

# Ferroelectric Switching in Multiferroic Magnetite ( $\text{Fe}_3\text{O}_4$ ) Thin Films

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Recently, multiferroic materials, that is, materials that possess two or more ferroic properties, such as spontaneous electric polarization and magnetization in the same phase, have attracted a renewed interest of the scientific community.<sup>[1,2]</sup> Since the discovery of an unusual two-orders-of-magnitude increase in resistivity at around 120 K by Verwey,<sup>[3]</sup> magnetite has been studied intensively. While the magnetic properties of  $\text{Fe}_3\text{O}_4$  are relatively well known and understood, the electronic properties, mostly at temperatures below the Verwey transition  $T_V$ , are still under debate.<sup>[4]</sup> Above  $T_V$ , magnetite has an inverse spinel structure in which the iron occupies both the octahedrally and tetrahedrally coordinated cation positions. Relevant for the properties of magnetite seem to be the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions, which equally occupy the octahedrally coordinated cation sites (in the oxygen octahedra). At room temperature,  $\text{Fe}_3\text{O}_4$  is a ferrimagnetic material with a critical temperature as high as 860 K and metallic behavior. At the Verwey temperature, magnetite undergoes a first-order phase transition from a pseudocubic to a monoclinic structure. The concurrent metal-insulator transition has been related to a charge-ordering pattern consisting of an alternation of the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions on the octahedrally coordinated sites.<sup>[5,6]</sup> Magnetite was also one of the first materials studied regarding the magnetoelectric (ME) effect, that is, inducing an electrical polarization by an externally applied magnetic field and vice-versa.<sup>[7]</sup> Early studies on the ME effect have suggested the existence of a spontaneous polarization at temperatures below 38 K,<sup>[8–10]</sup> but final proof of ferroelectricity in magnetite has not yet been given.<sup>[11]</sup>

In single-phase multiferroic materials, materials in which ferroelectricity and magnetism coexist, the control of the magnetic properties by an applied external electric field or, in

contrast, the control and switching of the electrical polarization by a magnetic field, are especially appealing.<sup>[12,13]</sup> Additionally, new mechanisms of ferroelectricity that are fundamentally different from the classical displacive ferroelectrics, such as  $\text{BaTiO}_3$  or  $\text{PbTiO}_3$ , are proposed. For instance, magnetization can induce a certain dielectric polarization, such as in multiferroic manganites or hexaferrites, where a coupling between the magnetic and dielectric properties occurs due to a complex spin structure, characteristic of frustrated magnets.<sup>[14–18]</sup> Alternatively, charge ordering (CO) in certain materials, such as in  $\text{LuFe}_2\text{O}_4$ , might also induce a spontaneous polarization.<sup>[19]</sup>

Ferroelectric switching is usually difficult to experimentally demonstrate in these materials, mostly due to an intrinsic high conductivity. With a noticeable exception, where dynamic hysteresis loops have been measured in epitaxially stabilized hexagonal  $\text{TbMnO}_3$ ,<sup>[20]</sup> the polarization values of the new multiferroic materials have not been directly measured by dynamic switching processes, but rather indirectly, for example by measuring the pyroelectric current or magnetoelectric signals. We have to notice that the definition of ferroelectricity is rather restrictive.<sup>[21]</sup> The spontaneous polarization should be effectively switchable by an externally applied electric field. In addition, ferroelectrics are different from other systems, showing bistable dipolar states, such as electrets, by the switching time, which usually is very short, down to the nanosecond range.

Here, we present real-time switching of ferroelectric polarization and other ferroelectric properties of magnetite epitaxial layers in the temperature range from 4.2 K to about 40 K. We found that magnetite, the prototype of magnetic (oxide) materials, which possesses only cations that carry a magnetic moment, shows a sizable switchable polarization ( $2P_r$ ) of about  $11 \mu\text{C cm}^{-2}$  in the low-temperature range.

Epitaxial thin magnetite films were deposited on niobium-doped (100)-oriented  $\text{SrTiO}_3$  (STON) single crystals using RF magnetron sputtering or pulsed-laser deposition (PLD). Figure 1A shows a transmission electron microscopy (TEM) cross-section bright-field image and an electron-diffraction pattern (inset) of a 150 nm thick, epitaxial  $\text{Fe}_3\text{O}_4$ /STON heterostructure. Other structural investigations as well as basic magnetic and electrical properties are given in the Supporting Information (SI) or were published elsewhere.<sup>[22,23]</sup> In order to measure the ferroelectric properties, capacitor-like metal- $\text{Fe}_3\text{O}_4$ -metal structures were fabricated by deposition of top metal (Me) electrodes on the  $\text{Fe}_3\text{O}_4$  films to form Me- $\text{Fe}_3\text{O}_4$ -STON heterostructures.

