

Growth and magnetic properties of single crystal $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$ ($x=0.35-1$)

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The pyrite $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$ ($0.25 \leq x \leq 0.9$) was predicted to be half metal, insensitive to Fe-Co disorder. To verify its half metallicity, we have grown single crystals of $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$ ($x=0.35, 0.5, 0.75, 0.9$, and 1). Crystals of up to a few mm in size by temperature gradient (923–873 K) solution growth from Te melts, which showed high crystalline quality by scanning electron microscopy, x-ray diffraction, and magnetic measurements. A half-metallic magnetization of $1 \pm 0.03 \mu_B$ per Co atom was found for $x=0.35-0.9$. Point contact Andreev reflection measurements, however, showed spin polarization of 47%–61% with the maximum around $x=0.5$, well below predictions. Ferromagnetic resonance measurements give $g \sim 2.08$ with large intrinsic damping, which indicates a reduced half-metallicity. Inductively coupled plasma and energy dispersive x-ray spectroscopy results confirm a sulfur deficiency of $\sim 1.5\% - 10\%$ [$(\text{Fe}, \text{Co})\text{S}_{2-y}$, $0.03 \leq y \leq 0.2$] and small amounts of Te. Electronic structure calculations show the extra electron provided by Co substitution to FeS_2 populates a sulfur-derived conduction band. Consequently, S deficiency and/or S site disorder are expected to affect the transport properties. This is consistent with the low polarization measurements and again indicates the importance of crystalline order in obtaining highly spin-polarized materials. [DOI: 10.1063/1.1555986]

I. INTRODUCTION

The development of half metallic (HM) materials for high spin polarization ($P=100\%$) is an important strategy in improving magnetoelectronic devices. A significant increase in P would have a profound effect on performance, and is expected to enhance the performance of other devices as well, such as the Johnson spin transistor, the spin-polarized light emitting diode, the Datta–Das spin-polarized field effect transistor (FET), and proposed realizations of quantum computers based on spin entanglement.

Of the materials predicted to be half metal, CrO_2 has spin polarization over 90%,¹ while half Heusler NiMnSb and full Heusler $\text{Co}_2\text{MnSi}(\text{Ge})$ alloys have P less than 60%.^{2,3} The usual explanation for the reduced half metallicity is the sensitivity of these materials to crystallographic disorder and stoichiometry,^{4,5} and to surface effects.⁶ Ferromagnetic $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$ ($0.25 \leq x \leq 0.9$) was recently predicted to be HM and insensitive to disorder in a metal sublattice.⁷

In this work we present initial results for spin polarization combined with structural and compositional analysis of the predicted half metal, $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$ for $0.35 \leq x \leq 1$, and provide experimental evidence that suggests the importance of sulfur defects in the spin polarization of this material.

II. EXPERIMENTAL PROCEDURE

A. Crystal growth

Single crystals of $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$ ($x=0.35, 0.5, 0.75, 0.9$, and 1) were prepared using temperature gradient solution growth with Te as the flux.⁸ The source materials used were commercial FeS_2 and CoS_2 powders from Alfa Aesar. Pow-

ders were mixed according to the desired composition and pressed into a 3 g pellet. The pellet was introduced into the end of a quartz tube [18 mm outer diameter (o.d.), 15 mm inner diameter (i.d.)] and about 75 g of tellurium lumps and 0.9 g of sulfur (5%) were then added to the tube. A quartz plug was placed against the tellurium and the tube was necked, evacuated and backfilled several times with argon and then sealed under vacuum. The distance between the source and the tip of quartz plug was about 14 cm. The ampoule was placed in a temperature gradient furnace for two weeks. To avoid peritectic decomposition of FeS_2 to S and FeS_x at 1016 K, the source material was maintained at 923 K and the growth zone at 873 K. The pyrite crystals were separated from the solidified melt by dissolving the Te of the growth zone in 30% nitric acid.

B. Crystal characterization

The morphology of the extracted crystals was examined using optical and scanning electron microscopies. To insure that a single phase of $(\text{Fe}, \text{Co})\text{S}_2$ alloy formed from the two phase powder mixture, crystals were crushed into powders to do a $2\theta-\theta$ x-ray diffraction ($\text{Cu } K\alpha$) measurement and compare it to the diffraction pattern of their parent material. The growth face of crystals was also examined by x-ray diffraction measurement of small random crystallites.

Elemental analysis was performed on all samples using standardless scanning electron microscopy (SEM)-based energy dispersive x-ray spectroscopy (EDS) on the surface and the interior of the fractured crystals of all compositions. CoS_2 crystals were also analyzed using induction coupled plasma (ICP) from a PerkinElmer Optima 2000 DV ICP-optical emission spectrometer (OES).

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C. Magnetic and transport measurements

The Curie temperatures and saturation magnetizations of the alloys at 5 K were measured using superconducting quantum interference device (SQUID) magnetometry. Ferromagnetic resonance (FMR) spectra were taken from 77 to 300 K using commercial spectrometers operating at 9.46 and 34.8 GHz. All samples confirmed the T_C derived from magnetometry and the approximate $M(T)$ was obtained by double integration of the derivative spectra.

