Experimental and computational investigation of structure and magnetism in pyrite Co_{1-x}Fe_{x}S_{2}: Chemical bonding and half-metallicity

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Bulk samples of the pyrite chalcogenide solid solutions Co_{1-x}Fe_{x}S_{2} (0 \leq x \leq 0.5), have been prepared and their crystal structures and magnetic properties studied by x-ray diffraction and SQUID magnetization measurements. Across the solution series, the distance between sulfur atoms in the persulfide (S^{2−}) unit remains nearly constant. First principles electronic structure calculations using experimental crystal structures as inputs point to the importance of this constant S−S distance, in helping antibonding S−S levels pin the Fermi energy. In contrast hypothetical rock-salt CoS is not a good half metal, despite being nearly isostructural and isoelectronic. We use our understanding of the Co_{1-x}Fe_{x}S_{2} system to make some prescriptions for new half-metallic ferromagnets.

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I. INTRODUCTION

The rapid development of spin valve-based magnetic read heads and the emergence of spintronics1 has thrown up a need for new half-metallic ferromagnets for spin injection, as well as the need for a better understanding of the underlying materials issues in half-metallic ferromagnets.2,3 The recognition that pyrite CoS_{2} is close to being a half-metallic ferromagnet,4,5 and that half-metallicity is robust across the solid solution Co_{1−x}Fe_{x}S_{2} (Ref. 6) has led to considerable renewed efforts to understand this material.7 However, there is as yet no report on why the solid solution Co_{1−x}Fe_{x}S_{2} is special: What are the unusual features in the crystal and electronic structure of the pyrites that result in its properties?

Benoit and Néel first showed that cobalt pyrite CoS_{2} is a ferromagnet.8,9 No other MX_{2} compound (X=chalcogenide), or even MXY (Y=pnictide) is ferromagnetic.8,9 Jarrett et al.4 made magnetic and transport measurements on Co_{1−x}Fe_{x}S_{2} which indicated itinerant electron ferromagnetism. FeS_{2} (x =1) is a d band semiconductor with filled octahedral S^{2−} levels of Fe^{2+} level separated from empty e_{g} levels. As electrons are added (0 \leq x \leq 1) the compounds become conducting and ferromagnetic, even for x values as large as 0.97 (or electron concentrations as small as 0.03 in the e_g band). Over a wide range of x, the magnetic moment (in Bohr magnetons) obtained from saturation magnetization is precisely equal to the number of e_g electrons. DiTusa et al.11 have recently argued that the dilute (x approaching 1) regions of the solid solution are worthy of closer examination and that near x=0.99, an insulator-metal transition is already observed. They report a quantum critical point in the ferromagnetic-paramagnetic transition between x=0.972 and x=0.964.

Spin-polarized electronic structure calculations by Zhao, Callaway, and Hayashibara3 found that CoS_{2} is ferromag-
cells Co$_{0.75}$Fe$_{0.25}$S$_2$ and Co$_{0.06}$Fe$_{0.94}$S$_2$. We use the crystal orbital Hamiltonian population (COHP) (Ref. 19) to examine details of spin-polarized chemical bonding across the solid solution series, and examine the relation between chemical bonding and half-metallicity. A comparison with rock-salt CoS (whose spin polarized crystal and electronic structure have been calculated from first-principles) confirms the special features of the electronic structure of the pyrites.

II. EXPERIMENT

Samples of Co$_{1-x}$Fe$_x$S$_2$ ($0 \leq x \leq 0.5$) were prepared starting from the elements taken according to stoichiometry, by heating well-ground powders in evacuated, sealed silica ampoules for 1 week at 673 K. The powders were then reground, pelletized, resealed in evacuated silica ampoules, and heated for 873 K for 4 d. A final heating was performed at 973 K for one week, of samples that had been ground up and pelletized again. Powder x-ray diffraction patterns were collected on powders using overnight runs on a Scintag X2 diffractometer operating in the Bragg-Brentano $\theta$-2$\theta$ geometry. Data were recorded using Cu $K\alpha$ radiation and a step size of 0.02$^\circ$ in 2$\theta$. The data were subject to Rietveld refinement$^{17}$ using the pyrite (space group $Pa\bar{3}$, No. 205) structural model with the transition metal (Co or Fe) at (0,0,0) and S at $(x_5,x_5,x_5)$ with $x_5 \approx 0.39$. The XND (Ref. 20) Rietveld program was employed for the refinements.

