

Ferromagnetism on the unpolished surfaces of single crystal metal oxide substrates

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It is shown that a variety of single crystal substrates (Al_2O_3 , LaAlO_3 , SrTiO_3 , TiO_2 , and ZnO), purchased from commercial suppliers, contain a ferromagnetic component to the magnetization in addition to the expected linear magnetic response. This ferromagnetic contribution is only observed on the unpolished surfaces and can be eliminated by either polishing or annealing at 600°C in air, but not by annealing at 600°C in a vacuum of 5×10^{-6} Torr. Particle induced x-ray emission spectra demonstrate that there is excess Fe on the unpolished surfaces of these single crystal substrates. While defect related ferromagnetic signals have been reported in some of these substrates, and while our results do not exclude this origin of ferromagnetism, we clearly show that the ferromagnetic signals observed in our samples are largely due to excess iron on the unpolished surfaces, possibly in the form of a mixture of Fe, Fe_3O_4 , and or $\gamma\text{-Fe}_2\text{O}_3$. © 2011 American Institute of Physics. [doi:10.1063/1.3611034]

I. INTRODUCTION

There has been much interest in recent years in the existence of ferromagnetism in metal oxides containing no magnetic ions, the so-called d^0 ferromagnetism.^{1–4} It has been suggested that the phenomena is produced by defects such as oxygen or cation vacancies.⁵ Alternatively, some researchers argue that it is due to sample contamination.⁶ Recently, Khalid *et al.* performed a study⁷ of several different diamagnetic materials (MgO , MgAl_2O_4 , SrTiO_3 , LaAlO_3 , LSAT , and ZnO) using a variety of complementary probes [magnetometry, electron paramagnetic resonance, x-ray magnetic circular dichroism, x-ray absorption spectroscopy, and particle-induced x-ray emission (PIXE)]. They concluded that there are three contributions to the magnetization: an intrinsic diamagnetic contribution, a paramagnetic contribution due to various transition-metal impurities, and a ferromagnetic contribution. The coercive fields of the ferromagnetic contribution were rather independent of the actual crystal material. No definite origin was given for this ferromagnetic contribution, although again, it was speculated to be associated with surface defects.

In addition, a search for defect related ferromagnetism in SrTiO_3 (STO) was recently published,⁸ in which ferromagnetic contributions to the total magnetic moment were observed in approximately fifty STO substrates purchased from four different commercial suppliers. These single crystal substrates of a typical dimension, $5 \times 5 \times 0.5 \text{ mm}^3$, could be purchased in two states: with either one (1sp) or both (2sp) of the $5 \times 5 \text{ mm}^2$ faces polished. It was observed that the ferromagnetic contribution to the total moment could be reduced by polishing additional faces as shown in Fig. 1. The lower panel, Fig. 1(a), shows the raw moment versus field data for the same sample in the “as purchased” (1sp)

state and with one additional face polished (2sp). If all six faces of a substrate were polished, then the moment versus field curves became completely linear. In the upper panel, Fig. 1(b), the same data is shown, however, with the linear diamagnetic response of the substrate removed. Note that there is approximately 35 mm^2 ($\approx 58\%$) of unpolished area in the 1sp state but approximately 10 mm^2 ($\approx 17\%$) in the 2sp state for this $5 \times 5 \times 0.5 \text{ mm}^3$ substrate and that the saturation moment is roughly in the same ratio as the unpolished area. In addition, the coercive field at room temperature was determined to be approximately 200 G, in agreement with many diamagnetic metal oxides.⁷ Furthermore, the effect of annealing STO on the magnetic moment is different depending on whether the heat treatment was performed in air or vacuum, as is illustrated in Fig. 2. Note that annealing in air effectively destroys the ferromagnetic contribution to the moment, while annealing in vacuum at the same temperature (600°C) does not destroy the ferromagnetic moment. It was speculated that the ferromagnetic moment on the unpolished surface was in the form of magnetic Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$ particles with saturation moments of approximately 50 emu/g at 300 K and that annealing in air drove the iron oxide particles into the form of the less magnetic $\alpha\text{-Fe}_2\text{O}_3$ with a saturation moment at 300 K of less than 0.5 emu/g. However, no direct evidence for the presence of excess iron oxide on the unpolished surfaces was presented. In fact, electron energy dispersive spectroscopy (EDX) did not detect any difference between the polished and unpolished surfaces,⁸ however, we now believe this was due to the lack of sensitivity to several trace elements.

