Bulk Spin Polarization of $Co_{(1-x)}Fe_xS_2$

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We report on a new method to determine the degree of bulk spin polarization in single crystal $Co_{(1-x)}Fe_xS_2$ by modeling magnetic Compton scattering with *ab initio* calculations. Spin-dependent Compton profiles were measured for CoS_2 and $Co_{0.9}Fe_{0.1}S_2$. The *ab initio* calculations were then refined by rigidly shifting the bands to provide the best fit between the calculated and experimental directional profiles for each sample. The bulk spin polarizations, P, corresponding to the spin-polarized density of states at the Fermi level, were then extracted from the *refined* calculations. The values were found to be $P = -72 \pm 6\%$ and $P = 18 \pm 7\%$ for CoS_2 and $Co_{0.9}Fe_{0.1}S_2$, respectively. Furthermore, determinations of P weighted by the Fermi velocity (v_F or v_F^2) were obtained, permitting a rigorous comparison with other experimental data and highlighting the experimental dependence of P on v_F.

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Spintronic materials are the subject of considerable research and rapid technological development. In these materials and devices, the goal is to exploit the electron spin for applications such as data storage and read heads. Some commercial devices exist, for example, magnetic random access memory devices being based on the concept of spin-dependent tunneling magnetoresistance [1]. Because of the potential for the development of novel devices using spin transport in semiconductors, so-called spin-injector materials (which would act as a source of highly spin-polarized electrons) currently attract considerable interest. An obvious choice for a spin injector is a ferromagnetic system since it naturally has an imbalance of the electron spin population at the Fermi level and thus possesses a degree of spin polarization. Ideally, materials for applications would be fully spin-polarized "half-metals" (HMs), where the density of states (DOS) at the Fermi energy (E_F) is finite for one spin but zero for the other, such that carriers of only one spin exist at the Fermi level. However, ferromagnets typically only possess partial spin polarization. Despite much theoretical and experimental effort, only a few promising candidates, such as CrO_2 [2,3], optimally doped $La_{0.7}Sr_{0.3}MnO_3$ [4], and $Co_2MnAl_{(1-x)}Sn_x$ [5,6] have been found to exhibit high polarizations. Recently, $Co_{(1-x)}Fe_xS_2$ has garnered interest resulting from predictions of half-metallicity and the potential to *tune* the polarization via Fe doping. The consensus is that doping simply adjusts the Fermi level [7–11] without altering the band structure. The possibility of altering the magnitude of the polarization makes this material ideal for fundamental research on spin polarization.

The spin polarization can be defined simply in terms of the spin-dependent DOS, $N_{\uparrow/\downarrow}$, at the Fermi level. However, in order to facilitate comparison with various experimental techniques, it is useful to expand this definition to weight $N_{\uparrow/\downarrow}$ with the Fermi velocity, $v_{F,\uparrow/\downarrow}$. Hence, following Mazin [12], P_n can be defined such that,

$$P_n = \frac{N_\uparrow v_{F,\uparrow}^n - N_\downarrow v_{F,\downarrow}^n}{N_\uparrow v_{F,\uparrow}^n + N_\downarrow v_{F,\downarrow}^n}. \tag{1}$$

For $n = 0$, as quoted by most theoretical studies, P_0 is solely defined by the DOS. Weighting with the Fermi velocity accounts for transport properties, with $n = 1$ in the ballistic or $n = 2$ in the diffusive regimes. Experimentally the direct measurement of the polarization has proven to be a challenge. In particular, except for the case of a HM where P_n is 100%, the appropriate value of n is often ambiguous; consequently, comparison with theory is possible but notoriously difficult [12–15]. In point-contact Andreev reflection (PCAR) measurements, for example, the value of n is not the same for all materials [14]. Bulk techniques such as saturation magnetization or transport measurements can only give an indication of half-metallicity, and techniques which give access to the magnitude of P directly such as spin-polarized photoemission or PCAR are heavily dependent on the surface quality of the sample.

In this Letter, we demonstrate that a magnetic Compton scattering study combined with *ab initio* electronic structure calculations can be used to extract P_n in the representative pyrite-type series $Co_{(1-x)}Fe_xS_2$. Fine-tuning the theory to experiment enables the spin polarization to be determined for $n = 0$ as well as the weighted values for $n = 1, 2$.

Magnetic Compton scattering is a valuable tool for the investigation of spin-dependent effects as the incoming hard x rays directly probe the twice-integrated momentum distribution of the unpaired electrons in the bulk [16]. A Compton profile (CP) represents the 1D projection of the electron momentum density. If the difference between the CPs is measured for opposite applied magnetic field directions, the resulting difference profile contains only the spin-dependent part of the momentum distribution; this is referred to as the magnetic Compton profile (MCP).