The spin polarization (P) values were measured using the point contact Andreev reflection (PCAR) technique.² The PCAR measurements were performed at ~ 1.5 K using a mechanically sharpened superconductor (Sn) with a superconducting gap of $\Delta = 0.6$ mV. A four-probe method and standard lock-in techniques were used to collect the measured conductance ($G = dI/dV$). Variable vertical positioning allowed several data points for each sample, which allowed the variation of contact resistance at the normal metal and superconductor interface. However, only about three points were collected for each sample due to low contact resistance, which was about 9Ω for the initial contact and less than 1Ω after the third contact.

III. RESULTS

A. Crystal morphology: Structural and chemical analysis

The crystals range from sub-mm to a few mm in size in each direction, with larger sizes for higher Co concentrations. Crystals have many different shapes and larger crystals are often in the form of lumps consisting of 1–2 mm thick intergrown plates or as agglomerates of small crystals that entrap the Te. Crystals show layer type growth with $[100]$ as the prominent growth direction.

The x-ray diffraction patterns of the powdered crystals confirmed the single phase nature of the crystals that formed from their parent FeS_2 and CoS_2 powder mixture. The cubic lattice parameters a determined from powders crushed from single crystals were 0.5453, 0.5471, 0.5503, 0.5516 and 0.5530 nm for $x = 0.35, 0.5, 0.75, 0.9,$ and 1 , respectively. They followed Vegard's rule, indicating a complete solid solution.

The composition was analyzed with EDS on the surface and the interior of the fractured crystals. The sulfur content varied from crystal to crystal but was generally deficient for all of the alloys. The chemical formula is $(\text{Fe,Co})\text{S}_{2-y}$ with y ranging from 0.03 to 0.2. The composition on the surface of the crystals was found to be the same as that of the interior. The tellurium concentration was about 0.1–0.2 at. %. An ICP experiment on several large crystals of CoS_2 gave a composition of $\text{CoS}_{1.92}$ of ~ 3 at. % Te. The larger amount of Te found using ICP may be due to residual Te between the crystals. EDS was performed on small individual crystals with cleaner surfaces. Several crystals of $x = 1$ and 0.9 were postannealed in sulfur atmosphere at 773 K for 72 h with no improvement in stoichiometry.

B. Magnetic properties

For magnetic measurements, small but true single crystals were used. The M vs T curves for the $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$ alloys showed a single magnetic phase nature indicating the high crystalline quality. T_C was determined to be 107, 120, 153, 145 and 125 K for $x = 0.35, 0.5, 0.75, 0.9$ and 1 , respectively, and agrees reasonably well with that of literature values.⁹ The saturation magnetization was 0.343, 0.496, 0.727, and $0.927 \mu_B$ for $x = 0.35, 0.55, 0.75$ and 0.9 , i.e., $1 \pm 0.03 \mu_B$ per Co consistent with the half metallicity. FMR was performed on all alloys with the best results obtained for $\text{Fe}_{0.1}\text{Co}_{0.9}\text{S}_2$, which had the most favorable shape for FMR, thin platelets with specularly reflecting surfaces. The result indicated below the ordering temperature a g value of 2.08 and linewidths of about 70 Oe at 9.5 GHz and near 200 Oe at 35 GHz, suggesting very large intrinsic spin precession damping. These are both indications of the considerable spin-orbit character of ferromagnetic electrons, which may interfere with the ideal half-metal character.¹⁰

C. PCAR results

The data were analyzed using modified Blonder–Tinkham–Klapwijk (BTK) theory¹¹ for the case of ferromagnetic metals.¹² The spin polarization, P , was obtained by fitting the data according to the theory of Ref. 12, including corrections for the spread resistance. The conductance versus bias voltage for a $\text{Fe}_{0.5}\text{Co}_{0.5}\text{S}_2$ crystal is plotted in Fig. 1, normalized to the conductance at $|V| \gg \Delta$. The measurement was repeated for another sample of the same composition with very good reproducibility. The interfacial scattering strength Z was small for this as well as for all measurements of this series of alloys. We found the highest $P = 0.61 \pm 0.03$ at $x = 0.5$, well below the theoretical value for a HM. The uncertainties arise mainly from the uncertainty in the temperature and superconducting gap (assumed here to be ~ 0.55 – 0.6 mV).

Figure 2 plots the measured values of P vs Co concentration. Our calculations predict for pure CoS_2 spin polarization $P = -20\%$ in the purely ballistic regime and $P = 55\%$ in the purely diffusive regime, consistent with the measured value of $|P| = 40\%$. The measured spin polarization does increase with the Fe concentration, as predicted by the calculations, it stops short of reaching 100%. At very high Fe concentration P decreases again, also qualitatively consistent with the calculations. However, the true reasons for this dependency are not clear at this moment.