The present work was performed to provide more direct evidence for the aforementioned hypothesis by measuring PIXE spectra on both polished and unpolished surfaces of STO in addition to a number of other commercially prepared metal oxide single crystal substrates. PIXE is more sensitive than the more typically used EDX because the bremsstrahlung

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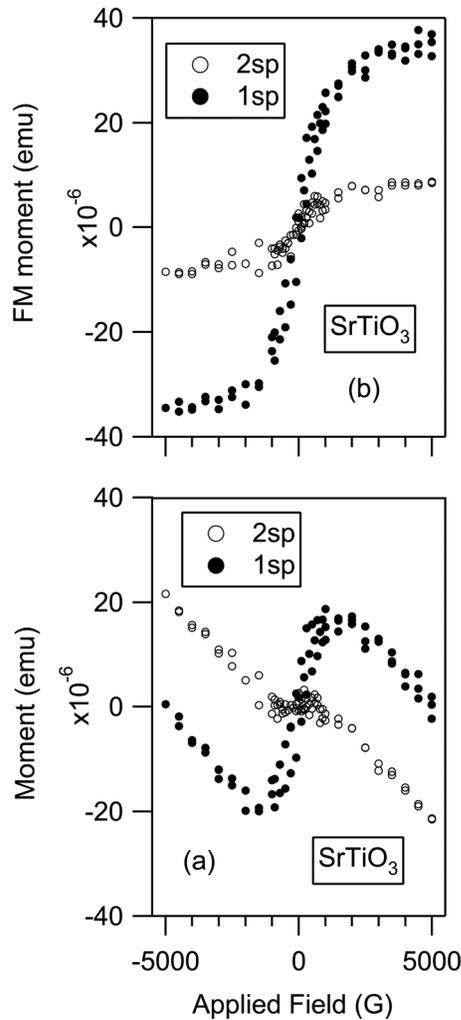


FIG. 1. (a) The magnetic moment vs applied field of a $5 \times 5 \times 0.5$ mm³ SrTiO₃ substrate with one (1sp) or both (2sp) of the 5×5 mm² faces polished. (b) The ferromagnetic moment determined by subtracting the linear diamagnetic contribution of the samples.

continuous background radiation is greatly reduced. In addition to the PIXE work, it is shown that a wide variety of metal oxides exhibit the same change in the magnetic properties after annealing, as shown by STO in Fig. 2.

II. EXPERIMENTAL DETAILS

The STO (001), Al₂O₃ (0001), LaAlO₃ (001), TiO₂ (001), and ZnO (0001-O face terminated) single crystal substrates ($5 \times 5 \times 0.5$ mm³ with one face polished) were purchased from either MTI Crystals, Inc. (USA) or CRYSTEC, GmbH, Berlin. The substrates were handled only with Teflon tweezers to avoid contamination of the samples. Measurements of the field dependent moment were made at room temperature using a Quantum Design superconducting quantum interference device (SQUID) magnetometer on the as-purchased substrates. The substrates were then treated in one of three ways: either (i) the second 5×5 mm² face was polished using the procedure described in Ref. 8, or the substrate was placed in a Coorstek high density AD998 Al₂O₃ boat with the unpolished surface face up and annealed at 600 °C (ii) in air, or (iii) in a vacuum of approximately