The directional MCPs can be directly compared to the spin-dependent momentum distributions which have been computed from the *ab initio* electronic structure calculation (from which the polarization may also be calculated). It has been demonstrated previously [17,18] that the agreement with experiment may be refined by iterating a rigid shift of the bands (with respect to the Fermi level) contributing to the spin moment. In the case described here, this optimization is performed by minimizing the χ^2 calculated simultaneously between the computed and measured MCPs along four crystallographic directions. The bulk polarization P and the weighted polarization P_n can then be calculated directly from the refined model band structure giving a direct experimental insight into not only the polarization but also the effect of the Fermi velocity on P. The ability to extract all possible permutations of the polarization allows simple comparison with results from other studies.

In order to test our method, we calculated the spin polarization of Ni. For Ni, a transport measurement determined P_2 to be $23 \pm 3\%$ experimentally [19], whereas *ab initio* calculations predict $P_2 = 0\%$ [12]. For our refinement, we used experimental MCPs for four crystallographic directions from Dixon *et al.* [20]. The refinement increased the value of P_2 from our *ab initio* value of 0% to $20 \pm 2\%$, which agrees well with the previous experimental result. This simple test shows that it is a robust method for determining P_n.

Band structure calculations predict CoS_2 to be a highly spin-polarized ferromagnet, just missing half-metallic behavior [21]. The Fermi level lies low in the conduction bands, and doping with the isostructural semiconductor FeS_2 results in a reduction in the occupation of one spin channel. It has been predicted that this would enable the polarization to be tuned to half-metallicity [9–11]. Saturation magnetization and transport measurements indicate a high spin polarization hinting towards possible half-metallicity at doping levels between 7%–10%. The trend in the total DOS at E_F extracted from heat capacity and nuclear magnetic resonance follows this conjecture [8,22]. However, PCAR measurements of the absolute value of the magnetization reveal magnitudes of up to $|P| = 64\%$ in the pure (single crystal, [23]) and $|P| = 85\%$ for $x = 0.15$ (polycrystalline, [11]) in the doped system. Complementing these results, anisotropic magnetoresistance measurements show a change in sign of the polarization on doping, as predicted by *ab initio* calculations [11,24]. Although the qualitative behavior of both experiment and theory are similar, the absolute values of P disagree [25]. This may be attributed in part to the sensitivity of PCAR to v_F (such that $n > 0$), as opposed to the theoretical values which refer to P_0.

For the current study, measurements were performed on CoS_2 and $Co_{0.9}Fe_{0.1}S_2$ single crystals to investigate polarization effects at low doping. High quality single crystals were prepared by the chemical vapor transport method [8]. Particular care was taken to ensure stoichiometry and to avoid sulfur deficiency, which is known to affect the measured polarization [7,26]. The magnetic Compton scattering experiments were carried out at the beam line (BL08W) of SPring-8, Japan. All experimental data were collected at a temperature of 10 K. The MCPs were subsequently corrected for detector efficiency, absorption, the relativistic cross section, and multiple scattering effects. The value of the saturation magnetization measured with a SQUID at 10 K was determined to be $0.83\mu_B/\mathrm{Co}$ and $1.04\mu_B/\mathrm{Co}$ for the pure and $x = 0.1$ samples.

The electronic structure of CoS_2 was computed using the linear muffin-tin orbital method (LMTO) within the atomic sphere approximation including combined correction terms [27]. The exchange correlation part of the potential was described within the local spin density approximation, and the effect of doping was incorporated via the virtual crystal approximation. As observed in previous calculations, the moment at the experimental lattice constant of 5.5 Å is substantially underestimated [28,29] and so the calculations presented here have been performed at 5.71 Å, producing moments which are $0.85\mu_B/\mathrm{Co}$ and $0.92\mu_B/\mathrm{Co}$ for the pure and $x = 0.1$ systems, respectively, in good agreement with the experimental values.

The results of the calculation for CoS_2 are depicted in Fig. 1. The spin-resolved DOS show the sulfur $2p$ states below the cobalt $3d$ manifolds. These states, which are hybridized with sulfur $2p$ states, are split by the crystal field into t_{2g} and e_g manifolds. The Fermi level lies low in the e_g manifold where two majority bands and four minority bands cross E_F (see inset of Fig. 1). The partial DOS contributed by each band are depicted in Fig. 2(a). In the undoped compound, in both the majority and minority spin channel, band 1 holds the largest DOS and is therefore expected to have the biggest impact on P_n. The calculation predicts a polarization $P_0 = -58\%$. The band structure and partial DOS for $x = 0.1$ are broadly similar to the pure case and lead to $P_0 = 40\%$ [see Fig. 2(b)]. Our calculations predict half-metallicity to occur for $x \geq 0.3$. Overall these results are consistent with other theoretical band predictions [24,28–30].

