Towards a full Heusler alloy showing room temperature half-metallicity at the surface

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Abstract
In this paper we investigate the surface spin polarization in a 100 nm Co\(_{2}\)Cr\(_{0.6}\)Fe\(_{0.4}\)Al film grown ex situ epitaxially on MgO(100) with a 10 nm Fe buffer layer by means of spin-resolved photoemission. We show that a careful in situ preparation of the sample surface leads to values for the room temperature spin polarization up to 45% at the Fermi level. To our knowledge, this is the highest value measured so far at the surface region of a full Heusler alloy at room temperature.

1. Introduction
The success of modern spintronics devices, i.e. devices relying on the electron spin as carrier of information, depends crucially on the ability to store, transport and manipulate the spin state of an electron within a properly chosen material system. While storage is traditionally accomplished by the use of magnetoresistive effects in magnetic multilayer systems (like in MRAMs), transport and manipulation of spin can be addressed through the use of (partly) semiconductive materials, where typical spin diffusion lengths are much larger and material properties can be tuned precisely to establish a coupling to external fields for coherent spin manipulation purposes [1]. However, the conductivity mismatch [2, 3] between ferromagnetic metals and semiconductors which hinders efficient spin injection is still an unsolved issue. There are two possible approaches to overcome this issue [4]: realize pure semiconductor devices (for which ferromagnetic semiconductors are needed) or search for new materials exhibiting large carrier spin polarization. A promising class of materials for the latter possibility consists of half-metallic Heusler alloys, exhibiting metallic behaviour for one spin direction and a band gap for the other. This should lead to a full spin polarization \( P \) at the Fermi level \( E_F \), which is more generally defined as the normalized difference of spin up and spin down electron occupation numbers with respect to a certain energy and given quantization axis:

\[
P(E) = \frac{N_{\text{up}}(E) - N_{\text{down}}(E)}{N_{\text{up}}(E) + N_{\text{down}}(E)}
\] (1)

In order to be attractive for technical applications, a Heusler alloy should satisfy, in principle, three requirements: such a material should show a full polarization: (i) at \( E_F \) (i.e. be a half-metal), (ii) not only in bulk but up to the very surface region, and (iii) at room temperature.

The fabrication quality of such alloys is improving steadily. This is shown, for example, in the case of Co\(_2\)FeSi by the increasing coherence between measured and predicted values for the element-specific number of magnetic moments \( \mu_B \) per unit cell [5, 6]. However, the connection to the spin polarization at \( E_F \) as the relevant parameter is not straightforward and relies heavily on the chosen model potential in calculations.

To our knowledge, a Heusler compound satisfying all conditions (i),(ii) and (iii) has not yet been reported. Half-metallicity has been experimentally verified in NiMnSb but only for the bulk material and at \( T = 27 \) K [7]. On the other hand, surface sensitive techniques failed to demonstrate half-metallicity of such a compound. It is not straightforward that the surface region of a Heusler alloy will show the same electron spin polarization (ESP) as the bulk material. In principle, extrinsic as well as intrinsic mechanisms may reduce
the spin polarization at the surface. Among the extrinsic mechanisms, chemical and magnetic disorder have been discussed to play a relevant role [8, 9]. Intrinsic mechanisms, which take place also at perfectly ordered surfaces, are for example magnetic fluctuations and modifications in the surface band structure with respect to the bulk one. In a recent publication, Kolev et al [10] have investigated the (100) surface of NiMnSb using spin-resolved appearance potential spectroscopy and found a significantly reduced spin asymmetry with respect to calculations based on the bulk electronic structure. By a careful analysis, the authors could exclude chemical disorder, structural defects at the surface as well as overall stoichiometric disorder as responsible mechanisms for the observed reduction of spin polarization. In another paper Wang et al [24] have investigated the CCFA film. The spin-resolved photoemission experiments were performed in a separate UHV system with a base pressure of \( <10^{-10} \) mbar, equipped with an Ar\(^+\) sputter gun. Surface characterization is achieved by LEED as well as Auger analysis and by identifying characteristic features of the photoemission spectrum. The latter is obtained by irradiating the sample with the s-polarized 4th harmonic (photon energy 5.1 eV) of a 100 fs Ti : Sapphire oscillator (Spectra Physics Tsunami). The laser light angle of incidence is set by geometry to 45°, while the spectra are taken in normal electron emission. Spin-resolved photoemission spectra are recorded by a commercial cylindrical sector analyzer (Focus CSA 300) equipped with an additional spin detector based on spin-polarized low-energy electron diffraction (Focus SLEED). The achieved energy resolution is 150 meV, the acceptance angle of the analyzer is ±13°. For the measurements the films are remanently magnetized by an external in-plane magnetic field.