Magnetic measurements were performed using a Quantum Design MPMS 5XL Magnetometer. Sample holders (gelatin capsules inserted in plastic drinking straws) held small solid pellets of the Co$_{1-x}$Fe$_x$S$_2$ phases. We have not corrected the measured magnetizations for any core or sample-holder diamagnetism. Demagnetization corrections have not been performed.

III. COMPUTATIONAL METHODS

Linear muffin-tin orbital (LMTO) calculations$^{21}$ within the atomic sphere approximation (ASA) were performed using the STUTTGART TB-LMTO-ASA program$^{18}$. Experimental crystal structures used as inputs for the calculations were obtained from x-ray Rietveld refinements from this study, unless otherwise mentioned. Typically, more than 300 irreducible $k$ points within the primitive wedge of Brillouin zone were employed in the calculations. The generalized gradient approximation (GGA) for calculation of exchange correlation was employed following the Perdew-Wang prescription.$^{22}$ This results in slightly larger moments over the von Barth-Hedin$^{23}$ LSDA, although not to the extent that CoS$_2$ is a perfect half metal as determined by Shishidou et al.$^{15}$ Calculations including the effect of the spin-orbit interaction were also performed using a modified version of the LMTO code.$^{24}$ The implementation of the spin-orbit coupling into the otherwise scalar-relativistic LMTO formalism is analogous to the implementation described in Ref. 25 for the APW method. It was found that neither the states near the Fermi energy, nor the magnetic moment in any way affected by the inclusion of spin-orbit coupling. For ferromagnetic, rock-salt CoS, the cell volume (which is the sole free structural parameter) was optimized using full-potential linearized augmented plane wave (LAPW) calculations using the $\text{WIEN2K}$ code.$^{26}$ Exchange correlation was considered following the Perdew-Burke-Ernzerhof$^{27}$ parametrization.

IV. RESULTS

A. Crystal structure

Powder x-ray diffraction revealed all compounds in the series to be single phase, and well-fitted by Rietveld profile refinement to the pyrite crystal structure described in Fig. 1. Results of the x-ray refinement are summarized in Fig. 2(a), which shows data for the two extreme compositions ($x=0.0$ and $x=0.5$) in the series studied here. The cubic $a$ cell parameter varies linearly with $x$, as shown in Fig. 2(b) indicating the formation of a homogeneous solid-solution. Careful analysis does however suggest a broadening in peak profiles as $x$ increases in Co$_{1-x}$Fe$_x$S$_2$. The decrease in the $a$ lattice parameter as a function of increasing $x$ (substitution of Co by Fe) arises from the different sizes of these ions; six-coordinate, low spin Co$^{2+}$ has an ionic radius of 0.65 Å, whereas the corresponding radius for Fe$^{2+}$ is 0.61 Å.$^{28}$ The single internal parameter in the pyrite crystal structure is the position $(x_5,x_5,x_5)$ of S. We have used refined values of $x_5$ and $a$ to calculate S-S distances across the solid solution series. Within experimental error, we find nearly no change in the S-S distance as a function of $x$ as seen in Fig. 2(b). This is an important experimental observation, which we discuss at length at a later stage. In Fig. 2(b) we also show for comparison, structural data for the end-members CoS$_2$ (Ref. 29) and FeS$_2$.$^{30}$

B. Magnetism

Zero field cooled (ZFC) and field-cooled (FC) magnetization $M$ as a function of temperature recorded on Co$_{1-x}$Fe$_x$S$_2$
These are also shown in Fig. 3. Data (circles), the Rietveld fit (fit reliability $R_{\text{Bragg}} \lesssim 8\%$ for all samples) and the difference profiles are shown for each compound. Vertical lines at the top of the plot indicate expected peak positions. (b) Filled circles: Evolution of the $a$ cell parameter (in Å) with $x$ of the solid solution Co$_{1-x}$Fe$_x$S$_2$. Error bars are smaller than the circles. The dashed lines connect published crystal structure (Refs. 29 and 30) data on the end members (squares). Open circles: S-S distances as function of $x$. The dashed line connects published (Ref. 29) data (squares).

