

## Robust half metallicity in $\text{Fe}_x\text{Co}_{1-x}\text{S}_2$

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(Received 7 July 2000; accepted for publication 11 September 2000)

The  $\text{Fe}_x\text{Co}_{1-x}\text{S}_2$  system is predicted, on the basis of density functional calculations, to be a half metal for a wide concentration range. Unlike most known half metals, the half metallicity in this system is expected to be very stable with respect to crystallographic disorder and other types of defects. [S0003-6951(00)04445-4]

Half metals (HMs), i.e., metals in one spin channel and insulators in the other, are attracting substantial interest recently, mostly because of potential application in spintronic devices like spin valves.<sup>1</sup> A few dozen various materials have been predicted to be HM on the basis of band structure calculations, but hardly any have been convincingly confirmed to be such by an experiment. A possible exception is  $\text{CrO}_2$  where a spin polarization of up to 95% was measured by the Andreev reflection technique<sup>2</sup> (in some other materials there is indirect evidence, such as integer magnetic moment or optical spectra consistent with half metallic bands). The usual explanation of such a discrepancy between the theory and the experiment is that half metallicity in these materials is very sensitive to crystallographic disorder and stoichiometry (see, e.g., Ref. 3). Indeed, no materials have been calculated to be HM in a wide range of concentrations of the constituents, and insensitive to disorder.

In this letter, we predict that the pyrite alloys  $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$  are HM for most of concentrations ( $0.25 \leq x \leq 0.9$ , at least), and not sensitive to ordering of Fe and Co in the metal sublattice. The reason for such robustness with respect to crystallographic disorder is that the half metallicity in this compound is not due to some fine tuning of the band structure, but to the competition between the kinetic (band) energy, and Stoner (Hund) interaction, both relatively independent on the details of the band structure.

Experimentally, the system of pyrite solid solutions,  $(\text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn})(\text{S}, \text{Se})_2$ , is amazingly rich, despite the fact that all these materials form in the same crystal structure with relatively small changes in the only internal parameter, the S–S bond length.  $\text{FeS}_2$  is a nonmagnetic semiconductor, in agreement with the band-structure calculations.<sup>4,5</sup> With as little as 0.1% Co, by some data,<sup>6</sup> it becomes a ferromagnetic metal, and remains ferromagnetic all the way through  $\text{CoS}_2$ , and further on until approximately  $\text{Co}_{0.9}\text{Ni}_{0.1}\text{S}_2$ . It was noted that the magnetic moment  $M$  per Co atom in  $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$  solid solutions stays close to  $1 \mu_B$  in an extremely wide range from  $x \approx 0.1$ – $0.2$  to  $x = 0.9$ – $0.95$ . In the original paper,<sup>6</sup> this was interpreted as extreme localization of magnetic moment on Co, with the nonmagnetic  $\text{FeS}_2$  matrix. The same interpretation was used in a number of subsequent papers, although it was noted also<sup>7</sup> that half metallicity is another possibility.

At larger  $x$ ,  $M$  decreases to  $\approx 0.85 \mu_B$ .<sup>6</sup> Starting from  $\text{CoS}_2$ , one can also substitute S with Se. The Curie temperature rapidly decreases, and magnetism disappears at Se concentration of 10%–12%, while  $M$  decreases only slightly.<sup>8</sup> At larger concentrations, the material shows metamagnetic behavior with no sizable spontaneous magnetization, but with magnetization of  $0.82$ – $0.85 \mu_B$  appearing abruptly when applied magnetic field in tesla exceeds approximately  $(220x_{\text{Se}} - 25)$  T. Very similar behavior was observed in pure  $\text{CoS}_2$  under pressure,<sup>8</sup> suggesting that the magnetic effect of Se is just reducing the density of states (DOS). Further substitution of Co by Ni leads to a Mott–Hubbard transition, which, in contrast to the system considered here, is poorly described by the local spin density approximation (LSDA). Further doping by Cu leads to a superconductivity, presumably due to high-energy sulfur vibrons.<sup>9</sup>