The experimental and calculated MCPs, resolved along different crystallographic directions, are shown

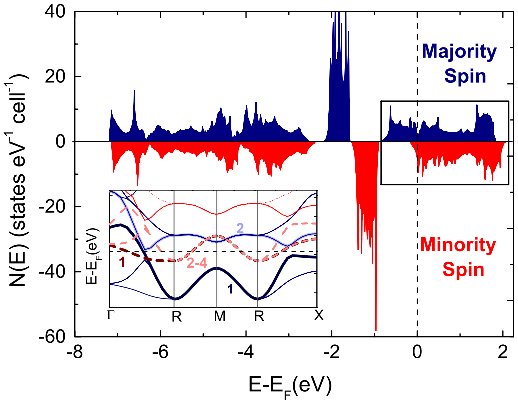

FIG. 1 (color online). The DOS of CoS_2, where the sulfur p and cobalt d manifolds are depicted for the majority and minority spin states. The inset shows the band structure of the e_g manifold around the Fermi level along a high symmetry path in the cubic Brillouin zone. Overall six bands composed of two in the majority (blue solid lines) and four in the minority (red dashed lines) channel cross the Fermi level.

in Figs. 3(a) and 3(b) for CoS_2 and $Co_{0.9}Fe_{0.1}S_2$. The *ab initio* theoretical results are in excellent agreement with the experimental MCPs. The characteristic structures in the directional differences of the magnetic Compton profiles serve as a rigorous check on the calculation, and these are shown for the pairs of directions [100]–[110] in the insets of Fig. 3. In order to optimize the agreement between theory and experiment, the energy bands were refined, as described earlier, to provide the best fit to the experimental MCPs. Small energy shifts of the bands crossing E_F change the detailed shape of the resultant MCP; the band positions were refined to give the best fit between the theoretical and experimental MCPs simultaneously for four crystallographic directions for CoS_2 and three for $Co_{0.9}Fe_{0.1}S_2$. The spin moments calculated from these fits agree well with the experimental values, providing an independent consistency check.

Despite small energy shifts of the bands (20–60 meV), the fitting procedure sees the χ^2 parameter reducing by 30%–50% from its starting value to the minimum and has an appreciable impact on the polarization. In the undoped case, the polarization decreases from the original value of $P_0 = -58\%$ to $P_0 = -72(\pm 6)\%$. Here the error (which is generally larger for more dispersive bands) reflects the uncertainty of the fit. This decrease can be mainly attributed to majority band 2 being shifted above E_F and the DOS of band 1 being decreased. For the $x = 0.1$ compound, the polarization decreases from the original value of $P_0 = 40\%$ to $P_0 = 18\%(\pm 7)$, which is primarily due to the lowering of majority band 2 and an increased DOS for the minority band.

The fitted bulk polarization P_n obtained for CoS_2 and $Co_{0.9}Fe_{0.1}S_2$ is depicted in Fig. 4 along with the results from the unfitted calculation for different compositions. The results of the original calculation for P_0 at different x are in good agreement with previous theoretical studies [24]. However, the weighting with the Fermi velocity has a significant effect on the nominal value of the polarization, particularly in the pure system where a weighting with v_F^2 results in a positive polarization. The evolution of the fitted P_n is qualitatively consistent with indirect measurements

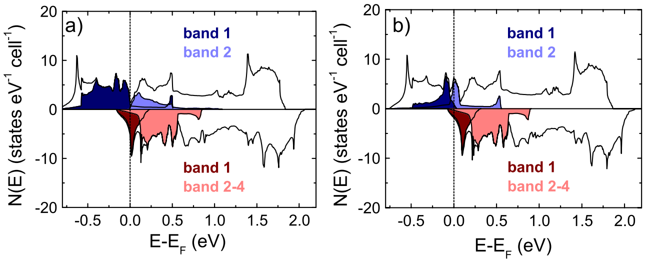

FIG. 2 (color online). The DOS in the e_g manifold of (a) CoS_2 and (b) $Co_{0.9}Fe_{0.1}S_2$ is composed of six bands around the Fermi level. As in Fig. 1, the DOS of the majority and minority bands are blue and red, respectively. The dark and light colors signify band 1 and band 2 (or in the minority channel, the combination of bands 2–4), respectively.

