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Resonant photoemission and spin polarization of Co$_{1-x}$Fe$_x$S$_2$

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Abstract
The valence band occupied state electronic structure of Co$_{1-x}$Fe$_x$S$_2$ in the region of the Fe/Co 3d bands has been investigated using photoemission and spin-polarized photoemission. As measured by using spin-polarized ultraviolet photoemission, the surface Fermi level spin polarization of Co$_{1-x}$Fe$_x$S$_2$ thin films at 50 K, specifically at $x = 0, 0.05, 0.10$ and $0.15$, was found to be much reduced compared to that of the bulk. The spin polarization nonetheless increases with Fe concentration. The resonant photoemission spectroscopy provides evidence that S bands have a strong resonance at the photon energy corresponding to the Co 2p core level, indicating strong hybridization between Co and S bands in Co$_{1-x}$Fe$_x$S$_2$ (at small $x$). Similar evidence exists for Fe hybridization with the S bands.

1. Introduction

Although a ferromagnetic metal with 100% Fermi level spin polarization at elevated temperature, is forbidden [1–4], high polarization materials remain of great interest as a component in devices that require great spin fidelity. Among high polarization ferromagnets, Co$_{1-x}$Fe$_x$S$_2$ has attracted much attention [5–16]. In such transition metal disulphides, with the pyrite structure, the metal 3d bands are split into $t_{2g}$ and $e_g$ subbands by the significant crystal field. The metal 3d electron configuration varies from $t_{2g}^6e_g^0$ in FeS$_2$, a semiconductor with an energy gap of $E_g = 0.95$ eV [17, 18] to $t_{2g}^6e_g^1$ for the ferromagnetic metal CoS$_2$ which has a $T_C$ of 120–123 K [10, 16, 19, 20]. The mixed transition metal pyrite Co$_{1-x}$Fe$_x$S$_2$, a solid solution of CoS$_2$ and FeS$_2$ has a composition-controlled spin polarization up to 85% [12, 13], generally confirming the theoretical predictions of Mazin [9]. Different $x$ values lead to different spin polarizations, as the Fermi level is tunable in Co$_{1-x}$Fe$_x$S$_2$ by Fe doping [12, 13]. The highest spin polarization measured in these materials is 85% at low temperatures, for $x = 0.15$.

Spintronic devices such as magnetic tunnel junctions, spin injection devices, and spin transistors are known to exhibit superior performance if high spin polarization can be obtained at the interface with the ferromagnetic spin polarizer [4]. This is problematic, as most high polarization materials are plagued by minority spin surface states [1–4], including CoS$_2$ [21]. Such surface states tend to decrease the measured surface or interface polarization, diminishing the advantage provided by the high bulk polarizations. Here we show that while the metal sulfur hybridization in Co$_{1-x}$Fe$_x$S$_2$ is very strong, as expected, indeed the surface polarization is significantly diminished with respect to bulk.

2. Experimental details

The Co$_{1-x}$Fe$_x$S$_2$ films were fabricated via a two-step synthesis [15, 22], by first deposition of the Co$_{1-x}$Fe$_x$, of thickness 14–80 nm, then the Co$_{1-x}$Fe$_x$ films were sulfidized.
by exposure to a sulfur atmosphere at elevated temperatures. A contamination-free surface of the Co$_{1-x}$Fe$_x$S$_2$ thin films were prepared by ion-beam sputtering followed by annealing. The possible failings of this surface preparation approach is that preferential segregation [23] and sputtering of one or more of the constituent components is possible. While the complications of preferential sputtering or segregation are considered in the discussion that follows, there is no evidence to indicate either occurs in a significant manner in these experiments: resonant photoemission ratio of intensities, discussed below, are consistent with the nominal composition. The alternatives of cleaving the sample (as in [21, 23–25]) or scraping the surface (as in [26]), to prepare a clean surface, were not an option here.