To understand better the behavior of the  $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$  system, we performed several series of density functional LSDA calculations: First, virtual crystal approximation (VCA) was used in conjunction with the linear muffin tin orbital (LMTO) method.<sup>10</sup> Then, we did several calculations using rhombohedral supercells of 4 or 8 formula units. Finally, we checked the results against full-potential linear-augmented plane-wave (LAPW) calculations<sup>11</sup> for pure  $\text{CoS}_2$ ,  $\text{FeCo}_3\text{S}_8$ , and  $(\text{Fe}_{0.25}\text{Co}_{0.75})\text{S}_2$  in VCA. The results were consistent with the LMTO calculations. All calculations were performed in the experimental crystal structure of  $\text{CoS}_2$ . In reality, the S–S bond in  $\text{FeS}_2$  is 4% longer. The effect on the band structure is not negligible, particularly near the bottom of the conductivity band. However, the difference is not important for the half metallicity of  $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$  alloys, and understanding the basic physics of its magnetic phase diagram. The results of the calculations are summarized in Fig. 1. In good agreement with the experiment, the magnetic moment per Co is exactly  $1 \mu_B$  for  $0.3 \leq x \leq 0.9$ . This is true for both virtual crystal and supercell calculations (Fig. 1), demonstrating stability of the HM state with respect to crystallographic disorder. We performed calculations for ordered  $\text{Fe}_7\text{CoS}_{16}$ ,  $\text{Fe}_3\text{CoS}_8$ ,  $\text{FeCoS}_4$ , and  $\text{FeCo}_3\text{S}_8$ , and found that already the former compound (i.e.,  $x = 0.125$ ) has magnetization of  $1 \mu_B$  per Co. Although the original paper<sup>6</sup> implied that this magnetic moment resides on Co, this is not true: for instance, in  $\text{Fe}_7\text{CoS}_{16}$  less than 30% of total magnetization ( $0.45 \mu_B$ ) resides on Co. The nearest-neighbor Fe (6 per cell) carry  $\approx 0.15 \mu_B$  each. 8% of the total moment resides on S, about the same relative amount as

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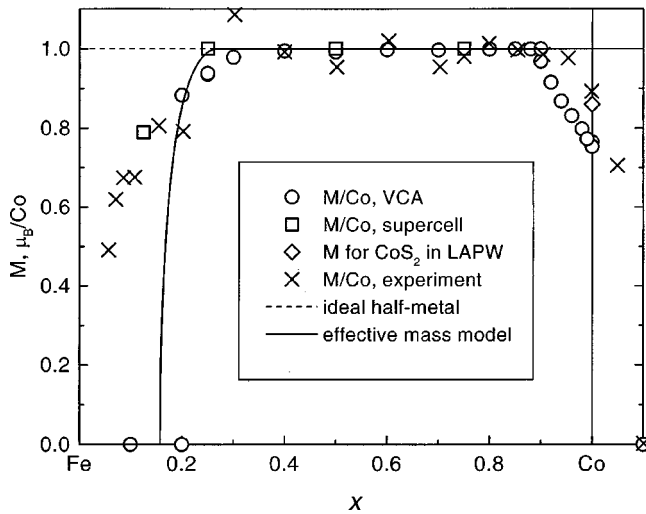


FIG. 1. Experimental and calculated magnetization in  $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$  alloys. VCA: virtual crystal approximation; s/cell: supercell calculations. Experimental data are from Ref. 6.

in  $\text{CoS}_2$ .<sup>12</sup> Therefore, one cannot view the low-doping  $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$  alloys as magnetic Co ions embedded in the nonmagnetic  $\text{FeS}_2$  background.