3. Sample preparation and pre-characterization

The CCFA thin films were prepared on an Fe buffer layer on MgO(1 0 0) substrates and capped by an Al layer. Details on sample preparation and characterization can be found in [25]. Briefly, the substrates were annealed \( \text{ex situ} \) in an oxygen atmosphere at \( T = 950 \) °C immediately before loading into the UHV chamber. The 10 nm Fe buffer was deposited by electron beam evaporation and grows epitaxially in (1 0 0) orientation as shown by RHEED. The CCFA films (typical thickness 100 nm) were deposited by dc magnetron sputtering in argon at a pressure of \( 6 \times 10^{-2} \) mbar from a stoichiometric target. The substrate temperature amounted to \( T = 100 \) °C during deposition. Those samples already show the B2 structure as demonstrated by x-ray diffraction [25], but the degree of order is improved by an annealing step at \( T = 600 \) °C at a pressure of \( p \approx 10^{-4} \) mbar. After annealing a well ordered surface of the samples is observed by RHEED [26]. The Al capping layer with a thickness of 4 nm was deposited by dc magnetron sputtering after the annealing step. The thickness of all layers was determined by x-ray reflectometry. Before characterization with spin-resolved photoemission, the magnetic properties of the sample were studied \( \text{ex situ} \) using the magneto-optical Kerr effect. A fourfold in-plane anisotropy was reported [27], reflecting the crystallographic symmetry of the CCFA film.

4. In situ sample treatment

In order to obtain reproducible results with spin resolved photoemission, the (1 0 0) surface of the the sample has to be carefully prepared \( \text{in situ} \). Since this experimental technique is sensitive to the surface region [28], the protecting Al cap layer has to be carefully removed. A further reason requiring a careful preparation is that the crystal structure of CCFA easily allows for atomic disorder, either by interchange of atoms or by partial occupancy [12].

Due to the critical role played by the preparation procedure, we will describe it in detail.

(A) As a first step, the Al cap layer was removed from the sample by means of 5 to 10 cycles of Ar\(^+\) sputtering at moderate rates. More in detail, in each sputtering cycle the sample was sputtered with Ar ions with a kinetic energy of 500 eV and an angle of incidence of respectively +65° and −65° with respect to the surface normal. The sputtering time was 10 min for each angle of incidence. In general, 5 to 10 cycles were sufficient to remove the Al cap layer. Its successful removal was checked by means of Auger spectroscopy and by monitoring the changes in the photoemission spectrum.

(B) The sample was heated at 300 °C for 12 h before the first characterization attempts.

(C) Without further treatment, the prepared surface shows no LEED patterns, and the measured polarization is identically zero over the whole spectral range of about 2 eV below \( E_F \).
(D) As a next step, the sample was treated with further (again 5 to 10) sputtering cycles with the same parameters as those described in (A). After every sputtering cycle, the sample was heated at 300 °C for 10 min. After these sputter/heat treatments, a first LEED pattern was observable: this gives a clear indication that this preparation step is needed in order to achieve a certain degree of surface geometrical order.

(E) In the last step, a sputtering cycle (same parameters as in (A)) was applied while the sample was held at 300 °C. After sputtering the sample was heat flashed for approximately 1 min to 450 °C. The last step was repeated before each measurement and assures the reproducibility of the obtained results.

5. Experimental results and discussion

Figure 1(a) shows a LEED image obtained from the sample after the steps (A) to (D) of the in situ preparation procedure described in section 4. The picture was recorded at 88 eV primary electron energy and demonstrates a clear fourfold symmetry in correspondence with the cubic bulk lattice. If the step (E) is also applied, then the LEED pattern obtained from the sample is shown in figure 1(b). The picture was recorded at 100 eV primary electron energy. Compared with figure 1(a), figure 1(b) shows a clearer LEED pattern, demonstrating that the preparation step (E) leads to a better rearrangement of the surface atoms.

