

Half-metallic electronic structures of quaternary ferromagnetic chalcospinels: $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{S}_4$ and $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$

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First-principles calculations indicate that the chalcogenide spinels $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{S}_4$ and $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ can be ferromagnetic metals, half-metals, or semiconductors depending on the Cd concentration x . In particular, $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{S}_4$ can be tuned to be effectively half-metallic for x values between 0.25 and 0.875 and $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ can be half-metallic for x between 0.625 and 0.875. For $x < 0.25$ for $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{S}_4$ and for $x < 0.625$ for $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$, these materials are predicted to be ferromagnetic metals. For $x > 0.875$ both systems are predicted to be ferromagnetic semiconductors. © 2008 American Institute of Physics. [DOI: 10.1063/1.2841848]

The chromium-based spinel chalcogenides, ACr_2X_4 ($\text{A} = \text{Cu}, \text{Cd}, \text{Hg}, \text{Fe}, \text{Co}$; $\text{X} = \text{S}, \text{Se}, \text{Te}$) were first studied more than forty years ago.^{1–4} Among these compounds, CdCr_2S_4 and CdCr_2Se_4 are known to be ferromagnetic semiconductors with Curie temperatures of 85 and 129 K, respectively. On the other hand, CuCr_2S_4 , CuCr_2Se_4 , and CuCr_2Te_4 are metallic and have Curie temperatures (T_C) well above room temperature, with T_C 's of 377, 430, and 360 K, respectively. There have been several investigations of the properties of these chalcospinels and their alloys motivated in large part by their unique magnetic and optical properties. The doped Cu-chromium chalcogenides have been revisited in recent years because of their unusual transport properties characterized by a large, temperature dependent magnetoresistance.⁵ More recently, relaxor ferroelectricity and colossal magneto-capacitance have been observed in the ferromagnetic semiconductors CdCr_2S_4 and HgCr_2S_4 .⁶

The chromium-based compounds are *normal* spinels that have a face-centered cubic lattice and belong to the centrosymmetric space group $Fd\bar{3}m$. A basic structural component of the chalcospinels is an anion bonded to one A cation and three Cr ions. The nominally divalent metal ions A occupy the tetrahedral sites (1/8 filled by A), while the trivalent Cr ions occupy the octahedral sites (1/2 filled by Cr). The positions of the cations are fixed by the symmetry of the structure, but the anion positions are variable and are specified by the parameter u . A local structural deformation induced by the cation-anion interaction is observed in these materials and is characterized by a small deviation of the anion u -parameter from the ideal value of 0.375. These distortions along with cation valence play an important role in determining the properties of these materials.

Although the properties of the chalcospinels have been the subject of recent experimental studies, their electronic structure has received less attention, at least in part due to their rather complicated crystal structure. The electronic structure of CuCr_2X_4 ($\text{X} = \text{S}, \text{Se}, \text{and Te}$) chalcogenides was discussed in the past,^{2,3} but until recently no detailed band

structure calculations were reported. Band structure calculations suggest that a number of chalcospinels are highly spin-polarized.^{7–10} Indeed, complete spin polarization—the so called half-metallic (HM) materials—where there is a gap in one spin band at the Fermi level and no gap in the other spin band have been predicted in the $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ system.⁷ Shanthi *et al.* have reported the *ab initio* band structure of CdCr_2S_4 and CdCr_2Se_4 , calculated for both the nonmagnetic and the ferromagnetic states.⁸ Their calculations predict CdCr_2S_4 to be a ferromagnetic insulator and CdCr_2Se_4 to have a ferromagnetic semimetallic ground state with very low density of states at the Fermi energy and a nearly gapped structure. Strong exchange splitting in both the compounds suggests the tantalizing possibility of realizing a half-metallic ferromagnetic state in the Cr-chalcospinels. In this letter, we report such a state by performing systematic spin-polarized electronic calculations of quaternary $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{S}_4/\text{Se}_4$ chalcospinels. We show that their properties can be tuned from ferromagnetic metal/semiconductor to half-metal by changing the cadmium concentration in these two systems. The $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{Te}_4$ system is explored as well, but it appears to differ in its behavior from the Se and S systems.

