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Spin-resolved photoelectron spectroscopy of Fe₃O₄—revisited

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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.

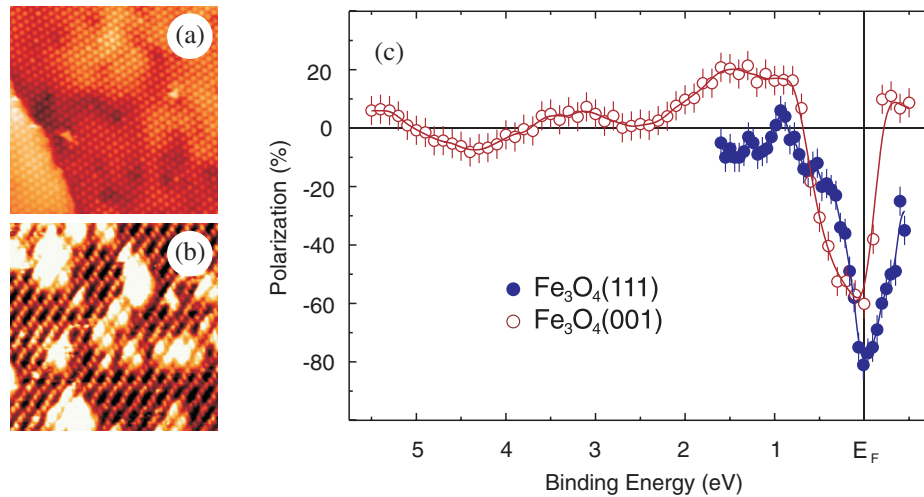


Figure 1. (a) $20 \times 20 \text{ nm}^2$ atomically resolved STM image of the $\text{Fe}_3\text{O}_4(111)$ surface. (b) $50 \times 50 \text{ nm}^2$ STM image of a $(\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ reconstructed $\text{Fe}_3\text{O}_4(001)$ surface. (c) The spin polarization as a function of binding energy of $\text{Fe}_3\text{O}_4(111)$ (full circles) and $\text{Fe}_3\text{O}_4(001)$ (open circles).

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

Tobin *et al* [5] performed SP-PES measurements on $\text{Fe}_3\text{O}_4(001)/\text{MgO}(001)$ 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 Fe_3O_4 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 *ab initio atomistic* thermodynamics study based on density-

functional theory (DFT) calculations [6, 10] identified the lowest energy configuration of the $\text{Fe}_3\text{O}_4(001)$ 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 *modified B layer* exhibiting a Jahn–Teller distortion of the surface atoms [6] reproduces the *wavelike* $(\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ 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 $\text{Fe}_3\text{O}_4(001)/\text{MgO}(001)$ 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 $\text{Fe}_3\text{O}_4(001)$ 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 Fe_3O_4 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.

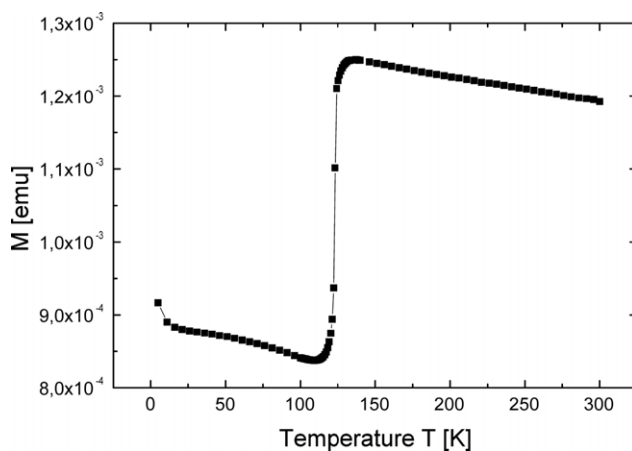


Figure 2. Temperature-dependent magnetization measurement of a 50 nm thick $\text{Fe}_3\text{O}_4(001)$ film. Measurements of magnetization were performed upon warming up the samples in a magnetic field of 200 Oe applied in-plane along the [100] direction.

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