Figure 2 shows on the left scale the spin resolved photoemission spectra recorded from CCFA after the steps (A) to (D) of the in situ preparation procedure described in section 4, i.e. corresponding to the LEED pattern of figure 1(a). The spectra for the majority electrons ($N_{up}$) are represented with filled triangles, the one for minority electrons ($N_{down}$) with filled squares. They show the Fermi level $E_F$ (showing up at 0 eV in the chosen binding energy scale) and a monotonous increase in the photoemission yield up to $\sim$0.9 eV. The low-energy cutoff is approximately at 1.2 eV. The ESP, calculated from those two curves using equation (1), is shown in the same picture on the right scale (filled circles). Overall, the ESP does not reach values higher than 10%. In particular, it starts from 2.5% at the low-energy cutoff, and shows three peaks at 0.6, 0.4 and 0.2 eV. Then, it decreases again towards $E_F$ to reach $P(E_F) \sim 5\%$, well below the expected value of 100%.

Figure 3 shows on the left scale the spin resolved photoemission spectra recorded from CCFA after the full in situ preparation procedure (steps (A) to (E)), i.e. corresponding to the LEED pattern of figure 1(b). Again, the spectra for the majority electrons are represented with filled triangles, the one for minority electrons with filled squares. In this case, the two spectra have remarkably different intensities, resulting in the ESP depicted with filled circles on the right scale. Between the low-energy cutoff ($\sim$1.1 eV) and 0.4 eV binding energy, the ESP assumes values between approximately 35% and 30%, then it increases more or less steadily and reaches the value $P(E_F) \sim 45\%$. This value is to our knowledge the highest spin polarization at the surface region reported so far by means of spin-resolved photoemission from a full Heusler alloy at room temperature. The remarkable difference
in the absolute value and energy dependence of the ESP in figures 2 and 3 is a clear indication for the extreme importance of the surface preparation procedure prior to the measurements. Indeed, Correa et al [29] have reported for the half Heusler alloy NiMnSb(100), that an optimized annealing process after sputtering is essential to restore the bulk stoichiometry of the surface, disturbed by the previous sputtering. Evidence for such behaviour was taken from the analysis of normal-emission ultraviolet photoemission spectra.

The specific surface treatment described in our paper is the result of an empirical optimization of the surface preparation prior to the measurements, aimed to reach the highest possible value of the surface spin polarization. The achieved results show that for this particular Heusler alloy, the reduction of the surface spin polarization can be—at least partially—circumvented by selecting an adequate preparation procedure. This is of course very important also for the production of spintronics devices, where surface and interface between different materials play a crucial role for the injection of spin polarization.

At this point, we would like to spend some words about the reproducibility of the obtained results. We have measured different CCFA films, all prepared under the same conditions. Indeed, by following the steps (A) to (E) of the in situ preparation procedure described in section 4, the measured ESP and the spin-resolved photoemission spectra shown in figure 3 are obtained every time. Moreover, if after the measurements the sample is exposed to air for up to 1 day, and afterwards the step (E) is applied (2 or 3 times), then the spin polarization can be fully recovered.

The fully reproducible increase in the ESP towards E_F in figure 3 is a clear indication of the presence of a band gap (at least partial) for the minority electrons, as expected from theoretical calculations [20]. However, at this point we have to note that photoemission from a single crystal gives information only about direct transitions taking place near the surface Brillouin zone center. Thus, the comparison of our experimental data with density of states (DOS) calculations, as the one reported in [20], can be only qualitative. Further angle- and spin-resolved measurements are planned in the next future. Together with band structure calculations (including correlations effects) this will give further precious information about the electronic band structure of the CCFA Heusler alloy.

6. Conclusions

In this paper we have found an optimized preparation procedure for the (100) surface of the full Heusler alloy Co2Cr0.5Fe0.4Al. Applying such a procedure, we have obtained a room temperature surface spin polarization of 45% at the Fermi level by means of spin-resolved photoemission. To our knowledge, this is the highest value reported so far by means of a surface sensitive experimental technique. We proposed that implementing such a procedure could lead to a better performance of spintronics devices based on Heusler alloys.

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