We used the Vienna *ab initio* simulation package,¹¹ which is based on density functional theory with generalized gradient approximation,¹² for the exchange correlation potential and projector augmented wave based pseudopotentials.¹³ The largest chalcospinel unit cell used in our calculations contains 56 atoms, which include 32 S/Se anions, 8 A-site Cd/Cu cations, and 16 B-site Cr cations. The Cd/Cu ions occupy the tetrahedral sites, while the octahedral sites are occupied exclusively by Cr. Because of the clear octahedral preference for the Cr^{+3} ions, a normal spinel structure is assumed to be adopted for all these compounds. We have used a 56-atom supercell for the calculations involving A-site Cd substitution in 1/8th increments of x . No significant change in the results is observed when arbitrary changes are made in the choices of the A sites for making the Cd substitutions. For x increments of 1/4th, we have used a 28-atom supercell to simplify the calculations. As a test, we calculated the end members ($x=0$ and 1) with 14, 28, and 56 atoms and verified that the calculated densities of states

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TABLE I. Calculated structural and magnetic properties of relaxed $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ and $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{S}_4$ supercells, along with comparison with the experimental data: lattice parameters, u parameters, and low temperature magnetic moment.

Supercell	Lattice parameter (\AA)		u parameter		Magnetic moment ($\mu_B/\text{f.u.}$)		Number of electrons	
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	N^\uparrow	N^\downarrow
CuCr_2Se_4	10.337	10.374	0.382	0.383	5.20	5.10	26.05	20.95
$\text{Cd}_{0.25}\text{Cu}_{0.75}\text{Cr}_2\text{Se}_4$...	10.497	...	0.384	...	5.32	26.285	20.965
$\text{Cd}_{0.5}\text{Cu}_{0.5}\text{Cr}_2\text{Se}_4$...	10.557	...	0.390	...	5.50	26.5	21.00
$\text{Cd}_{0.625}\text{Cu}_{0.375}\text{Cr}_2\text{Se}_4$...	10.662	...	0.390	...	5.63	26.63	21.00
$\text{Cd}_{0.75}\text{Cu}_{0.25}\text{Cr}_2\text{Se}_4$...	10.722	...	0.389	...	5.75	26.75	21.00
$\text{Cd}_{0.875}\text{Cu}_{0.125}\text{Cr}_2\text{Se}_4$...	10.786	...	0.391	...	5.87(5)	26.875	21.00
CdCr_2Se_4	10.721	10.839	0.390	0.390	5.98	6.00	27.00	21.00
CuCr_2S_4	9.814	9.812	0.383	0.383	4.85	5.00	26.005	20.995
$\text{Cd}_{0.125}\text{Cu}_{0.875}\text{Cr}_2\text{S}_4$...	9.873	...	0.383	...	5.13	26.1275	20.9975
$\text{Cd}_{0.25}\text{Cu}_{0.75}\text{Cr}_2\text{S}_4$...	9.946	...	0.386	...	5.25	26.25	21.00
$\text{Cd}_{0.5}\text{Cu}_{0.5}\text{Cr}_2\text{S}_4$...	10.050	...	0.392	...	5.50	26.5	21.00
$\text{Cd}_{0.75}\text{Cu}_{0.25}\text{Cr}_2\text{S}_4$...	10.212	...	0.389	...	5.75	26.75	21.00
$\text{Cd}_{0.875}\text{Cu}_{0.125}\text{Cr}_2\text{S}_4$...	10.223	...	0.391	...	5.87(5)	26.875	21.00
CdCr_2S_4	10.207	10.295	0.390	0.391	6.00	6.00	27.0	21.00

(DOS) per formula unit is essentially independent of the cell size.

As a first step, we fully relaxed the structures in shape and volume to determine the lowest energy configuration. The calculated relaxed positions of the S/Se away from the ideal u value of 0.375 are in very good agreement with the experimentally determined values of u (Table I). Figures 1(a) and 1(b) display the calculated total DOS of the majority and minority spin bands for CuCr_2S_4 and CdCr_2S_4 , respectively. The partial DOS of the Cu/Cd d , Cr d , and S p for the two systems are shown in Figs. 1(d) and 1(e). Similarly, the calculated DOS for CuCr_2Se_4 and CdCr_2Se_4 are shown in Figs. 2(a) and 2(b), respectively, and the partial DOS of Cu/Cd d , Cr d , and Se p shown in Figs. 2(d) and 2(e). It is apparent for all cases that the total DOS for energies around the Fermi level originate almost completely from the Cu and Cr d

bands and S/Se p bands for both spin bands. These calculations are in qualitative agreement with previously reported results.⁷⁻¹⁰