To understand the physics of this alloy, let us start with  $\text{FeS}_2$ .  $\text{FeS}_2$  is a nonmagnetic semiconductor with a gap between the  $t_{2g}$  and  $e_g$  states.<sup>4,5</sup> The reason for this is that the sulphur forms  $\text{S}_2$  molecules with the  $pp\sigma$  states split into a bonding and an antibonding state. The latter is slightly above the Fe  $e_g$  states, and thus empty. The other 5 S  $p$  states are below the Fe  $t_{2g}$  states, hence, the occupation of the Fe  $d$  bands is 6, just enough to fill the narrow  $t_{2g}$  band. Magnetizing  $\text{FeS}_2$  would require transfer of electrons from the  $t_{2g}$  into the  $e_g$  band, at an energy cost of the band gap  $\Delta$  per electron. The Stoner parameter  $I$ , which characterizes the gain of Hund energy per one electron transferred from the spin-minority into the spin-majority band, appears to be smaller than  $\Delta \approx 0.75$  eV.<sup>13</sup> However, if we populate the same band structure with  $x \ll 1$  additional electrons per formula unit, we can either distribute them equally between the two spin subband, or place  $x'$  in the spin majority band and  $x'' = x - x'$  in the spin-majority band (the total magnetic moment in  $\mu_B$  is then  $M = x' - x''$ ). In the latter case, we gain a Hund energy of  $-IM^2/4$ , but we lose some kinetic (band-structure) energy because some states have only single occupancy and thus more high-energy states have to be occupied. This energy loss can be computed in a manner entirely analogous to the classical Tomas-Fermi calculation.<sup>14</sup> The result is  $\Delta E = -IM^2/4 + B[(x')^{5/3} + (x'')^{5/3}]$ , where  $B = 3\hbar^2/10m^*(3/4\pi V)^{2/3}$ , and  $m^*$  is the effective mass in the conductivity band, and  $V$  is the volume per formula unit. This can be conveniently expressed in terms of the relative magnetization  $\beta = M/x$ :

$$\Delta E(\beta) = -Ix^2\beta^2/4 + B(x/2)^{5/3}[(1+\beta)^{5/3} + (1-\beta)^{5/3}].$$

Minimizing this with respect to  $\beta$  one finds:

$$\beta = A[(1+\beta)^{2/3} - (1-\beta)^{2/3}]/x^{1/3},$$

$$A = 5B/3I2^{2/3}.$$

The solution is a universal function  $\beta(A/x^{1/3})$ . Note that  $\beta(p) = 0$  for  $p > 3/4$ , and  $\beta(p) = 1$  for  $p < 1/2^{2/3}$ . Corre-

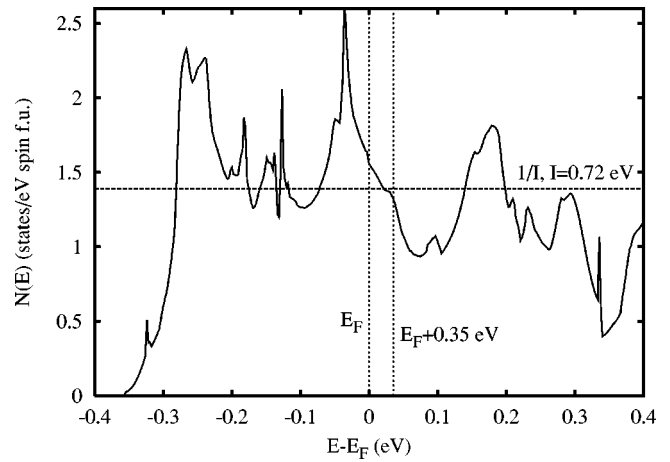


FIG. 2. Density of states for paramagnetic  $\text{CoS}_2$ , calculated by the LAPW method.  $E - E_F = 0.35$  eV corresponds to  $\text{Co}_{0.9}\text{Ni}_{0.1}\text{S}_2$  in the rigid-band approximation.

