Persistent optically induced magnetism in oxygen-deficient strontium titanate

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Trace Impurity Detection and Quantification Using Particle-Induced X-Ray Emission (PIXE)

As discussed in the main text, the nominally pure commercial SrTiO$_3$ substrates used in this study are known, based both on vendor specifications [1] and prior work [2, 3], to contain impurities at tens of part-per-million (ppm) levels. Such impurities could play a role in the effects we report in this paper, particularly in terms of complexes with oxygen vacancies, with Fe impurities being of particular interest. We thus undertook a thorough trace element analysis of the crystals used in this work, seeking to evaluate the major impurities and to quantify their concentration where possible.

The specific crystals used in this study were nominally >99.99% purity undoped SrTiO$_3$ substrates obtained from MTI Corporation [1]. Table 1 summarizes the main impurities one could expect to be present in such substrates, based on vendor specifications [1] and some prior work on similar crystals [2, 3]. Mg, Si, Ca, Fe, Cr, Mn and Al are anticipated, Al, Mg, Si, Ca, and Fe at approximately 10-50 ppm, Cr and Mn at levels that have not been previously quantified. In order to reliably detect and measure such ppm concentrations, Particle-Induced X-Ray Emission (PIXE) was employed. In this technique, high-energy particles (in our case He ions at 4 MeV energies) are used to induce inner shell ionization and subsequent relaxation, resulting in emission of X-rays with energies characteristic of the atomic species. In comparison to Energy Dispersive Spectroscopy (EDS) the absence of primary Bremsstrahlung results in significantly higher signal-to-noise ratios, enabling detection and quantification of trace impurity concentrations at ppm levels. In our set-up, an energy-dispersive Si(Li) detector is employed, and the 4 MeV ions are calculated to result in a probe depth of approximately 5 $\mu$m. The total dosage for each spectrum shown was 83 $\mu$C.
| Element | Expected Concentration (ppm) | Concentration from PIXE (ppm) |
|---------|-----------------------------|------------------------------|
| Mg [1]  | 20                          | Not detectable, likely present |
| Si [1]  | 40                          | Not detectable, likely present |
| Ca [1]  | 50                          | Present, not quantifiable    |
| Fe [1, 2, 3] | 30                  | 35±5                         |
| Cr [2]  | ?                           | < 100                        |
| Mn [2]  | ?                           | 10’s-100’s (upper bound)     |
| Al [1, 3] | 20                          | Not detectable, likely present |

**TABLE I. Trace impurities in the SrTiO$_3$ crystals used in this work.** The expected elements (first column) and concentrations (second column) are based on vendor specifications [1] and prior work on related crystals [2, 3]. The third column shows the results from our PIXE studies.

PIXE spectra are shown in Figure S1. In Figure S1a we show the spectrum from a nominally undoped SrTiO$_3$ crystal measured with and without an Al filter in the path of the detected beam. The magenta spectrum was calculated based on pure SrTiO$_3$ using the GUPIX software package [4], and it can be seen that each of the predicted peaks for the SrTiO$_3$ host is indeed observed, along with a significant number of others. (Note that oxygen possesses too low an atomic number to be probed by PIXE). That a significant fraction of these other peaks are simply artifacts due to the detector and/or Al filter was established via detailed and careful comparisons between the filtered and unfiltered spectra, in addition to data taken on other oxide single crystals. Specifically, the unfiltered spectrum reveals a large Si peak from the Si(Li) detector, in addition to four other detector artifacts, which are labeled on the figure. These erroneous signals (including the Si peak) are attenuated or eliminated in the filtered spectrum, but an Al peak is introduced due to the Al filter. As a consequence of these issues, the expected presence of Si and Al (Table 1) cannot be directly verified. Similarly, the low atomic number element Mg, while likely present, cannot be confirmed. Nevertheless, after acknowledging the Sr and Ti “sum peaks” and “escape peaks”, also labeled in Figure S1a (at positions in agreement with GUPIX), a number of identifiable impurity peaks remain (in the 5-8 keV range), and are labeled with question marks. We identify these peaks as signatures of Cr, Mn, and Fe.

This situation is summarized in Figure S1b, where the Al-filtered spectrum is shown with
FIG. S1. Identification and quantification of trace impurities in nominally undoped SrTiO$_3$ using PIXE. 

a, PIXE spectrum of a nominally undoped SrTiO$_3$ crystal measured with and without an Al filter. The expected spectrum from the SrTiO$_3$ host (calculated by GUPIX [4]) is shown in magenta. Peaks due to the Si(Li) detector and the Al filter are labeled, in addition to peaks subsequently deduced to be detector artifacts. 

b, Fully labeled PIXE spectrum from nominally undoped SrTiO$_3$. 

c, Comparison between PIXE spectra for nominally undoped, 0.01% Fe-doped, and 0.25% Cr-doped SrTiO$_3$ crystals. All scans were acquired with an Al filter present.
all peaks indexed. In addition to Cr, Mn, and Fe, a shoulder due to Ca is also visible, but the overlap with the strong Ti Kα peak precludes quantification of the Ca concentration. In order to quantify the Cr and Fe concentrations, we compared the PIXE spectrum from the nominally undoped SrTiO₃ with spectra from commercial 0.01 wt. % Fe-doped and 0.25 wt. % Cr-doped SrTiO₃. These comparisons are shown in detail in Figure S1c. Using the 0.01% Fe-doped crystal as a standard we deduce an Fe concentration of 35±5 ppm in our nominally pure SrTiO₃. Note that the specified 0.01% Fe content in the Fe-doped sample was also checked with quantitative analysis via GUPIX, and was found to be 0.01% within error. Similarly, using the 0.25% Cr-doped crystal as a standard we deduce an upper bound of 100 ppm for the Cr concentration. Finally, in the case of Mn, where no such standard was available, we used GUPIX to estimate the Mn concentration, resulting in 10-100 ppm. Note however that a small but noticeable detector artifact overlaps with the Mn peak; 10-100 ppm is therefore an upper bound.