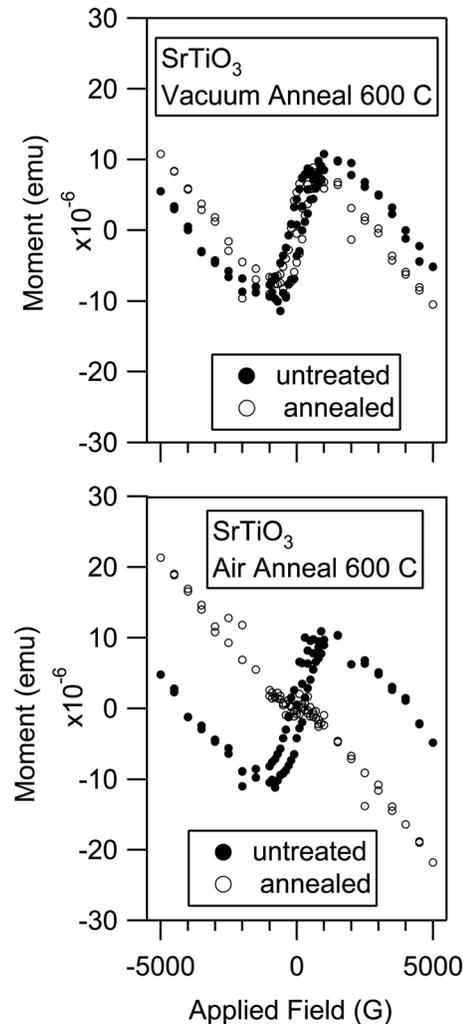


FIG. 2. (b) The magnetic moment vs applied field of a $5 \times 5 \times 0.5$ mm³ SrTiO₃ substrate before and after annealing in air at 600 °C (lower panel) or in vacuum at 600 °C (upper panel).

5×10^{-6} Torr. After treatment, the SQUID magnetometry measurements were repeated. In addition, complementary PIXE spectra were collected using 1 MeV protons at the University of Western Ontario Tandemron Accelerator lab from both polished and unpolished surfaces of substrates on samples with a ferromagnetic component to the magnetization determined by SQUID magnetometry. This incident energy is sufficient to excite an ≈ 10 μ m thick surface layer of a substrate. The PIXE spectra were acquired with a LN₂ cooled HPGe detector (resolution 135 eV at 5.9 keV) having a 5 mm diameter Be entrance window 13 μ m in thickness positioned at the angle of 90° relative to the incident beam. The low energy x-ray flux was attenuated by Al and or Be thin foils with the total thickness of ≈ 240 μ m. The samples were mounted on acrylic disks to avoid any surface contacts with metals, and covered with a thin carbon layer to prevent charging.

III. RESULTS AND DISCUSSION

Figures 3–5 present the SQUID magnetometry data for substrates before and after treatment (polishing, air annealing, vacuum annealing). Note that the moment versus field

