromagnetic metals and ferromagnetic semiconductors. Our calculations indicate

that for both  $A=\text{Cu}$  and  $\text{Cd}$ -based chalcospinels the magnetic moment scales approximately linearly with anion substitution concentration.

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