Our calculations for CdCr_2Se_4 differ in an important detail, however, from those reported in Refs. 8 and 9. The material has been experimentally determined to be a direct band gap semiconductor with a gap of 1.3 eV.¹⁴ Our calculations yield a direct band gap semiconductor with a somewhat smaller gap (0.4 eV). The calculations of Refs. 8 and 9 yield a semimetallic ground state. The disagreement with the experiment was ascribed in both cases to inadequacies of density functional theory (DFT). Although the tendency of DFT to underestimate band gaps is well documented, we suggest that the band gap error may be less than originally believed. Possible reasons for the disagreement between our calculations and those cited are the use of the atomic sphere

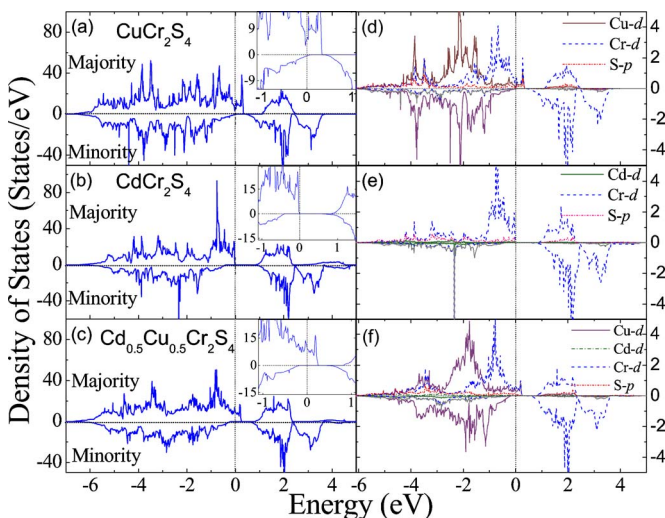


FIG. 1. (Color online) Calculated total (a–c) and individual Cu d , Cr d , and S p densities of electronic states (DOS) (per atom) of the $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{S}_4$ system for both the majority and minority spin bands; (a) and (d) are for CuCr_2S_4 ; (b) and (e) are for CdCr_2S_4 ; and, (c) and (f) are for $\text{Cd}_{0.5}\text{Cu}_{0.5}\text{Cr}_2\text{S}_4$. Results shown are for 28 atoms unit cell.

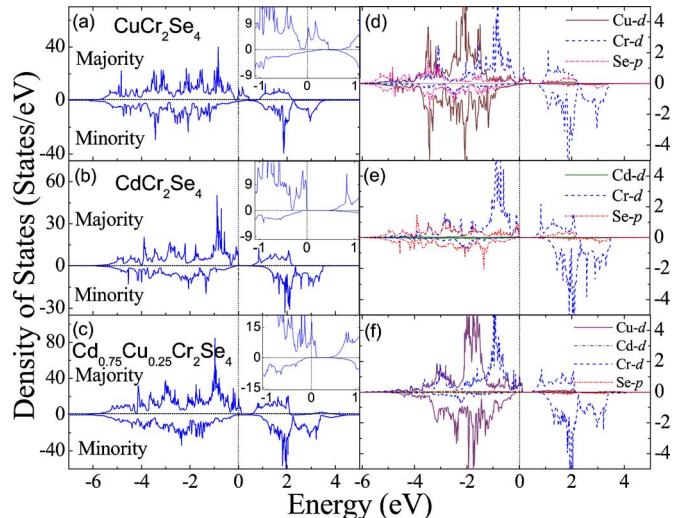


FIG. 2. (Color online) Calculated total (a–c) and individual Cu d , Cr d , and Se p densities of electronic states (DOS) (per atom) of $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ system for both the majority and minority spin bands; (a) and (d) are for CuCr_2Se_4 ; (b) and (e) are for CdCr_2Se_4 ; and, (c) and (f) are for $\text{Cd}_{0.75}\text{Cu}_{0.25}\text{Cr}_2\text{Se}_4$. Results shown are for 28 atoms unit cell.

approximation in Ref. 8 and the use of ultrasoft pseudopotentials in Ref. 9. The atomic sphere approximation is severe for spinel structure materials. Ultrasoft pseudopotentials may not be as reliable for transition metal ions as the Projector Augmented Wave pseudopotentials used in the calculations reported here.