are indicated in Fig. 3(a). ZFC data were recorded in a field of 1000 Oe upon warming from 5 K after cooling from room temperature under zero field. FC data were also collected upon warming from 5 K, after the samples were cooled under a 1000 Oe field. All samples show evidence for ferromagnetism, with $T_c$ below 155 K. There is almost no ZFC/FC separation in any of the samples, suggesting the samples are homogeneous, and also that they combine high permeability with low saturation fields. Clear ferromagnetic $T_c$ onsets as well as widths of the transition are best seen from plots of $MT$ vs $T$ displayed in Fig. 3(b). The $T_c$ onset does not seem to depend very much on $x$, and after an initial increasing with $x$, almost remains constant as seen in Fig. 3(c). Data were acquired under relatively high field (1000 Oe) so even small clusters of spins are sufficient for the magnetization to rise. The midpoints of the $MT$ vs $T$ traces are therefore better indication of ferromagnetic $T_c$. These are also shown in Fig. 3(c), and are seen to initially increase with $x$ and then decrease. The constant width of the transition [difference between $T_c$ (onset) and $T_c$ (midpoint)] for the different values of $x$ reflects that all the samples are homogeneous, and the transition is not due to small ferromagnetic clusters.

Magnetization at 5 K is displayed in Fig. 4(a). None of the samples showed any significant hysteresis implying $Co_{1-x}Fe_xS_2$ is a soft ferromagnet. Therefore only the positive $M$ vs $H$ quadrant is displayed. All the samples display saturation at fields well below 1 T. The saturation magnetization in Bohr magnetons ($\mu_B$) is plotted as a function of $x$ in Fig. 4(b). The dashed line is the expected spin-only value assuming each $e_g$ electron contributes 1 $\mu_B$ per formula unit to the magnetization. Only the parent CoS$_2$ phase is seen to have a saturation magnetization less than the spin-only value. Starting from $x=0.1$ through $x=0.5$, all samples display spin-only behavior. This is an indication that all the samples except $x=0.0$ are within experimental error, perfect half-metals in terms of their being no “leak” in the magnetization from majority to minority spin states. Such leaking is prevented by the complete absence of there are no minority spin states at the Fermi energy. Our results, for both ferromagnetic $T_c$ (midpoint) as well as saturation magnetization are nearly identical with those obtained by Jarrett et al.\textsuperscript{4}

C. Electronic structure

A number of authors have provided detailed electronic structure descriptions of CoS$_2$.\textsuperscript{5,13-15} Mazin\textsuperscript{6} has examined magnetism across the series Co$_{1-x}$Fe$_x$S$_2$. The purpose of this section is to use structure refinements as inputs to obtain first principles electronic structures, and in particular, to calculate COHPs so that trends in spin-polarized bonding across the solid solution series can be obtained.
compounds. FeS\(_2\) is a semiconductor with a calculated band gap of about 0.8 eV.\(^{31}\) In both FeS\(_2\) and CoS\(_2\), \(p\) states of S below \(E_F\) extend from about −8 eV to −2.5 eV. In CoS\(_2\), Co \(d\) states (the \(t_{2g}\) manifold) start at −2.5 eV, where \(S\) \(p\) states terminate. In FeS\(_2\), there is a gap between occupied \(S\) \(p\) states and the metal \(t_{2g}\) manifold. Comparing the DOS of FeS\(_2\) with CoS\(_2\), we observe that the \(d\) manifold in the former is shifted to higher energies. This is indicative of the general trend amongst the first row transition metals that as one goes to the right (from Sc through Cu), metal \(d\) levels are stabilized. To some extent, this trend is reflected in the Pauling electronegativities which are 1.83 for Fe and 1.88 for Co. It is the same trend which shifts MX\(_2\) crystal structures from being layered (with M\(^{4+}\)) to being three-dimensional (with M\(^{2+}\)) in a process referred to as redox competition.\(^{32}\) In oxide materials, the descent of cation \(d\) levels as one traverses first row transition metals results in the famous Zaanen-Sawatzky-Allen phase diagram.\(^{33}\) In making solid solutions of CoS\(_2\) and FeS\(_2\), we believe the distinctly shifted \(d\) levels of FeS\(_2\) have a role to play. While substitution of Co by Fe in the series Co\(_{1-x}\)Fe\(_x\)S\(_2\) results in electrons being removed from the \(e_g\) manifold, the \(d\) levels themselves are pushed to higher energies; the species (Fe) which “removes” electrons actually creates donor states. This is one of the factors which affects the electronic structure across the solid solution. A more electronegative substituent might remove electrons from \(p\) states of S, and this would be disastrous for the magnetism as demonstrated presently.