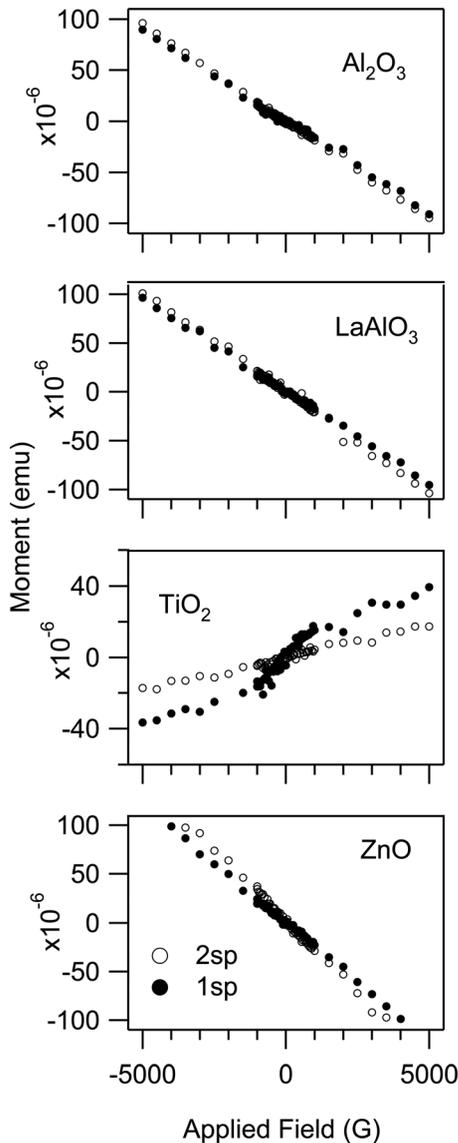


FIG. 3. The magnetic moment vs applied field for various $5 \times 5 \times 0.5 \text{ mm}^3$ single crystal substrates with one (1sp) or both (2sp) of the $5 \times 5 \text{ mm}^2$ faces polished. Note the different vertical scale for TiO_2 . The effect of polishing is most clear for TiO_2 for two reasons. Not only is the linear susceptibility smaller, but also because there is demonstrably more Fe on the unpolished surfaces than for other materials.

relations for all the substrates before treatment are nonlinear. The magnetization before treatment is composed of the sum of a linear component and a nonlinear ferromagnetic component, an example of which is shown in Fig. 1(b). The linear component is due to the intrinsic diamagnetic or paramagnetic susceptibility along with contributions from isolated paramagnetic impurities.⁷ This linear component can be extracted by making linear fits in the higher field regions ($-5000 \leq H \leq -2000$ or $2000 \leq H \leq 5000$ G). The saturation moments are equal to the y-intercepts of linear fits to the moment versus field data in the high field range. The average saturation moments and linear susceptibility contributions to the total moment are presented in Table I. The uncertainties listed in Table I are the standard deviations in the measurements for the whole set of samples before treatment. For example, in the case of TiO_2 , eight samples were tested and

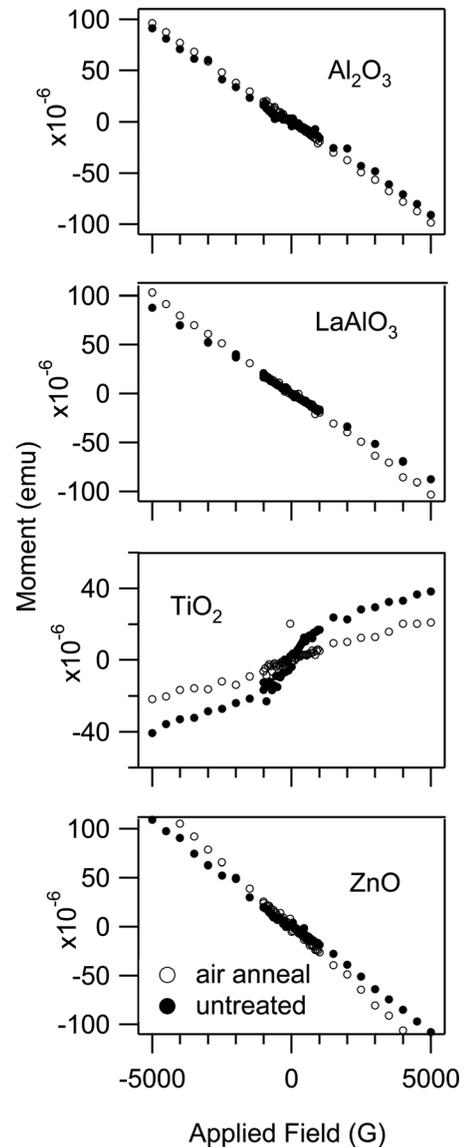


FIG. 4. The magnetic moment vs applied field for various $5 \times 5 \times 0.5 \text{ mm}^3$ single crystal substrates (with one side polished) before and after annealing in air at 600°C .

in the case of SrTiO_3 , the average data of 16 1sp substrates are used. The linear contributions to the magnetization that are listed in Table I are approximately equal to the values listed in Ref. 10. Note that the measured saturation moments for TiO_2 and SrTiO_3 are almost an order of magnitude larger than those of Al_2O_3 , LaAlO_3 , and ZnO .

