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To cite this article: M Fonin et al 2008 J. Phys.: Condens. Matter 20 142201

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Spin-resolved photoelectron spectroscopy of Fe₃O₄—revisited

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Received 12 February 2008
Published 7 March 2008
Online at stacks.iop.org/JPhysCM/20/142201

Abstract
Recently Tobin et al (2007 J. Phys.: Condens. Matter 19 315218) reported on the spin-resolved photoemission study of Fe₃O₄(001) films, claiming magnetite being a case against half-metallicity. In the present communication we re-examine recent spin-resolved photoemission experiments on Fe₃O₄ and explain why their criticism is unfounded.

The materials class of half-metallic ferromagnets comprising Heusler alloys [1, 2] and transition metal oxides such as CrO₂ [3] and Fe₃O₄ [4, 5] attracts continued interest because of its intriguing potential as spin-injector material in magnetic tunnel junctions or in spintronic devices. A particular challenging case is Fe₃O₄, which can be grown epitaxially as thin films with (111) and (001) orientation. The spin polarization values of both orientations at the Fermi energy determined by spin-polarized photoelectron spectroscopy (SP-PES) have given rise to different conclusions. Interpretations were put forward in the framework of either the ionic-configuration-based approach [5] or a band-type approach [4]. Such data have also been interpreted as proof against half-metallicity of Fe₃O₄ [5]. However, STM and electronic structure calculations provided evidence of surface reconstructions, at least for the (001) orientation [6], pointing to the limited applicability of surface sensitive PES measurements at low photon energies to elucidate bulk properties.

Our SP-PES investigations of Fe₃O₄(111)/W(110) showed at room temperature a spin polarization of −80% near the Fermi energy, $E_F$ [7] (see figure 1). In this paper we pointed out (p 64417-3, second-to-last paragraph) that a ‘spin polarization value by itself is no proof of a half-metallic state’. This caution on our part was obvious in view of the reference material Fe(110) showing also −80% spin polarization near $E_F$. In contrast, Tobin et al [5] claimed that we had concluded from the small region in $k$-space accessible by our experiment the half-metallic nature of Fe₃O₄. This is definitely incorrect. Instead, we took the result of $P = −80\%$ as indicative to abolish the ionic-configuration-based approach [8], setting an upper limit of $P = −66.6\%$, and followed a band-type description. Indeed, distinct dispersion was found for O(p)-derived and Fe(d)-derived bands of Fe₃O₄(111) [9]. By correlating spin-resolved features in the photoemission spectra with those in the electronic band structure calculations, very good agreement was found along the [111] direction [7]. We took these facts and the observed emergence of a band gap in the spin-up spectra upon oxidation of the Fe(110) film to yield Fe₃O₄(111) [7] as evidence for a half-metallic state of Fe₃O₄ with a (111) orientation.

The (001) orientation of Fe₃O₄ is yet another interesting case in the present context. It has been pointed out in the literature that strain in Fe₃O₄ films may play a crucial role and affect the electron spectroscopy data. A good measure of strain relief in thin films is the sharpness of the temperature-dependent Verwey transition near 120 K. As an example we show in figure 2 the magnetization as function of temperature of one of our epitaxial Fe₃O₄(001) films grown on MgO(001), confirming the very high quality of the films. In contrast, the Verwey transition of a so-called strain relieved Fe₃O₄ film in figure 2 of [5] is very much smeared out.

Tobin et al [5] performed SP-PES measurements on Fe₃O₄(001)/MgO(001) thin films, prepared by dc sputtering or evaporation in oxygen and transferred ex situ to the UHV system. It is well known that transport through air inevitably leads to surface contamination and/or to reconstructed magnetically dead surface layers. For these samples an overlayer attenuation model with several assumptions was used to estimate the spin polarization of the underlying bulk as \( P_{\text{bulk}} = -65\% \pm 35\% \). This rather crude estimate was considered as supporting the ionic-configuration-based approach [8], arriving at the final conclusion that Fe₃O₄ is not a half-metallic ferromagnet. However, ill-defined surface properties may obscure the intrinsic properties. Moreover, the structural model of the surface reconstruction plays an important role in the interpretation of results. A recent \textit{ab initio} atomistic thermodynamics study based on density-functional theory (DFT) calculations [6, 10] identified the lowest energy configuration of the Fe₃O₄(001) surface to be a ‘polar’ termination with octahedral (B) iron and oxygen. This new insight has, unfortunately, not been taken into account in [5] which considered rather a tetrahedral iron termination with 50% occupation (half A layer). The predicted \textit{modified B layer} exhibiting a Jahn–Teller distortion of the surface atoms [6] reproduces the \textit{wavelike} \((\sqrt{2} \times \sqrt{2})\)R45° structure along the [110] direction found by STM as shown in figure 1(b). It is also supported by a quantitative LEED analysis [11]. This surface termination is also responsible for a half-metal-to-metal transition at the (001) surface [6]. Hence, in the SP-PES of Fe₃O₄(001)/MgO(001) we observe at room temperature near \( E_F \) a spin polarization of \(-55 \pm 10\%\) (see figure 1), which compares favorably with the theoretical value of \(-40\%\) [6]. The DFT-GGA polarization value results due to states appearing in the band gap of the spin-up band. However, while the Fe₃O₄(001) surface has lost half-metallicity, the calculated bulk spin-split electronic structure is still half-metallic.

Hence, we find a qualitatively different electronic behavior of Fe₃O₄ surfaces with the (001) and (111) crystal orientations, possibly reconstructing differently. Moreover, there is evidence that the intrinsic bulk properties are still consistent with half-metallicity.

References


Figure 1. (a) 20 × 20 nm² atomically resolved STM image of the Fe₃O₄(111) surface. (b) 50 × 50 nm² STM image of a \((\sqrt{2} \times \sqrt{2})\)R45° reconstructed Fe₃O₄(001) surface. (c) The spin polarization as a function of binding energy of Fe₃O₄(111) (full circles) and Fe₃O₄(001) (open circles).

(This figure is in colour only in the electronic version)

Figure 2. Temperature-dependent magnetization measurement of a 50 nm thick Fe₃O₄(001) film. Measurements of magnetization were performed upon warming up the samples in a magnetic field of 200 Oe applied in-plane along the [100] direction.