At temperatures below the Verwey metal-insulator transition  $T_V$ , the magnetite becomes rather a semiconductor than an insulator, and the heterostructure becomes a metal-

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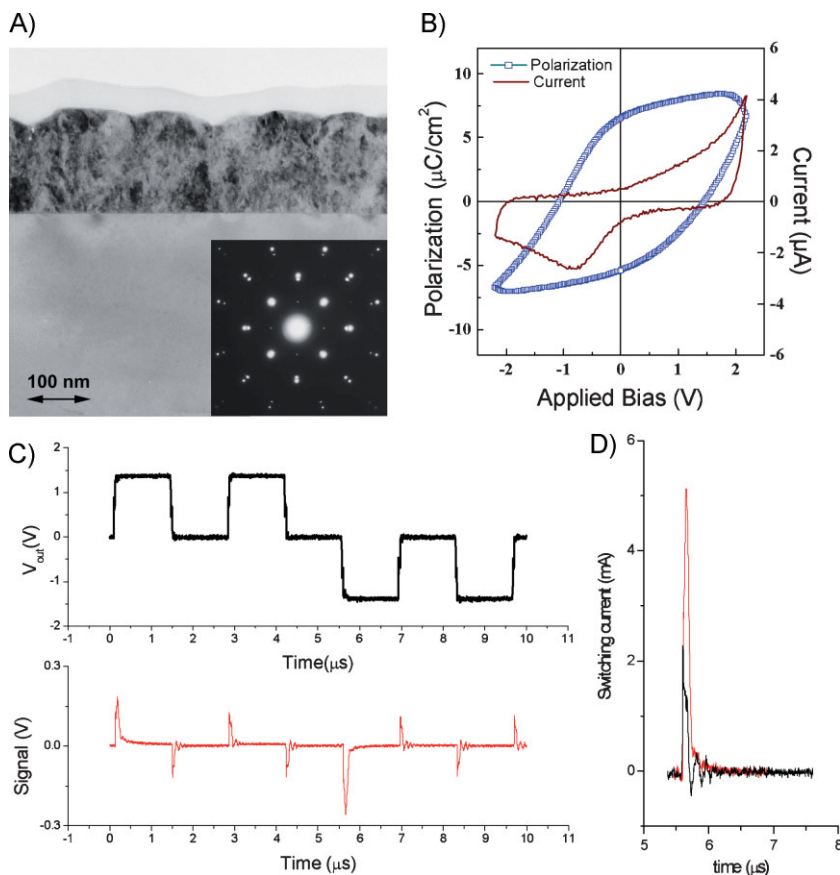
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semiconductor–metal structure. The resistivity of  $\text{Fe}_3\text{O}_4$  even at temperatures well below  $T_v$  is rather low and the leakage currents are hindering direct polarization measurements. Fortunately, at temperatures below  $T_v$  the  $\text{Fe}_3\text{O}_4$ -STON heterojunctions show Schottky behavior, with a barrier of about 0.11 eV and an ideality factor approaching unity, which corresponds to fairly good rectifying properties.<sup>[24]</sup>

As it was pointed out by Vanderbilt, an insulating or blocking interface would be sufficient to show the presence of polarization.<sup>[25]</sup> The blocking contacts minimize the free-carrier transport, rendering the discrimination of displacive currents from leakage possible, thus enabling polarization measurements, as in the case of InP.<sup>[26]</sup> Furthermore, by choosing an appropriate metal for the top electrode, the band alignment can be tuned such as to optimize the leakage, as we have shown in the case of epitaxial PZT layers.<sup>[27]</sup>