The data of Fig. 3 provide more evidence for the claim that the nonlinear ferromagnetic contributions to the magnetization is associated with the unpolished surface of the substrate. Note that, for all samples, the moment is more positive for positive fields and more negative for negative fields before polishing than it is after treatment, which is exactly the same as was shown for the STO in Fig. 1(a). The effect shown in Fig. 3 is most clear for the TiO_2 substrates for two reasons. Not only is the linear susceptibility of TiO_2 smaller than the other substrates (see Table I and note the different vertical scale in Fig. 3) but also because there is demonstrably more Fe on the unpolished surface of TiO_2

than on the other substrates, as will be seen in the PIXE data. In Ref. 8 it was speculated that the amount of Fe on the unpolished surfaces was related to the Mohs hardness of the substrate, however, the new data show that this is not correct. It is curious and perhaps worthy of further study that the substrates containing titanium have larger quantities of Fe on the unpolished surfaces.

A comparison of Figs. 3 and 4 shows that the effect of annealing in air at 600 °C is similar to polishing for a wide variety of substrates. That is, annealing in air essentially removes the ferromagnetic contribution to the magnetization. On the contrary, as shown in Fig. 5, annealing in a vacuum of approximately 5×10^{-6} Torr reduces slightly, but does not totally remove, the ferromagnetic component of the magnetization. One possible interpretation for the difference in annealing behavior is that the ferromagnetic component is associated with oxygen vacancies on the surface and near-surface region. For example, it was demonstrated⁹ that epi-

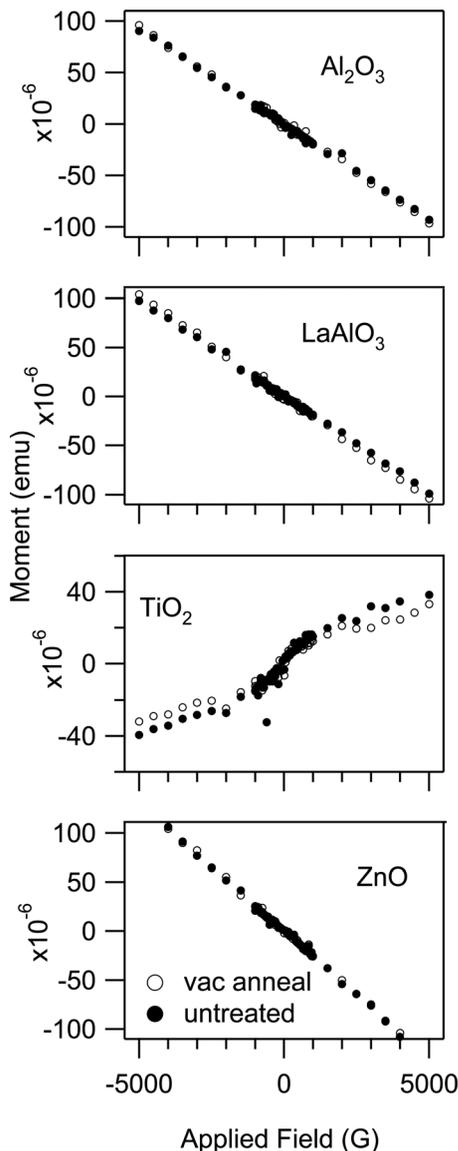


FIG. 5. The magnetic moment vs applied field for various $5 \times 5 \times 0.5$ mm³ single crystal substrates (with one side polished) before and after annealing in vacuum at 600 °C.

taxial STO films on Si are stable toward annealing in vacuum up to ≈ 550 °C. However, at higher temperatures, surface partial reduction occurs accompanied by SrO and O₂ desorption and the initially flat surface starts to roughen. In fact, the connection between oxygen vacancies and ferromagnetism was specifically studied in Ref. 8 for STO. It was shown that, *if all the faces of a substrate are polished*, even highly reduced samples showed a linear dependence of magnetization upon the applied field. No evidence of the ferromagnetic moment was observed in samples containing in the range of 10^{19} to 10^{21} per cm³ of oxygen vacancies.

