Bulk Spin Polarization of Co\(_{(1-x)}\)Fe\(_x\)S\(_2\)

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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\(_x\)S\(_2\) by measuring magnetic Compton scattering with \textit{ab initio} calculations. Spin-dependent Compton profiles were measured for CoS\(_2\) and Co\(_9\)Fe\(_9\)S\(_2\). The \textit{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\(_9\)Fe\(_9\)S\(_2\) respectively. Furthermore, determinations of \(P\) weighted by the Fermi velocity (\(v_F\) or \(v_F^n\)) 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 (MRAM) 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\(_2\)MnAl\(_{(1-x)}\)Sn\(_x\) \(^5\)\(^6\) have been found to exhibit high polarizations. Recently, Co\(_{(1-x)}\)Fe\(_x\)S\(_2\) has garnered interest resulting from predictions of half-metallicity and the potential to \textit{tune} the polarization via Fe doping. The consensus is that doping simply adjusts the Fermi level \([7\)\(8\)\(9\)\(10\)\(11\)] without altering the bandstructure. 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 density of states (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,

\[
P_n = \frac{N_{\uparrow}v_{F\uparrow}^n - N_{\downarrow}v_{F\downarrow}^n}{N_{\uparrow}v_{F\uparrow}^n + N_{\downarrow}v_{F\downarrow}^n}
\]  

(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 \(P_n = 100\%\), the appropriate value of \(n\) is often ambiguous, and consequently comparison with theory is possible, but notoriously difficult \([12]\)\([13]\)\([14]\)\([15]\). 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 \textit{ab initio} electronic...
structure calculations can be used to extract \( P_n \) in the representative pyrite-type series \( \text{Co}_{(1-x)} \text{Fe}_x \text{S}_2 \). 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 \textit{ab initio} electronic structure calculation (from which the 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 \( \chi^2 \) calculated simultaneously between the computed and measured MCPs along four crystallographic directions. The bulk polarization \( P_2 \), and the weighted polarization \( P_n \) can then be calculated directly from the refined model bandstructure giving a direct experimental insight into not only the polarization but also the effect of the Fermi level on \( P_2 \). 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 \textit{ab initio} calculations predict \( P_2 = 0\% \) [12]. For our refinement, we used experimental MCPs for four crystallographic directions from Dixon \textit{et al.} [20]. The refinement increased the value of \( P_2 \) from our \textit{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 \( P_n \).

Bandstructure calculations predict \( \text{CoS}_2 \) 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 \( \text{FeS}_2 \) 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] [10] [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 follow 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) 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 \textit{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 \( \text{CoS}_2 \) and \( \text{Co}_{0.9}\text{Fe}_{0.1}\text{S}_2 \) single crystals to investigate polarization effects at low doping. High quality single crystals were prepared by the chemical vapor trans-
port method [8]. Particular care was taken to ensure stoichiometry and to avoid sulphur deficiency, which is known to affect the measured polarization [7, 20]. The magnetic Compton scattering experiments were carried out at the beamline (BL08W) of SPring-8, Japan. All experimental data were collected at a temperature of 10K. 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 10K was determined to be 0.83 $\mu_B$/Co and 1.04 $\mu_B$/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 (LSDA) and the effect of doping was incorporated via the virtual crystal approximation (VCA). 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 $\mu_B$/Co and 0.92 $\mu_B$/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 sulphur 2p-states below the cobalt 3d manifolds. These states, which are hybridized with sulphur 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. 2a). 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 bandstructure and partial DOS for $x = 0.1$ are broadly similar to the pure case and lead to $P_0 = 40\%$ (see Fig. 2b). Our calculations predict half-metallicity to occur for $x \geq 0.3$. Overall these results are consistent with other theoretical band predictions [21, 22, 23, 30].

The experimental and calculated MCPs, resolved along different crystallographic directions, are shown in Fig. 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 $\chi^2$ 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

![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 the [100] and [110].]
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$_2$ are 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 such as saturation magnetization, but imply 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 Co$_{1-x}$Fe$_x$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 $P_{PCAR} = [64\%]$ 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 sulphur 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 bandstructure 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 Co$_{0.9}$Fe$_{0.1}$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 Co$_{1-x}$Fe$_x$S$_2$ demonstrate the importance of this.

Acknowledgments

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