Here, in the case of  $\text{Fe}_3\text{O}_4$ , we have established that, among several noble metals (Au, Pt, Ag, and Pd) as well as  $\text{SrRuO}_3$ , palladium showed the lowest leakage behavior when used as top electrode. This has enabled the direct measurement of dielectric hysteresis loops on Pd- $\text{Fe}_3\text{O}_4$ -STON heterostructures at low temperatures using a commercial ferroelectric tester. The dielectric hysteresis loop shown in Figure 1B is well saturated at negative applied bias, whereas at positive biases a significant contribution of the leakage current inflates the hysteresis loop, although at temperatures well below  $T_v$  the intrinsic conductivity of  $\text{Fe}_3\text{O}_4$  decreases further. Knowing that in certain cases a not-well-saturated loop might not be a proof of ferroelectricity,<sup>[28]</sup> we have used the fast voltage pulses, that is, the so-called positive-up-negative-down (PUND) test, to evaluate the switchable ferroelectric polarization.<sup>[29]</sup>

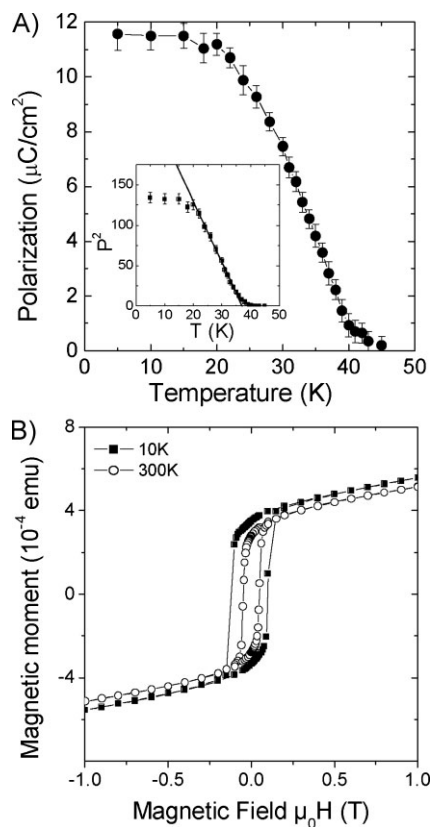
The applied voltage waveform and a raw switching signal are shown in Figure 1C. Switching current pulses and the corresponding nonswitching pulse are shown in Figure 1D. The switching current peaks are about 250 ns wide and several times higher than the corresponding nonswitching currents. The variation of the switchable polarization with temperature, calculated by integration of the current peaks and subtracting the nonswitching contribution, is shown in Figure 2A.<sup>[29]</sup> As is known, below the Verwey temperature  $\text{Fe}_3\text{O}_4$  lowers its symmetry from cubic to monoclinic. Magnetoelectric and X-ray studies showed that below 38 K magnetite lowers once more its symmetry to triclinic.<sup>[9,30]</sup> In our case of epitaxial thin  $\text{Fe}_3\text{O}_4$  films on (100)  $\text{SrTiO}_3$ , most probably the c-axis is in-plane; this is consistent with results on single crystals, showing that after cooling through the Verwey transition under compressive stress the c-axis is oriented along an axis of compressive stress<sup>[31]</sup> and further with results on magnetite films on MgO that are under tensile strain and have a preferential c-axis orientation along the film normal.<sup>[32]</sup> Thus, the



**Figure 1.** Ferroelectric characterization of a Pd- $\text{Fe}_3\text{O}_4$ -STON heterostructure. The 150 nm thick  $\text{Fe}_3\text{O}_4$  epitaxial film was deposited by PLD (most similar results for a sputtered film are shown in Fig. S5, SI). A) Cross-section TEM bright-field image, and corresponding selected area diffraction pattern demonstrating epitaxial growth. B) Dielectric hysteresis loop and switching current acquired at 4.2 K and a frequency of 1 kHz; the hysteresis loops acquired from 100 Hz to 2 kHz are essentially the same, except for a higher contribution of the leakage current at lower frequencies. C) PUND waveform and switching signal obtained on a 50  $\Omega$  load resistance at 15 K; D) current peaks associated with the switching polarization (red) and corresponding non-switching polarization (black). The ripples in the signal are due to the impedance mismatch between the pulse generator and the cryogenic probing station.

measured polarization in the present work is the value of the polarization projected on the a–b plane, although an intricate ferroelastic domain pattern cannot be ruled out.