In addition to predicting the correct ground state structural properties for CdCr_2S_4 and CdCr_2Se_4 , the calculated magnetic moments match very well with the experimental values reported for these systems (Table I). For example, the calculated magnetic moment of both CdCr_2S_4 and CdCr_2Se_4 is $6.0 \mu_B/\text{formula unit}$, which would be expected for the t_{2g}^3 ($S=3/2$) electron configuration of Cr^{3+} in octahedral coordination. This is in excellent agreement with the experimentally reported values of 6.0 and $5.98 \mu_B/\text{formula unit}$, respectively, for single crystal samples.^{6,15} It should be noted that the experimentally reported saturation moment values for polycrystalline samples are generally lower, particularly for those exhibiting stoichiometry deviations.¹⁶

For the Cu chalcogenides, the DOS at the Fermi level (E_F) is consistent with metallic behavior and suggests a high degree of spin polarization, as shown in Figs. 1(a) and 2(a). However, they cannot be considered to be true half-metals because of the small but finite density of minority states at E_F . The results for CuCr_2Se_4 are also in good agreement with those reported by Ramesha and Seshadri.¹⁰ Our calculated moments for CuCr_2S_4 and CuCr_2Se_4 are 5.0 and $5.1 \mu_B/\text{formula unit}$, respectively, are again close to the experimentally reported values of 4.85 and $5.2 \mu_B/\text{formula unit}$, respectively. While the value quoted for CuCr_2S_4 is for a polycrystalline sample,¹⁷ that for CuCr_2Se_4 is for a single crystal.¹⁸ Unlike the Cd chalcogenides, for which the magnetization arises almost exclusively from the B site Cr, the magnetic moment of the A site Cu 3d state in the Cu chalcogenides is finite and is aligned antiparallel to that of Cr. This results in a reduction of the total moment for the latter.

We have also calculated the electronic structure of the quaternary systems $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ and $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{S}_4$, assuming a spinel structure over the entire composition range. These calculations employed supercells consisting of 28 and 56 atoms, as mentioned previously. While the unmixed cases (end members) are metallic ($x=0$) and semiconducting ($x=1$), respectively, consistent with experimental results, we find that half-metallicity can be induced in both systems for a range of Cd-Cu compositions. Specifically, for the $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{S}_4$ system, while $x=0.125$ is predicted to be metallic, the compositions with $x=0.25, 0.375, 0.5$ [Fig. 1(c)], 0.625, 0.75, and 0.875 are predicted to be half-metallic, with the minority gap at the Fermi energy increasing with increasing cadmium concentration. For $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ we observe that $x=0.125, 0.25, 0.375$, and 0.5 show metallic behavior, while $x=0.625, 0.75$ [Fig. 2(c)], and 0.875 are half-metallic. Similar to the case of $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{S}_4$ system, the energy gap increases with increasing cadmium concentration. This picture is corroborated by a systematic analysis of the band structures of both $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ and $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{S}_4$ we performed, which clearly shows an increase of the minority gap combined with the shift of the Fermi level as a function of x .

Among the two quaternary systems that we have investigated so far, the $\text{Cd}_{0.25}\text{Cu}_{0.75}\text{Cr}_2\text{S}_4$ tends to favor formation of a half-metallic state at lower cadmium concentrations. Since the experimentally determined ferromagnetic Curie

temperatures of the sulfospinel end members CdCr_2S_4 and CuCr_2S_4 are 85 and 377 K, respectively, it may be possible for the quaternary system with low Cd concentrations to be half-metallic at room temperature.

We have also calculated the magnetic moment per formula unit as a function of composition for both of the quaternary systems $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{S}_4$ and $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$. The calculated values are listed in Table I. The moment is found to increase and scale linearly with increasing Cd concentration. For completeness, we have performed similar calculations on the analogous Te compounds. Unlike the Se and S cases, no half-metallic behavior was observed for $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{Te}_4$. The end members CdCr_2Te_4 and CuCr_2Te_4 both show metallic behavior.

In conclusion, we have studied the electronic band structure of ferromagnetic semiconducting and metallic spinels, $\text{CdCr}_2\text{Se}_4/\text{S}_4$ and $\text{CuCr}_2\text{Se}_4/\text{S}_4$. For the two quaternary systems, $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ and $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{S}_4$, the magnetotransport properties can be tuned by varying the Cu/Cd composition, with half-metallic behavior being predicted for a range of Cd concentration. Our calculations indicate that for both the S and Se-based quaternary chalcospinels, the spin magnetic moment scales approximately linearly with x until the system becomes half-metallic, at which point it scales perfectly linearly with x .

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