Spin-polarized angle-resolved photoemission spectra were acquired at the U5UA undulator spherical grating monochromator (SGM) beamline at the National Synchrotron Light Source (NSLS) [27–29]. Linearly polarized light from an undulator source was dispersed using a spherical grating monochromator (SGM) and the ultra-high-vacuum photoemission end station was equipped with a commercial angle-resolved hemispherical electron energy analyzer (EA125, Omicron GmbH), and a post-electron energy analyzer Mott detector for spin polarization analysis [27–29].

The spin polarization, $P$, for the collected data was determined according to

$$P = \frac{1}{2} \frac{\sqrt{I_L^+ I_R^-} - \sqrt{I_L^- I_R^+}}{\sqrt{I_L^+ I_R^+} + \sqrt{I_L^- I_R^-}}$$

where $I_L$ and $I_R$ represent the number of electrons scattered into the left and right channels of the Mott detector, respectively, and the superscript ‘+’ or ‘−’ refers to the sample being magnetized ‘up’ and ‘down’, respectively. The sample was cooled down to roughly 50 ± 15 K in a 300 Oe magnetic field applied parallel to the sample surface. We note at this stage that this is larger than the coercive field of 125 Oe at 50 K, although the issue of the actual polarization obtained will be discussed in more detail below. The spin-resolved photoemission spectra were measured repeatedly at an incident photon energy of $h\nu = 35$ eV and combined energy resolution of $\Delta E = 120$ meV. The photon energy resonant photoemission spectra were taken in the range of 45–70 eV at a light incidence angle, with the samples at room temperature. Throughout, the photoelectrons were collected along the surface normal.

3. Surface polarization

For two different iron doping concentrations in CoS$_2$, i.e. Co$_{1-x}$Fe$_x$S$_2$ with $x = 0.1$ and 0.15, we obtained a surface spin polarization via spin-polarized ultraviolet photoemission spectroscopy. In the spin-polarized photoemission spectra, there is a relatively small but quite clear spin asymmetry between majority spin (red) and minority spin (green), as seen in figures 1(a) and (b). The measured spin polarizations vary with binding energy but remain less than 10% (figures 1(b) and (d) for $x = 0.1$ and 0.15, respectively). These values for the surface spin polarization are significantly smaller than the bulk polarization (up to 85%) that was measured.

Figure 1. Spin-polarized photoemission of the mixed transition metal pyrite Co$_{1-x}$Fe$_x$S$_2$ (a) and (b) $x = 0.10$; (c) and (d) $x = 0.15$, at roughly 50 K. Red (up pointing triangles) and green (down point triangle) represent the signals for spin-up and spin-down, respectively. In the bottom panels (b), (d), we plot the net spin polarization $P$. 

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for Co$_{1-x}$Fe$_x$S$_2$ at $x = 0.15$ [12, 13] and liquid helium temperatures. Based on the measured bulk polarization at 4.2 K, we would still expect polarizations greater than 40% at 50 K for Co$_{0.85}$Fe$_{0.15}$S$_2$ given the 300 Oe applied field, which we clearly do not obtain. The spin polarizations are greatest in the region of the Co/Fe 3d bands near the Fermi level, and this is expected as the magnetic moment resides largely on the transition metal atoms, not sulfur.

There are several possible reasons for this smaller than expected spin polarization. These include a failure to saturate the Co$_{1-x}$Fe$_x$S$_2$ thin films into a single domain state, so that the net sample polarization does not truly reflect the polarization of a single ferromagnetic domain, or the possibility that the surface magnetization is oriented normal to the surface, thus causing a diminished signal. It should also be stated that of course the critical issue is the saturation field, if full polarization is to be measured, and this is much higher than the coercivity, in the region of 2500 Oe. Yet 300 Oe is still well beyond the coercive field $H_c$ of about 125 Oe at 50 K. Given that 300 Oe was applied during cooling through the Curie temperature, the magnetization of the samples should be close to 65% of the maximum saturation (verified by magnetometry measurements), so we would still expect, at a minimum, about 40% or more spin polarization at 50 K. Moreover, magnetization measurements also confirm in-plane magnetization, and thus a large out-of-plane component of the magnetization is unlikely to be responsible for the reduced polarization measured.