We have performed LMTO calculations on ordered supercells of pyrite CoS\(_2\) after systematically replacing some of the Co by Fe. Lattice \(a\) and internal structural parameters \(x_S\) for the calculations were taken from structure refinements of the nearest compositions as summarized in Fig. 2(b). Figure 6 shows densities of state for Co\(_{1-x}\)Fe\(_x\)S\(_2\) for (a) \(x=0.00\), (b) \(x=0.25\), and (c) \(x=0.50\). In all three compounds, the shape of unfilled states just above \(E_F\) is “boxlike” rising sharply with
energy. The evolution of $t_{2g}$ states with Fe substitution (in both spin directions) seems to result from a weighted superposition of the $t_{2g}$ states of spin-polarized CoS$_2$ and nonmagnetic FeS$_2$ [shown in Figs. 5(b) and 5(c)]. Filled $t_{2g}$ levels below $E_F$ seem pinned firmly in place. Partially filled $e_g$ levels are shifted up in energy, to near (the respective) Fermi energies.\textsuperscript{34} A feature of note is that at $E_F$ (the few) states in the minority states are progressively removed as $x$ increases in Co$_{1-x}$Fe$_x$S$_2$. This result, as previously reported in the calculations of Mazin,\textsuperscript{6} explains the less-than-perfect $[(M/\mu_B)/C<1]$ saturation magnetization of pure CoS$_2$ ($x=0$), and the increased $[(M/\mu_B)/C=1]$ magnetization as $x$ increases, seen in our magnetic measurements, and in the measurements of Jarrett et al.\textsuperscript{4} From a magnetism viewpoint, the extent of half-metallicity in this system can be obtained as the ratio of the saturation magnetic moment in Bohr magnetons to the number of unpaired $e_g$ electrons. Computationally, the magnetic moment, or more precisely, the polarization index $P$ given by\textsuperscript{35}

$$P = \left| \frac{N_s(E_F) - N_d(E_F)}{N_s(E_F) + N_d(E_F)} \right|$$

provides an indication of the half-metallicity, though this cannot easily be applied directly to Andreev reflection studies.\textsuperscript{16} We calculate $P=1$ for both the $x=0.25$ and the $x=0.5$ compounds. Correspondingly, magnetic moments per formula units were, respectively, obtained to be 0.75 $\mu_B$ and 0.50 $\mu_B$; whereas for CoS$_2$ ($x=0$) it was 0.90 $\mu_B$. These have been plotted in Fig. 4(b) in comparison with experiment, and are seen to correspond precisely to what is measured.

The COHP (Ref. 19) is a very useful tool for mapping the energy dependence of pairwise bonding and antibonding interactions between atoms from first-principles electronic structure calculations, including in systems which are spin-polarized.\textsuperscript{36,37} Figure 7(a) shows pairwise Co-S and S-S COHPs of parent nonmagnetic CoS$_2$, scaled by 0.5. We have verified that the spin-orbit coupling is negligible. Interactions are therefore confined to separate spin channels. Nonmagnetic CoS$_2$ has sharply antibonding states at the $E_F$. Switching on spin-polarization decreases these antibonding states, in keeping with the suggestion of Landrum and Dronskowski\textsuperscript{36} that sharply peaked antibonding COHPs in nonmagnetic calculations can be an indicator (the equivalent of a Stoner criterion) of the electronic instability associated with spin polarization and ferromagnetism.

From Fig. 7(b), we observe bonding Co-S COHPs in the region of $t_{2g}$ states and antibonding COHPs corresponding to the region of $e_g$ states. $E_F$ in spin-polarized CoS$_2$ falls in a gap flanked by antibonding Co-S($e_g$) and antibonding Co-S($t_{2g}$). The S-S COHP in Fig. 7(c) shows the strongly bonding region where the $p$ states of S are found. The effect of spin-polarization on S-S COHPs is small but
important. Interestingly, the antibonding region of the S-S
s
d
COHP just above
E_F
is slightly stabilized by spin-
polarization, just as antibonding S-S
s
#
d
is slightly desta-
bilized. Antibonding S-S
s
#
d
state are what pin the Fermi
energy, and are perhaps the most significant states for
discussing half-metallicity in these compounds. S-S states
are pseudomolecular so they not disperse very greatly.
They can be expected to remain in place because there is
no great change in the charge state or in the degree of
charge-transfer in the system as
x
is increased, as was
observed from the constancy of the S-S distance. For an-
tibonding S-S
s
#
d
states to descend through the Fermi en-
sity, the S-S bond would have to be elongated.