spondingly, with doping the material remains paramagnetic until  $x$  reaches  $x_1 = (20B/9I)^{3/4}$ . Then, the magnetic moment gradually grows until it reaches  $1 \mu_B/\text{Co}$  at the concentration  $x_2 = (5B/3I)^3$ . At larger dopings the material remains half metallic with  $\beta = 1$ . Eventually, DOS starts to deviate from the effective-mass model and the polarization  $\beta$  may become smaller than 1 again. One can estimate the critical concentrations  $x_{1,2}$  using the following values, extracted from the band-structure calculations for  $\text{FeS}_2$ :  $m^* \approx 0.8$ ,  $I \approx 0.55$  eV. This gives  $x_1 \approx 0.16$  and  $x_2 \approx 0.26$ , in qualitative agreement with Fig. 2.

This explains the on-the-first-glance unexpected result that unlike most known half metals  $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$  remains a HM for a large range of concentrations, is insensitive to crystallographic disorder,<sup>15</sup> and probably not very sensitive to the state of the surface either: the behavior qualitatively described by the universal function  $\beta$  above is determined by the competition of two large energies: The band gap  $\Delta$ , which is a measure of crystal-field splitting, and the Stoner factor  $I$ , a measure of the Hund coupling. As long as  $\Delta > I$  and  $x_1 \ll 1$  a large region of half metallicity exists. Both conditions are related primarily to the atomic characteristic of constituents and gross features of the crystal structure, and are not sensitive to details.

The same competition between the band energy and the Stoner energy leads to very different magnetic properties in the case of stoichiometric  $\text{CoS}_2$ , and of  $\text{CoS}_2$  doped with Ni ( $x > 1$  region in Fig. 1). The experimental magnetization in  $\text{CoS}_2$  is  $0.85\text{--}0.9 \mu_B$ , in perfect agreement with full potential LAPW calculations, and in reasonable agreement with LMTO results. External pressure, or substituting S by Se, rapidly reduces magnetization.<sup>8</sup> As shown in Ref. 16, Se doping increases the width of the conductivity band (because the  $\text{Se}_2$  dimer has smaller  $pp\sigma$  splitting than  $\text{S}_2$  and, therefore, the Co  $e_g$  states are better aligned with the chalcogen  $pp\sigma^*$  states). Thus, Se doping has the same effect as external pressure. Doping with Ni has a similar effect and concentrations of Ni of the order of 10% make the system nonmagnetic. The large magnetic moment of  $\text{CoS}_2$  suggests that the ferromagnetism in this system is robust and the fact that it disappears so rapidly with pressure and doping is puzzling.

On the other hand, this effect is correctly reproduced by

regular LSDA calculations (cf. Fig. 1 at  $x > 1$ , and Ref. 16). This tells us that it has to find its explanation in the peculiarities of the electronic structure of this compound. Indeed, fixed magnetic moment calculations at different pressures, and their detailed analysis (to be published elsewhere) show that the rapid disappearance of magnetism in this system, as well as its metamagnetic behavior, can be traced down to a specific structure of DOS, mostly the sharp peak just below the Fermi energy. We will only mention here that not only do the calculations yield a rapid decrease of the equilibrium magnetic moment with pressure, they also predict a noticeable *increase* of  $M$  at *negative* pressure. An expansion of 3%–4% in volume increases the calculated moment to nearly  $1 \mu_B$ . This suggests that the spin fluctuations at high temperature (above  $T_C$ ) may have larger amplitude than the ordered moments at zero temperature, a very unusual situation in magnetic metals. This kind of behavior has also been observed,<sup>17</sup> and discussed in the literature.<sup>18</sup> Yet another important observation from these calculations is that the position of the chalcogen  $p$  bands strongly depends on the chalcogen–chalcogen bond length, and, in turn, substantially affects the width of the conductivity band. This suggests strong magnetoelastic coupling.