IV. DISCUSSION

It was pointed out that this $(\text{Fe,Co})\text{S}_2$ alloy series is insensitive to disorder in the metal sublattice, and that the large magnetic moment makes it a very robust half metal. Furthermore, unlike some oxide materials, such as CrO_2 ,¹ for which the value of P seems to depend on Z , there was no evidence linking the underestimation of P to a spin-mixing effect. The most likely reason is the sulfur deficiency, which was not taken into account in Ref. 7. Fiechter *et al.*¹³ showed that synthetic iron-pyrite crystals frequently deviate from ideal stoichiometry by a sulfur deficiency of up to 7.5 at. %

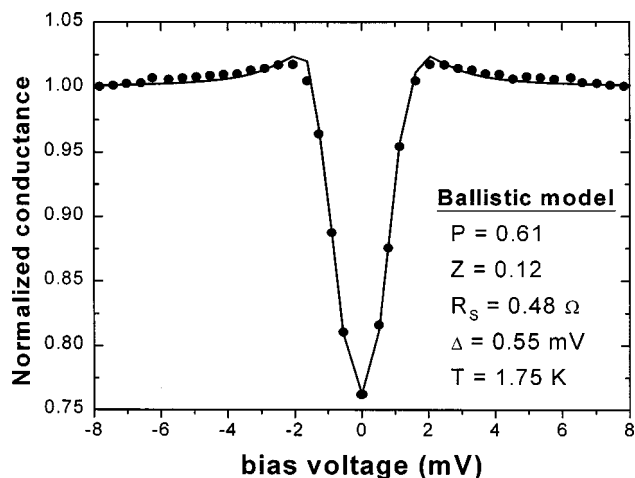


FIG. 1. Measurement of the spin polarization using PCAR for $\text{Fe}_{0.5}\text{Co}_{0.5}\text{S}_2$. The solid line is the fitted curve. R_s is the spread resistance fit across the sample.

($\text{FeS}_{1.85}$) and that this deviation does not greatly affect either lattice perfection or the cube edge of the material. The deficiency was explained by a high number of S vacancies that are homogeneously distributed in the lattice without forming a superstructure. In $\text{FeS}_{1.9}$, coordination of the 25% of the iron ions would be affected.¹⁴ The density of defect states in the gap is so high they may combine and form a defect band. This mechanism may be operative for our (Fe,Co) S_2 alloys, reducing the half metallicity. Our electronic structure calculations (similar to those described in Ref. 7) show that the lowest unoccupied states in FeS_2 have a mostly sulfur character. Extra electrons provided by Co populate these states. Consequently, sulfur deficiency is expected to affect the transport properties. The sulfur concentration is not optimized in this experiment and might be improved in future work by increasing the temperature gradient and/or by increasing the S content added.

Another possible cause for the low P is the antisite defect between sulfur and transition metal atoms. Tomm *et al.* pointed out that here antisite defects are geometrically allowed.¹⁵ However, different charge states of the Fe and S ions may actually lead to a high cost in energy for such an antisite defect. In any case, a high density of antisite defects would have caused band edge fluctuations at the bottom of the conduction band and the top of the valence band.¹⁵ Such defect might reduce P as well. Structural work is needed to verify the existence of this type of defect.

The effect of tellurium inclusion on P probably is small because of its low concentration, although being much larger than S, it would cause substantial lattice distortion, unfavorable for magnetism. Even CoFeSe_4 is, according to our calculations, not a half metal, due to the geometrical effect of the large Se ions, and the size of Te is even larger.

Finally, we would like to point out that the temperature dependence of the resistivity in the (Co,Fe) S_2 alloy is highly

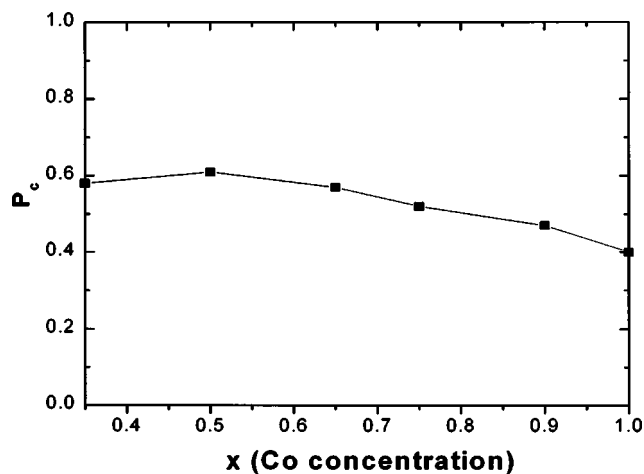


FIG. 2. Spin polarization (P) vs Co concentration of $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$.

unusual.^{16,17} For intermediate concentrations the resistivity is semiconducting like below T_C and metallic above T_C , with a minimum at T_C . The reason for this behavior is not understood yet-but it indicates that the electric transport in this system may be more complex than was assumed in conventional theories of Andreev reflection.

V. SUMMARY

We synthesized single crystals of $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$ ($x = 0.35-1$). Even though the crystals showed a high crystal-line quality, the chemical analysis using EDS and ICP confirmed a sulfur deficiency of 1.5%–10% and small amounts of Te inclusions. This sulfur defect is believed to be the cause of the low spin polarization (47%–61%) value.

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