In support of our argument that the S
2
2− units play a cru-
ial role in determining the electronic structure of CoS2 and
the series Co
1−
Fe
x
S
2
, we have performed first-principles cal-
culations on hypothetical rock-salt CoS, which has approxi-
mately the same atomic topology, and the same formal Co
valence as pyrite CoS2 . Figure 8(a) shows the results of the
structure optimization by plotting total energy as a function
of the cubic cell parameter, as well as the corresponding
magnetic moment of Co. The GGA-optimized cell parameter
was determined to be 4.67 Å. The corresponding magnetic
moment is about 4.67
m_B
per Co.

FIG. 8. (a) Total energy and magnetic moment per Co atom in
rock-salt CoS as a function of the cubic cell parameter, as obtained
from spin-polarized LAPW calculations. (b) Total densities of state
in the two spin directions of ferromagnetic CoS, calculated for a
rock salt (Fm3m) structure with
a=4.67 Å.

(b)

FIG. 9. (a) Summary of the nonmagnetic electronic structure of
Co
1−
Fe
x
S
2
for large
x
values (low
e_g
filling). As
x
becomes slightly
less than 1, the
e_g
levels are filled and descend below
E_F.
The
p
states remain above
E_F
however. The boxlike shape of the unfilled
d
states ensures the Stoner criterion is satisfied even for small fill-
ing. (b) Even at larger
e_g
filling (smaller
x
), only
d
states descend
below
E_F,
and
E_F
is pinned to the bottom of the unfilled
p
states. (c) Schematic nonmagnetic states in a more usual material such as
CoS, where unfilled states grow gradually, and the Stoner criterion
is satisfied only for large filling.

V. CONCLUSIONS

The low Curie temperatures of Co
1−
Fe
x
S
2
make their use
as spin injectors in spintronic circuitry unlikely.38 This sys-
tem does however offer insights into the design of new half-
metallic ferromagnets. There are two questions which our
results help to address. The first is, what renders a compound
half-metallic? From observing changes on going from ferro-
magnetic Co metal to CoS2, we learn that
s
and
p
states at
E_F
(present in Co
)
are not good for half-metallic behavior since
they are only poorly exchange split. Compound formation
through removal of
s
and
p
electrons is therefore useful. This
suggests that even in systems such as the Heusler com-
ounds, X
2
YZ, where X and Y are usually transition ele-
m ents and Z is a main group element, it might help to have
electron negative substituents at Z (for example, Si rather than Al).40

The second question is how the system retains ferromag-
netism and half-metallicity across the substitution range. We
summarize our findings on the unusual electronic structure of
the pyrites solid solutions Co$_{1-x}$Fe$_x$S$_2$ in the scheme displayed in Fig. 9. For low filling of $e_g$ states (x approaching 1), the electronic structure is characterized by “boxlike” states above $E_F$, with a very sharp rise in the number of states with energy, as depicted in Figs. 9(a) and 9(b). The origins of this sharp rise, as we have demonstrated, are S-S antibonding states, which persist just above the $E_F$ through the solid solution series. The states are sharp because they are pseudomolecular. Even small filling of empty states results in the Stoner criterion being fulfilled$^6$ and the rapid onset of ferromagnetism.$^{4,11}$ The details of the insulator-metal transition at very low filling of the $e_g$ band have not been examined by us. Within density functional theory, any finite filling of the $e_g$ levels would result in metallic behavior, and correctly describing the localization near the FeS$_2$ composition would require methods that go beyond the present treatment. The important role played by the shape of the DOS in fulfilling the Stoner criterion has been examined in detailed for transition metals by Andersen et al.$^{41}$

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33. We find, using s states of $S$ as a reference, that the calculated position of the Fermi energy shifts only very little across the solid solution series.


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