The other important consideration here is that spin-polarized photoemission is a surface technique, and thus has a significant signal contribution from the surface. The surface is not the bulk for high polarization materials [2–4]. There is certainly the possibility that the surface is not stoichiometric [2, 3], and thus that the surface polarization reflects the lower polarization of a more Fe or Co rich pyrite, or the possibility that while the surface is on average stoichiometric, the mixed metal pyrite phase separates at the surface. In either case, the surface would essentially not be the same material as the bulk. What must be considered however is that this small spin polarization might occur due to minority spin states close to the Fermi level, which have been identified to exist for the pure CoS$_2$(100) surface [21]. These minority spin states would provide a surface signal that would diminish the net spin polarization observed from the majority spin states, causing a decrease in the measured surface spin polarization. Consistent with this hypothesis is the fact that we find strong evidence for Fe–S and Co–S hybridization that scales as expected with the respective iron and cobalt concentrations.

### 4. Sulfur–cobalt and sulfur–iron hybridization

Figure 2 shows broad features in the photoemission spectra with binding energies between $-3$ and $-8$ eV with strong S 3p band weight [6, 21, 24] and strong dispersion with photon energy [24]. To demonstrate that these valence band features do contain some Co and Fe contributions, and hence show the essential transition metal hybridization with the S bands, resonant photoemission experiments were undertaken. Figure 2 illustrates some of the normal emission photoemission spectra of Co$_{1-x}$Fe$_x$S$_2$ thin films with $x = 0$ and 0.15 for photon energies from 45 to 75 eV, although it must be noted that films with $x = 0, 0.05, 0.10$ and 0.15 all exhibit similar behavior. After flux normalization, the data of figure 2 show a sharp peak in the intensity of the largely S-based initial state around 62 eV, as plotted in figure 3. This
Figure 3. Photoelectron intensities of the dispersing sulfur bands from $-3$ to $-8$ eV binding energy, as a function of photon energy, for the mixed transition metal pyrite $\text{Co}_{1-x}\text{Fe}_x\text{S}_2$, $x = 0$ (a), 0.05 (b), 0.10 (c) and 0.15 (d).

clear resonant photoemission enhancement of the valence band that begins at a photon energy near the Co 3p shallow core edge around 59 eV, and is indicative of a photoemission resonance due to excitations involving the cobalt 3p $\to$ 3d super-Coster–Kronig transition [24, 30]. With increasing Fe concentration in $\text{Co}_{1-x}\text{Fe}_x\text{S}_2$, there is another small resonant enhancement of the sulfur bands from $-3$ to $-8$ binding energy at a photon energy of about 56 eV, as seen in the photoemission intensity plots of the sulfur weighted bands (figure 3). This is yet another clear resonant photoemission enhancement occurring near the Fe 3d core edge around 52 eV, caused by excitations from the Fe 3p–3d transition [30].

The hybridization between both Fe and S and Co and S is thus demonstrated and the resonant photoemission ratio of intensities is consistent with the nominal stoichiometry.

5. Conclusion

We have measured a significantly smaller spin polarization ratio than the measured bulk value of 85% in $\text{Co}_{0.85}\text{Fe}_{0.15}\text{S}_2$ [12, 13], and significantly smaller than the expected polarization of more than 40%, given the experimental conditions. The surface of these mixed metal pyrites are spin polarized at least to the extent of 8–10%, but may well be dominated by minority spin surface states. The resonant photoemission data for different Fe concentrations in $\text{Co}_{1-x}\text{Fe}_x\text{S}_2$ demonstrate that the sulfur bands have both cobalt and iron contributions, i.e. both iron and sulfur and cobalt and sulfur hybridize. The valence band photoemission enhancement contribution, due to the characteristic iron 3p $\to$ 3d super-Coster–Kronig transition, increases with increasing Fe concentration relative to the valence band photoemission enhancements caused by the cobalt 3p $\to$ 3d super-Coster–Kronig transition.

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