Alternatively, it has been suggested by multiple authors^{6,8,11} that the ferromagnetic contributions to the magnetization are associated with iron and iron compounds. The PIXE measurements in this study provide direct confirmation of the fact that there is more iron on the unpolished than the polished surfaces. The PIXE emission spectrum for an STO substrate purchased from Crystec is shown in Fig. 6. Note, especially, that there is more Fe and Ca on the unpolished surface than the polished surface, while the major constituents (Sr and Ti) contribute the same number of counts from both the polished and unpolished surface. An almost identical spectrum was observed for the STO substrates purchased from Alfa-Aesar. The peaks near 9 keV, labeled “Ti pile-up,” are not x-ray emission peaks, but rather artifacts of a high count rate. A similar discrepancy in the amount of iron between polished and unpolished surfaces was clearly seen for TiO₂, as shown in Fig. 7(a). The PIXE spectra of the polished/unpolished faces of Al₂O₃ are also shown in this figure. There are traces of Fe on both surfaces. On the polished side, the trace iron acts as an isolated paramagnetic impurity incorporated in some fashion into the Al₂O₃ crystal. On the unpolished side, in addition to the aforementioned lattice defects, there is a small amount of excess Fe which is likely due to the diamond saw cuts made in shaping the substrate from the crystal boule. As expected, because the saturation moment on the Al₂O₃ is much smaller than TiO₂ for these particular samples, the difference in the Fe *K*α counts between the polished and unpolished surfaces of Al₂O₃ is much smaller and verging on the noise level. Specifically, for the samples shown in Fig. 7(a), the number of counts associated with the Fe *K*α peak (between 6.21 and 6.60 keV) for TiO₂ is 748 ± 56 while for Al₂O₃ it is only 29 ± 16 . It was impossible to see any difference between the polished and unpolished sides of LaAlO₃ and ZnO not only because the small amount is about the same size as in the samples of Al₂O₃, but also because the background is higher in the Fe

TABLE I. Room temperature magnetic properties of 1sp single crystal substrates in the as-purchased condition.

Material	Manufacturer	χ (emu/g-G) (all entries: $\times 10^{-7}$)	μ_{sat} (emu) (all entries: $\times 10^{-6}$)
Al ₂ O ₃	MTI	-3.4 ± 0.2	3.9 ± 2.3
LaAlO ₃	MTI	-2.08 ± 0.02	3.8 ± 2.3
SrTiO ₃	Crystec	-0.89 ± 0.08	19 ± 5
TiO ₂	MTI	$+1.01 \pm 0.09$	12 ± 2
ZnO	MTI	-3.5 ± 0.2	4.4 ± 2.5

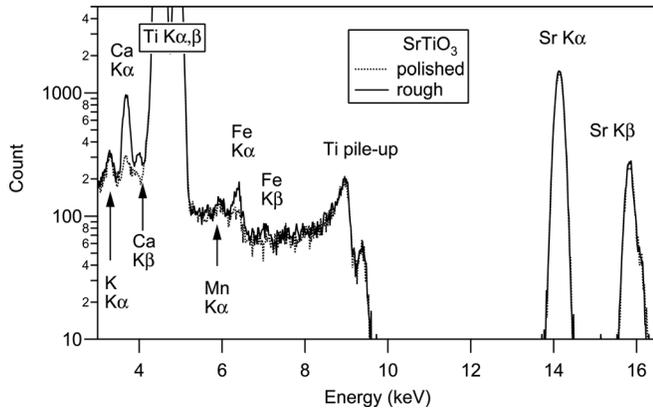


FIG. 6. X-ray emission spectrum induced by 1 MeV protons from the polished (dashed line) and unpolished surface (solid line) of a 1sp substrate purchased from Crystec, GmbH, Berlin.