The switchable polarization decreases continuously from about  $11 \mu\text{C cm}^{-2}$  at 20 K to zero at about 38 K. The measured polarization values might be influenced by the residual strain due to epitaxial growth, as in the case of single crystals the mechanical stress has been proven to have an important influence on crystal twinning and the magnetoelectric effect.<sup>[9]</sup> The relatively good linear fit of  $P^2$  versus  $T$  at temperatures close to (below) the transition temperature (inset in Fig. 2A) suggests that the phase transition at about 38 K is second-order. The large polarization values and the second-order-like phase transition might let to speculate on a pure electronic ferroelectricity based on itinerant  $d$  electrons, as proposed by Portengen et al.<sup>[33]</sup> However, the dielectric constant (Fig. S7 of SI) does not diverge as expected for a second-order phase transition as in the case of normal ferroelectrics. It behaves similarly to  $\text{LuFe}_2\text{O}_4$ ,<sup>[19]</sup> suggesting that



**Figure 2.** A) Switching polarization ( $2P_s$ ) measured using the PUND waveform shown in Figure 1C as a function of temperature. The plotted values are average values obtained in ten consecutive measurements and the error bar represents the corresponding statistical error; above the transition temperature the leakage increases drastically hindering proper measurements. The inset shows a plot of  $P^2$  versus  $T$  and the linear fit (red line) suggests a second order phase transition with a critical temperature of about 38 K. B) Magnetization hysteresis curves recorded at 10 and 300 K of the same magnetite film as in A).

the electronic behavior and the origin of ferroelectricity in both  $\text{Fe}_3\text{O}_4$  and  $\text{LuFe}_2\text{O}_4$  might be related.

Magnetic moment versus magnetic field loops as presented in Figure 2b show a clear hysteresis and therefore the presence of (ferri-) magnetic domains simultaneously with the ferroelectric domains. The magnetic coercive field at room temperature is relatively large, with values of 48 mT. This is attributed to strain anisotropy due to the large lattice mismatch. The PLD film shows a considerable change in the value of the coercive field below and above the Verwey transition, as is expected from the change in the magneto-crystalline anisotropy constants.

In order to clarify the origin of ferroelectricity in  $\text{Fe}_3\text{O}_4$ , we have performed simulations based on density functional theory (DFT), focusing on the relation between polarization and charge ordering, much as in the case of charge-frustrated  $\text{LuFe}_2\text{O}_4$ .<sup>[19]</sup> A model of polarization was recently proposed by van der Brink and Khomskii.<sup>[6]</sup> Accordingly, the charge ordering induces an alternation of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions on the octahedrally coordinated sites of the inverse spinel structure, simultaneously with an alternation of the Fe–Fe bonds along the b-direction of the monoclinic cell. The resulting polarization would then be given by the coexistence of

both bond- and charge-centered charge ordering. Considering the fact that the iron ions on the octahedrally coordinated sites form a network of iron tetrahedra (Fig. S4 of SI), Brink's and Khomskii's model assumes each tetrahedron to have a "3:1" CO pattern (three  $\text{Fe}^{2+}$  and one  $\text{Fe}^{3+}$  ions in a tetrahedron, or vice versa), in contrast to Anderson's criterion,<sup>[34]</sup> where each tetrahedron has a "2:2" pattern (two  $\text{Fe}^{2+}$  and two  $\text{Fe}^{3+}$  ions). However, recent DFT calculations<sup>[35]</sup> have predicted the ground state not to have fully "3:1" CO, but to show a mixed-CO pattern (25% 2:2 and 75% 3:1), as obtained in a base-centered monoclinic noncentrosymmetric  $Cc$  structure (see Fig. S4 of SI). In that case, the centers of mass of the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions do not coincide, therefore paving the way to an electronic origin for the observed ferroelectricity. Indeed, we performed a Berry phase calculation of the polarization and obtained  $P = (-4.4, 0, 4.1) \mu\text{C cm}^{-2}$ , with finite  $a$  and  $c$  components. The effective value  $|2P_a| = 8.8 \mu\text{C cm}^{-2}$  is in good agreement with corresponding experimental values measured in the  $a$ – $b$  plane. We note that every calculation of polarization needs a centrosymmetric reference structure. Here, we considered a fully "3:1" CO pattern in the  $P2/c$  symmetry (including inversion symmetry). The  $P2/c$  cell is shown by DFT to be a competing state, being rather close in energy (by about 20 meV/formula unit) to the  $Cc$  structure. One might possibly conjecture that just below the Verwey transition, the CO would mostly show a "3:1" CO with a  $P2/c$  symmetry, where no polarization is observed; subsequently, below 38 K, one might observe the "mixed" CO with a  $Cc$  symmetry leading to ferroelectricity.