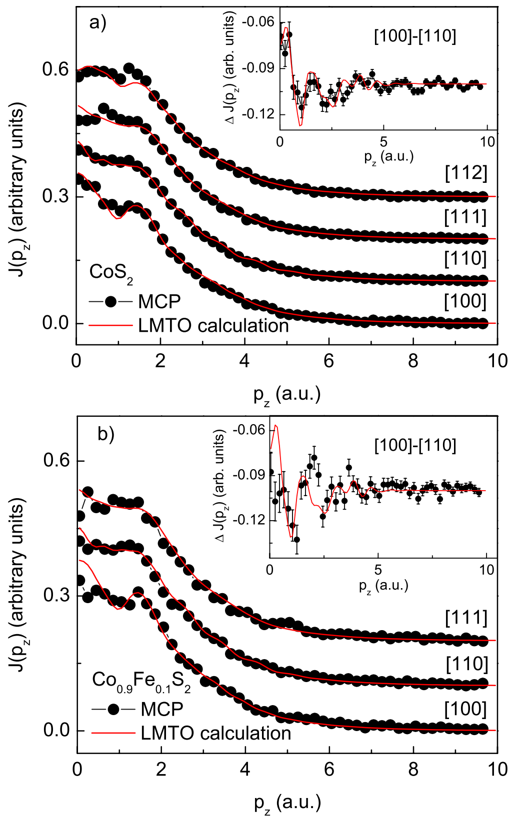

FIG. 3 (color online). Experimental and LMTO MCPs for (a) CoS_2 and (b) $Co_{0.9}Fe_{0.1}S_2$ resolved along different crystallographic directions. For clarity the profiles are offset by 0.2 and statistical errors are smaller than the symbol size. The insets of both graphs show the directional differences for each composition between [100] and [110].

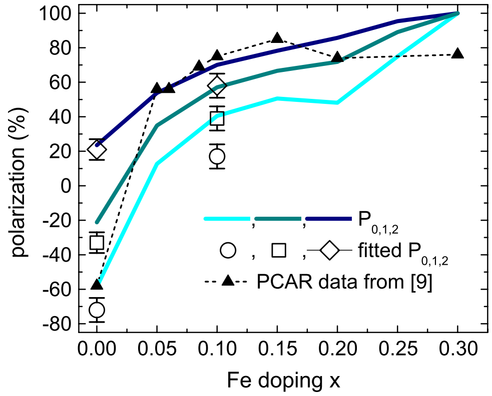

FIG. 4 (color online). Experimental PCAR (▲) polarization data compared to $P_{0,1,2}$ from the LMTO calculation (lines) as a function of composition in 5% steps. The tuned calculations are also shown, where the bare P is also weighted by the Fermi velocity (open symbols). Note that the sign change in the PCAR data has been inferred from AMR measurements.

such as saturation magnetization but implies that the maximum P is not obtained at $x = 0.1$.

Our results demonstrate the tunability of the different polarization functions across the series of $\mathrm{Co}_{(1-x)}\mathrm{Fe}_x\mathrm{S}_2$. The data confirm that P_0 is negative in the pure and positive for the doped compound. It is instructive to compare our values for P_n with the PCAR results. In the case of the pure compound, the value of $P_{\mathrm{PCAR}} = |64\%|$ is between P_0 and P_1. However, for the $x = 0.1$ composition, P_{PCAR} is in close proximity to P_2 found in our study. This could indicate a doping dependent crossover from the ballistic to the diffusive regime in PCAR measurements, which is consistent with the increase in resistivity observed for higher Fe doping [8]. Alternatively, these discrepancies could be due to surface effects playing a role in the PCAR measurements as pointed out by Leighton *et al.* [7]. Although PCAR has a penetration depth corresponding to the coherence length of the superconductor, the electrons crossing the interfacial barrier experience the surface potential. Studies on the surface state of CoS_2 show that sulfur degradation could influence polarization measurements [31,32]. However, so far the surface stoichiometry of the alloyed composites has not been investigated.

In summary, we present a new method to determine the bulk spin polarization. Although harder to put into practice, this novel technique calculates P_n from a refined model band structure that is fitted to experimental MCPs. Moreover, it is free from surface effects. The case of Ni shows that this approach is a rigorous method of determining the bulk P_n. More importantly, the results on CoS_2 and $\mathrm{Co}_{0.9}\mathrm{Fe}_{0.1}\mathrm{S}_2$ illustrate the applicability of the approach in a more complex system and highlight the degree to which the polarization is dependent on v_F. We speculate that there is a crossover from the ballistic to the diffusive transport regimes on doping with Fe on the basis of the comparison with PCAR measurements. The new method can be used to determine P_n in such a way that its dependence on v_F is unambiguous, and our results for $\mathrm{Co}_{1-x}\mathrm{Fe}_x\mathrm{S}_2$ demonstrate the importance of this.

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