

# Hybridization-induced charge rebalancing at the weakly interactive $C_{60}/Fe_3O_4(001)$ spinterface



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## ABSTRACT

Spin injection in organic and molecular spintronic devices is largely defined by the electronic and magnetic structure of the constituting organic/ferromagnetic “spinterfaces”. Unlike most of the previous studies involving highly interactive organic/metallic interfaces, we present here the valence electronic structure of a weakly hybridized interface between  $C_{60}$  and epitaxial  $Fe_3O_4(001)$ , which is unraveled for the first time by means of synchrotron-based photoelectron spectroscopy. Using resonant excitation of Fe  $2p$  core electrons into the unoccupied  $3d$  states, we are able to extract the effect of  $C_{60}$  adsorption on the different ionic sites of the mixed valence magnetic oxide. We elucidate, using a proposed model, that electron donation from  $C_{60}$  leads to surface charge rebalancing in  $Fe_3O_4$ , which is accompanied by an enhancement of the conductivity, where the half-metallic nature of the ferrite is largely preserved. These observations, which have so far not been reported for existing organic/metallic systems, are expected to play a significant role in spin transport across this novel interface. Our work showcases the fascinating physical phenomena unique to organic/magnetic oxide spinterfaces, and offers a new pathway towards interface engineering for organic spintronic applications.

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## 1. Introduction

Conventional electronics relies exclusively on electronic charge, which makes it difficult to fulfill the intensifying problem of downscaling electronic components. One of the existing research fields that could lead to viable alternatives is organic spintronics, exploiting both the charge and spin degrees of freedom of charge carriers in organic semiconductors [1–3]. On the one hand, spintronics provides approaches to achieve nonvolatile data processing and storage functionalities via manipulation and readout of spin as well as charge [4]. On the other hand, light carbon-based semiconductors exhibit weak spin-orbit coupling, which leads to intrinsically long spin lifetime, besides being low-cost, physically flexible, and chemically tunable [5,6].

In the context of organic spintronics, the “spinterface” between organic semiconductors and ferromagnetic materials plays a pivotal role in determining magneto-transport properties of spin devices [3,7–9]. As evidenced previously, the formed organic/ferromagnetic interfaces possess unique spin polarization, different from those of the magnetic layers, due to (strong) orbital hybridization at their interfaces [10–12]. When properly engineered, such interfacial hybridization effects can be employed to manipulate spin injection efficiency [13]. However, this necessitates in-depth knowledge of a range of organic/ferromagnetic interfaces exhibiting different interaction strengths, in which the weakly hybridized ones have been rarely investigated so far [14,15]. As a pilot study in this regard, we earlier demonstrated a novel interface formed by  $C_{60}$  molecules and ultrathin ferrimagnetic  $Fe_3O_4$  films, epitaxially grown on  $GaAs(001)$  [14]. The choice of this particular combination is largely motivated by a number of attractive attributes: (i)  $Fe_3O_4$  is known for its exceptionally high Curie temperature of 850 K, and (ii) its high spin polarization of 81% at the Fermi level measured at room temperature (RT) [16]; even though full polarization has been predicted by density-functional calculations [17]. (iii)  $C_{60}$  is highly stable and easily forms high-quality molecular films via thermal

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evaporation. In terms of device applications, exceptionally weak hyperfine interaction is present in  $C_{60}$ , due to an absence of hydrogen nuclei and low natural abundance of  $^{13}C$  nuclear spins [18–20]. Using X-ray magnetic circular dichroism (XMCD), we have previously confirmed a significantly weaker orbital hybridization at the  $C_{60}/Fe_3O_4$  interface, manifested as a carbon  $K$ -edge dichroic signal of only 1% [14], versus those for more interactive interfaces, such as 3% in  $C_{60}/Fe(001)$  [11] and 5% in graphene/ $Ni(111)$  [21]. Remarkably, due to the higher work function of  $Fe_3O_4$ , electron donation from the molecules, that is normally not occurring on  $3d$  transition metals, has been seen to trigger cation redistribution and modification of spin and orbital magnetic moments of the ferromagnetic surface [14].

In this article, using synchrotron-based photoelectron (PE) spectroscopy we paint a full picture of the  $C_{60}$ -induced electronic modifications in  $Fe_3O_4$ . By resonantly exciting  $Fe$   $2p$  core electrons into the unoccupied  $3d$  states, we unravel for the first time the effect of  $C_{60}$  adsorption on the valence electronic structure contributed by each of the three cation sites of an epitaxial  $Fe_3O_4(001)$  ultrathin film. Our results suggest that electron charge is transferred due to hybridization from  $C_{60}$  to the  $t_{2g}$ -band of B- $Fe^{2+}$ , followed by charge rebalancing occurring between this band and the  $t_{2g}$ -band of A- $Fe^{3+}$  site. These electronic processes then result in an enhancement of the charge conductivity and a preservation of half-metallic property of  $Fe_3O_4$ . These findings illustrate the intriguing properties unique to the weakly interactive interfaces, which are expected to play a significant role in spin transport in relevant organic spintronic devices.

## 2. Experimental

The experiments were performed on beamline D1011 at the MAX-IV Laboratory in Lund, Sweden. The end-station of D1011 houses a joint analysis/preparation chamber, with a base pressure of  $10^{-10}$  mbar, for core-level/valence-band PE spectroscopy, X-ray absorption (XA) spectroscopy, and XMCD. The PE spectroscopic measurements were carried out using a Scienta SES-200 hemispherical analyzer, at an incident angle of  $45^\circ$  of the X-ray beam relative to the sample normal, *i.e.*, at normal emission. XA spectra were collected at RT in total-electron-yield mode, in which the sample drain current is recorded, at the same photon incident angle, as a function of photon energy. XMCD spectra were obtained at remanence, after magnetization of the sample in an external field of 0.1 T along the X-ray beam, followed by taking the difference in absorption intensity measured for left- and right (75%) circularly polarized X-rays.