To summarize, our most important conclusions are:

(1) The  $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$  alloy is predicted to be a half metal in a large range of concentrations. Unlike most other known half metals, and very importantly for the applications, the half metallicity should be robust with respect to defects and crystallographic disorder.

(2)  $\text{CoS}_2$  is an itinerant ferromagnet. The Fermi level sits on a steep slope of the density of states. As a result, despite a large magnetic moment, ferromagnetism disappears easily by a first-order (“metamagnetic”) transition when DOS is reduced by Ni doping, by pressure, or by Se doping.<sup>8</sup> The structure of the density of states also manifests itself via an unusual temperature dependence of the amplitude of magnetic fluctuations.

(3) There is strong coupling between electronic, lattice, and magnetic degrees of freedom in  $\text{CoS}_2$ . Interesting transport properties are to be expected at and near this composition.

For such a rich and interesting system, the  $3d$  pyrites seem to be surprisingly little studied either experimentally or theoretically. Hopefully this letter will encourage further investigations.

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<sup>4</sup>V. Eyert, K. H. Hock, S. Fiechter, and H. Tributsch, *Phys. Rev. B* **57**, 6350 (1998).

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<sup>7</sup>G. L. Zhao, J. Callaway, and M. Hayashibara, *Phys. Rev. B* **48**, 15781 (1993); S. K. Kwon, S. J. Youn, and B. I. Min, *Phys. Rev. B* **62**, 357 (2000).

<sup>8</sup>T. Goto, Y. Shindo, H. Takahashi, and S. Ogawa, *Phys. Rev. B* **56**, 14019 (1997).

<sup>9</sup> $\text{CuS}_2$  has considerable density of states at the Fermi level, 1 st./eV spin f.u., and substantial electron–phonon interaction with high-frequency  $S_2$  vibrons. Our calculations for  $\text{CuS}_2$  will be published elsewhere. Note also that a very large electronic specific heat coefficient of 19.5 mJ/mol  $\text{K}^2$  was reported [S. Waki and S. Ogawa, *J. Phys. Soc. Jpn.* **32**, 284 (1972)], corresponding to a renormalization  $(1+\lambda) \approx 3$ . Of course, part of this renormalization should be coming from electron–magnon interaction, similar to, say,  $\text{SrRuO}_3$  [c.f., e.g., I. I. Mazin and D. J. Singh, *Phys. Rev. B* **56**, 2556 (1999)].

<sup>10</sup>The Stuttgart package LMTO-TB 4.7 (<http://www.mpi-stuttgart.mpg.de/ANDERSEN/LMTODOC/LMTODOC.html>) was employed. Six automatically generated empty spheres were used per formula unit, and the result agreed reasonably well with the full-potential calculations (better than the alternative setup recommended in Ref. 4).

<sup>11</sup>The WIEN-97 package was used [P. Blaha, K. Schwarz, and J. Luitz, Vienna University of Technology, 1997; improved and updated version of the code, P. Blaha, K. Schwarz, and P. Sorantin, *Comput. Phys. Commun.* **59**, 399 (1990)].

<sup>12</sup>Noticeable magnetization on S has been confirmed experimentally [A. Ohsawa, Y. Yamaguchi, H. Watanabe, and H. Itoh, *J. Phys. Soc. Jpn.* **40**, 992 (1976)].

<sup>13</sup>For the conductivity band in  $\text{FeS}_2$ , due to hybridization with S,  $I$  is smaller than in pure Fe and is  $\approx 0.55$  eV.

<sup>14</sup>N. H. March, in: *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundquist and N. H. March (Plenum, New York, 1983).

<sup>15</sup>While we did not formally perform any disordered calculation like in Ref. 3, it is clear that in our case it would not change any conclusion: the fact that various supercell calculations and virtual crystal approximations all produce a sizable energy gap in the minority channel (and no states in the gap) proves that more sophisticated treatment of disorder would have added finite lifetime to the one-electron states, but would not destroy the half metallicity in the way it does in Heusler alloys (see Ref. 3).

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