$K\alpha$ peak region and the statistical noise masks any difference. This is likely the same reason that Fe could not be seen in the earlier published EDX spectra⁸ on STO. The only

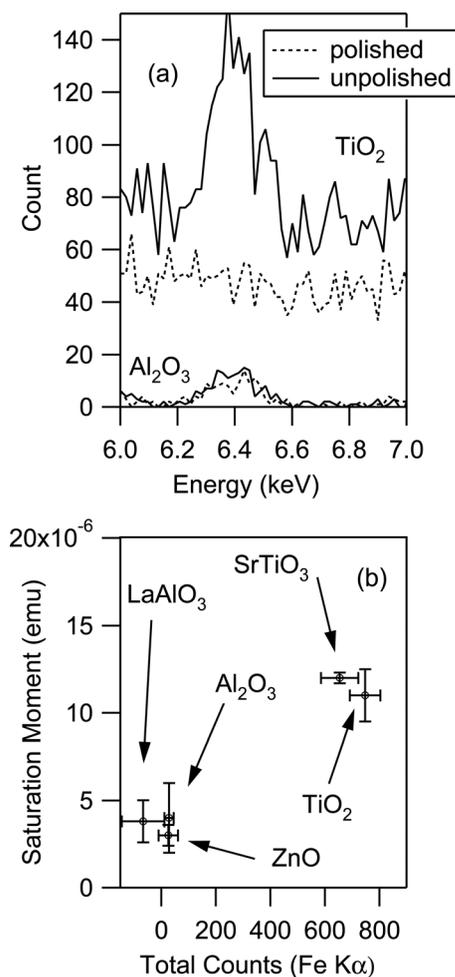


FIG. 7. (a) X-ray emission spectra in the vicinity of the Fe $K\alpha$ emission (6.40 eV) excited by 1 MeV protons from the polished (dashed line) and unpolished surfaces (solid line) of 1sp substrates purchased from MTI, Inc. (b) The room temperature saturation moment measured using SQUID magnetometry vs the difference in the number of counts in the vicinity of the Fe $K\alpha$ emission (6.21 to 6.60 keV) between the unpolished and polished sides of the substrate.

reason any difference is seen for Al₂O₃ is because there is negligible background in the region of the Fe $K\alpha$ emission.

Figure 7(b) is a plot of the ferromagnetic saturation moment versus the difference in the number of counts between the polished and unpolished sides in the Fe $K\alpha$ peak. Note that the uncertainties in the number of counts shown for LaAlO₃ and ZnO in Fig. 7(b) are larger than for Al₂O₃ and that this is related to the larger background for these two materials in the region of the Fe $K\alpha$ emission. However, also note that if one were to do a linear fit of the points in Fig. 7(b), the y-intercept would not be zero. This might be explained by the Fe being in different forms on the unpolished surfaces (ferromagnetic Fe, Fe₃O₄, or γ -Fe₂O₃.) With the present technology, except for, perhaps, high-resolution transmission electron microscopy coupled with electron energy loss spectroscopy, it would be almost impossible to disentangle the amount of Fe in each form. Most of the metal oxides examined here have a dielectric constant of 8 or higher, and therefore any surface analyses of these single crystals examined with electron beam techniques would be challenging due to charging effects. Again, we postulate that annealing in air drives all of the Fe on the unpolished surfaces into the form of α -Fe₂O₃ with a significantly smaller saturation magnetization. There were also trace amounts of Cr and Ni found on Al₂O₃ but it is not possible that the stable oxides of these elements contribute to the ferromagnetic magnetization observed in Figs. 3–5, since they are all anti-ferromagnetic, except CrO₂, which requires special high pressure synthesis to stabilize.

The ubiquitous presence of Fe on the unpolished surfaces of commercially prepared metal oxides would explain several puzzling observations. First, it is consistent with the observation that the coercive field of the ferromagnetic contribution to the magnetization of metal oxide substrates is insensitive to the actual crystal material.⁷ In addition, it might explain the fact that the temperature dependence of the saturation magnetization of TiO₂ thin films grown on LaAlO₃ substrates and measured at high temperature could be fit with a Curie temperature of 879 K¹², which is remarkably close to the ferromagnetic transition temperature of γ -Fe₂O₃.

In conclusion, it has been unequivocally demonstrated that a ubiquitous ferromagnetic contribution to the magnetization of many commercial single crystal substrates is largely, if not entirely, associated with iron or its oxides on the unpolished surfaces. This reality must be taken into account in any studies of ferromagnetism in metal oxide thin films or metal oxide films doped with magnetic impurities grown on such substrates.

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