The stoichiometric  $Fe_3O_4(001)$  ultrathin film was prepared as described previously [14,22–25]. Briefly, the epitaxial film was fabricated *in situ* by post-growth annealing of a 3 nm thick Fe film on a clean GaAs(001) substrate at  $230^\circ C$  in an  $O_2$  partial pressure of  $8 \times 10^{-5}$  mbar. Subsequent deposition of  $C_{60}$  molecules onto the oxide surface was done at RT, using a home-made Knudsen cell. The nominal  $C_{60}$  thicknesses were calibrated *in situ* by estimating the attenuation of the characteristic PE peaks of the oxide. All stages of the sample preparations were carefully monitored by low-energy electron diffraction (LEED) in combination with PE spectroscopy.

## 3. Results and discussion

Fig. 1(a) shows a schematic atomic arrangement of  $Fe_3O_4$  on GaAs(001). For hetero-epitaxy, the {100} surfaces of the oxide offer the best atomic registry [22]. With a cube-on-cube growth mechanism, a lattice mismatch as low as 5% can be achieved upon a  $45^\circ$  rotation between the two unit cells. Such an epitaxial growth has been verified by LEED, see Fig. 1(b). Both first- and half-order

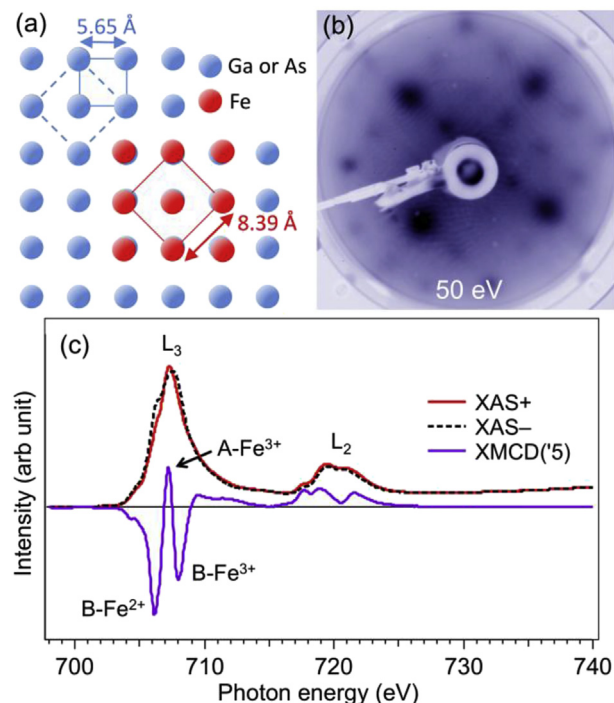


Fig. 1. (a) Atomic arrangement of  $Fe_3O_4(001)$  unit cell atop GaAs(001). (b) LEED pattern of  $Fe_3O_4(001)$ , taken at an electron energy of 50 eV, by *in-situ* oxidation of a 3 nm thick epitaxial Fe ultrathin film on GaAs(001). (c)  $Fe$   $L_{2,3}$ -edge XAS and XMCD spectra of the  $Fe_3O_4$  obtained at remanence by taking the difference between the XAS spectra recorded with opposite photon helicity. The sample has been magnetized *in-situ* in a 0.1 T external field prior to the dichroic measurements.

diffraction spots on a cubic plane are clearly observed, thus indicating the expected inverse spinel structure of  $Fe_3O_4$ . On the other hand, being a mixed-valence material with a well-defined  $Fe^{3+}/Fe^{2+}$  ion distribution, the stoichiometry and oxidation state of  $Fe_3O_4$  can be further confirmed by XMCD [22–25]. Fig. 1(c) shows the  $Fe$   $L_{2,3}$ -edge XA and XMCD spectra of the ferrite prior to  $C_{60}$  deposition. In the XMCD spectrum, the three peaks at the  $L_3$ -edge correspond to the three different Fe cation environments. The two negative peaks at 705.8 and 707.5 eV arise from the B- $Fe^{2+}$  and B- $Fe^{3+}$  cations, respectively, while the positive peak at 706.7 eV stems from the A- $Fe^{3+}$  sites, where B (A) indicates octahedral (tetrahedral) symmetry. The opposite sign of the peaks arises from the antiferromagnetic coupling between the A-site and B-site sublattices. These key features, which closely resemble those of their bulk counterpart [26], demonstrate the high quality of the initial  $Fe_3O_4(001)$  surface for subsequent  $C_{60}$ -related measurements as discussed below.

We first focus on the evolution of the  $Fe_3O_4$  surface electronic structure, upon stepwise  $C_{60}$  deposition, characterized by means of PE spectroscopy. The survey PE spectra in Fig. 2(b) reveal that, as the  $C_{60}$  thickness increases, the C 1s peak becomes more intense, while the Fe  $2p$  and O 1s intensities are suppressed. For completeness, the spectra corresponding to the clean GaAs(001) substrate and the Fe ultrathin film have been included in Fig. 2(b) as reference data. The valence band PE spectra of the same sample depositions are shown in Fig. 2(c). It is apparent that the as-deposited Fe film exhibits a sharp Fermi edge, typical for  $3d$  transition metals, and also a small bump at  $\sim 6$  eV, marked by a black arrow. The spectral weight of the later, which is absent in pure Fe, might originate from the  $2p$  orbitals of a tiny amount of O adsorbate, as previously seen in other studies [27]. The presence of such impurities, however, does not play a role here, since the metallic

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