Spintronics is the catch phrase for novel kinds of electronics that exploit the spin of charge carriers – electrons or holes – in addition to their charge. Massive efforts by scientists and engineers are underway to bring many exciting concepts in this field to fruition. It would be good if one could find a practical material where all the conduction electrons have the same spin orientation. Such a material could deliver electrical current that would be 100% spin-polarized, which could, for example, be used to flip magnetization domains in a device by simply sending a current through it. Magnetite, Fe₃O₄, is a presently considered one of the ‘hot’ magnetic materials. (It is, at the same time, a very old one. In fact, loadstone, as it is commonly known, was part of the earliest compasses. And bacteria synthesize magnetite and use it as a navigational tool to guide themselves into their preferred habitat [1]).

Density-functional theory (DFT) calculations for Fe₃O₄ predict that the minority spin band in Fe₃O₄ is metallic, while the majority band has a band gap [2]. This is exactly the property one is seeking; commonly called ferromagnetic half-metallic behavior. In addition, Fe₃O₄ has a high Curie temperature of over 800 K, which makes it particularly attractive for spintronics applications. It is still an issue of ongoing discussion whether or not this 100% spin polarization is really present in Fe₃O₄, see for example two articles in a recent focus issue on this topic [3,4]. (This matter is complicated by the fact that the material becomes insulating around 120 K, which makes it impossible to use Andreev reflection measurements as a litmus test for a ferromagnetic half-metal.) In any event, if one wants to use Fe₃O₄ as a spin source, the spin polarization would need to be preserved across its surface. Herein lies the crux of the problem: the most important low-index surface, Fe₃O₄(100), turns out to be polar.

Polar surfaces have a perpendicular, non-vanishing dipole moment, which in the established view leads to a high-energy, unstable situation [5]. In order to lift polarity, surfaces often reconstruct [6]. So does Fe₂O₄(100). A (\sqrt{2} \times \sqrt{2})R45° reconstruction has consistently been reported [7–10]. The models for this reconstruction vary, and so do the predicted consequences for ferromagnetic half-metallicity on the surface [11]. Based on DFT calculations, Pentcheva et al. [12] have previously made an interesting suggestion. They have proposed that the surface is fully stoichiometric and terminates with rows of octahedrally-coordinated Fe atoms, separated by oxygens (Fig. 1). (Fe₂O₄ contains both, octahedrally and tetrahedrally-coordinated Fe atoms in the bulk.) Their model contains a small, yet important modification to a bulk-like termination. Atoms are not aligned in straight rows, which is what one would get by just cutting the crystal. Instead, they form a wave with a periodicity that causes the (\sqrt{2} \times \sqrt{2})R45° symmetry. This structure is in very nice agreement with early STM studies [8] and an XRD analysis [12]. According to Pentcheva et al.’s previous DFT calculations, these ‘wiggles’ are sufficient to provide the lowest-energy surface for a wide range of oxygen chemical potentials. A Jahn–Teller-like distortion of the surface atoms was invoked as an explanation. This is a novel idea, and much different from other reconstructions of polar surfaces that typically involve non-stoichiometries and/or a re-arrangement of charges. Moreover, in Ref.

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Wiggling its way out of surface polarity: Fe₃O₄(100) (A Perspectives on the article: “A combined DFT/LEED approach for complex oxide surface structure determination: Fe₃O₄(011)” by R. Pentcheva, W. Moritz, J. Rundgren, S. Frank, D. Schrupp, M. Scheffler)

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[12], it was predicted that this modified structure has far less spin polarization than the bulk. In fact, it looses its half-metallicity. It is thus important that the proposed model be tested and confirmed experimentally.

Such an experimental verification is provided in a careful LEED study presented in this issue by Pentcheva et al. [13]. Compared to other structures that were tested, the ‘polaron’ structure shows by far the best agreement. A Pendry $R$-factor of 0.34 was achieved, which is a respectably low value for an oxide surface.

As an interesting technical aspect, the authors of Ref. [13] evaluate the effect of different scattering potentials on their LEED-I($V$) calculations. For multi-scattering calculations one typically uses muffin-tin potentials in order to calculate phase-shifts. Dividing up the crystal in muffin-tin spheres is a straightforward exercise for metals; one simply takes the neutral radii of the atoms. For ionic oxides it is questionable how this is best achieved, as an $O^2-$ ion is only stabilized by a solid’s Madelung potential, and the proper radius that one should use is not given a priori. It has recently been shown that estimating muffin-tin radii from DFT ground state charge distributions is a good approach. Lindsay et al. [14] describe how this reduced the $R$-factor by a factor of two for the $TiO_2(110)$ surface. For $Fe_3O_4$, as is shown in this article, virtually the same Pendry $R$-factors are obtained for both, DFT-derived and more traditional muffin-tin potentials, provided that the muffin-tin radii are chosen in a proper fashion [15].

The combination of first-principles DFT calculations and surface science experiments has become a very powerful tool to attack complex situations, and this article is a shining example. Reliable structure determinations of oxide surface are complicated by the fact that the unit cell is often large (certainly the case for $Fe_3O_4$), and that a surface can assume different terminations, depending on the preparation conditions. The authors have iterated between DFT calculations and LEED-I($V$) measurements to avoid getting stuck in local minima in the optimization process. Their study has provided much credibility to an unconventional solution of surface polarity in a technologically important material.

References


Fig. 1. (Fig. 10b in the article) Surface model of the ‘polaron’ structure of $Fe_3O_4(001)$-($\sqrt{2}\times\sqrt{2}$)R45°.