In summary, we have experimentally shown ferroelectric switching in magnetite thin films at temperatures below 38 K. The switchable polarization is about  $11 \mu\text{C cm}^{-2}$  below 20 K, and the thin film undergoes a second-order-like phase transition with a Curie temperature of about 38 K. Density functional simulations predict values of the polarization in very good agreement with corresponding experimental data, and suggest ferroelectricity to be driven by a non-centrosymmetric pattern for the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  charge ordering. Further studies are required to clearly unravel the origin of polarization and the switching mechanism. It is still to be investigated whether the ferroelectric phase transition is truly of second-order type, and whether the Curie temperature is a genuine critical point. In addition, the electronic properties, including band gap, trap levels, free-carrier generation-recombination, and conduction mechanism at low temperatures, need to be investigated in depth. The present work proves that magnetite is not only the first material in which humans observed magnetism and correlated electron properties, but that it is also ferroelectric with a value of the ferroelectric polarization approaching that of well-known ferroelectric materials, such as  $\text{BaTiO}_3$ . The ferroelectric properties and real-time switching of polarization in magnetite have experimentally been established. Magnetite is thus one of the rare multiferroic materials that at the same time possess a switchable ferroelectric polarization and a switchable magnetization. Therefore, this material can unquestionably be included in the group of multiferroic materials and may even be considered a prototype of multiferroic materials.

## Experimental

Epitaxial thin magnetite films were deposited on niobium-doped (100)-oriented  $\text{SrTiO}_3$  single crystals using RF magnetron sputtering

and pulsed laser deposition (PLD). In case of PLD, a KrF Excimer laser (Lambda Physik model LPX300) operating at a wavelength of 248 nm, a repetition rate of 10 Hz and pulse energy of 600 mJ was used. The substrate temperature was 430 °C and the oxygen partial pressure during deposition  $9 \times 10^{-6}$  mbar (1 mbar = 100 Pa). After the film deposition the oxygen flow was stopped immediately and the chamber was quickly pumped down to below  $10^{-7}$  mbar to avoid the oxidation of the magnetite film. The sample was rapidly cooled by switching off the substrate heater. X-ray diffraction using a Philips X'Pert diffractometer and transmission electron microscopy using a Philips CM20 Twin microscope were applied to structurally investigate the films. Magnetic properties were measured using a SQUID magnetometer (Quantum Design model MPMS7) and basic electrical properties are given in the Supporting Information (SI) or were published elsewhere [24].

Top metal electrodes ( $\sim 60 \mu\text{m} \times 60 \mu\text{m}$ ) were deposited by thermal evaporation (Pd, Au, and Ag) or magnetron sputtering (Pt) through a shadow mask. A cryo-prober (Lake Shore, TTP4) was used to contact the top electrode via Be-Cu tips and to vary the sample temperatures from 4.2 to 300 K.

Ferroelectric hysteresis loops were measured using a Ferroelectric Analyzer (TF2000, aixACCT). PUND measurements were performed by applying 100 ns to 5  $\mu\text{s}$  wide pulses of variable voltage using a pulse generator (Tektronix AFG3102) and measuring the signal generated by the current on a 50  $\Omega$  load resistance using an oscilloscope (Tektronix TDS684C). The a.c. impedance was measured by a Hewlett Packard impedance analyzer (HP4194A). The dielectric dispersion was measured dynamically by rising the temperature up with a speed of 2 K  $\text{min}^{-1}$ .

Density functional simulations were performed using the Vienna Ab-initio Simulation Package (VASP) [36], within the generalized gradient approximation [37] to the exchange correlation potential. A Hubbard U correction was added on Fe d states within the so-called "GGA+U" approach [38] (where  $U = 4.5$  eV and  $J = 0.89$  eV). The cutoff energy for plane waves was set at 400 eV whereas the k-point sampling was done using the  $4 \times 4 \times 2$  Monkhorst-Pack k-point grid. In order to compare the energy and the Berry phase [25,39] ferroelectric polarization for paraelectric ( $P2/c$ ) and ferroelectric ( $Cc$ ) states, we used the same primitive cell of the base-centered monoclinic  $Cc$  lattice (in this setting  $a = b \neq c$  and  $\alpha \neq \beta \neq \gamma$ , almost identical to triclinic, except for the  $a = b$  condition) and the experimental lattice parameters [40], with 112 atoms per unit cell with optimized internal positions. A ferrimagnetic configuration was imposed on Fe spins, with all Fe-B (Fe-A) sites as up (down) spins.

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