The third column of Table 1 summarizes these results. Mg, Si, and Al, while likely present at the 10’s of ppm concentration range, cannot be directly probed by PIXE. Ca is present (vendor analysis places it at 50 ppm) but cannot be reliably quantified by PIXE due to overlap with a host peak. Mn was confirmed as present and measured in the 10-100 ppm range (as an upper bound), while Fe and Cr concentrations were determined more accurately at 35±5 and <100 ppm, respectively. As a whole, the results are thus in good agreement with vendor specifications and prior work. Most importantly, the presence of a number of elements at 10 ppm levels is indeed confirmed and the Fe concentration is quantified at 35 ppm.
Temperature Dependent Absorption and Long-Wavelength MCD

As discussed in the main text, optically induced magnetic circular dichroism (MCD) in SrTiO$_{3-\delta}$ disappeared when the temperature was raised above $\sim$18 K. To determine if this coincided with any change in the $V_O$-related sub-bandgap optical absorption, we measured the optical density of both SrTiO$_{3-\delta}$ and SrTiO$_3$ samples over a broad temperature range.

![Temperature dependent optical absorption for SrTiO$_{3-\delta}$ and SrTiO$_3$.](image)

**FIG. S2.** Temperature dependent optical absorption for SrTiO$_{3-\delta}$ and SrTiO$_3$. The optical density for a, oxygen-deficient SrTiO$_{3-\delta}$ and b, re-oxygenated SrTiO$_3$ changes only minimally as the temperature is increased from 3 K to 60 K. In particular, the $V_O$-related sub-bandgap absorption at $\sim$430 nm remains largely unchanged, despite the disappearance of magneto-optical phenomena at temperatures exceeding 18 K.

Figures S2a and S2b show the sub-bandgap absorption spectra for a SrTiO$_{3-\delta}$ sample and for the same sample after it has been re-oxygenated. For both samples, the optical density is only minimally altered as the temperature is raised from 3 to 60 K; the sub-bandgap absorption features that are related to oxygen vacancies do not vanish above 18 K.

Additionally, we investigated MCD from SrTiO$_{3-\delta}$ at longer wavelengths out to 1000 nm. As shown in Fig. S3a, optical pumping at 405 nm with right- and left-circularly polarized light (RCP and LCP, respectively) does not induce any additional MCD features at wavelengths between 500 and 1000 nm. Furthermore, the MCD spectrum did not show any notable features in this range even when a 6 T magnetic field was applied (Fig. S3b).
FIG. S3. MCD spectra of SrTiO$_{3-\delta}$ at long wavelengths to 1000 nm. a, Optically induced magnetization for right- and left-circularly polarized (RCP and LCP, respectively) 405 nm pump light, as measured by MCD spectroscopy. MCD features are clearly observed from 400 to 500 nm, but not at longer wavelengths. b, MCD spectrum of SrTiO$_{3-\delta}$ at 5 K shows that no MCD signals exist in reduced samples between 500 and 1000 nm, even at 6 T applied magnetic field.

SQUID Studies of Optically Induced Magnetization

Optically induced magnetization in SrTiO$_{3-\delta}$ was measured using a commercial SQUID magnetometer (Quantum Design MPMS) operating at zero magnetic field. Fig. S4 shows the experiment. 405 nm pump light was coupled to the sample via a standard single-mode UV optical fiber (0.13 numerical aperture), using a three-axis fiber launcher (Thorlabs; MBT613D) with piezoelectric actuators. In these experiments, it was critical to produce and maintain circularly polarized light at the output of the fiber (i.e., at the sample) while the sample and probe were in situ. We used a linear polarizer and a variable waveplate (a Soleil-Babinet compensator on a rotation mount) to launch circularly polarized light into the fiber. We adjusted the polarization state of the light within the fiber by straining it and inducing birefringence with a manual fiber polarization controller (Fiber Control Industries; FPC-1). This is essential to correct for unwanted birefringence in the fiber (due to bends, etc.) to ensure circular polarization of the light at the output of the fiber.
FIG. S4. **Setup for SQUID measurements of optically induced magnetization.** Light from a 405 nm diode laser was coupled to a standard single-mode fiber. A linear polarizer, a variable waveplate (a Soleil-Babinet compensator on a rotation mount), and a manual fiber polarization controller were used to control the polarization of the light arriving at the sample. A photodiode monitored the polarization-dependent intensity of the back reflection from the end of the fiber, allowing for *in situ* control over the polarization at the sample.

Circular polarization of the light at the output of the fiber was confirmed and continuously monitored by measuring the intensity of the light that was back-reflected from the end cleave of the fiber (a good cleave is important). Upon back-reflection, RCP light (for example) changes to LCP light, which is then nulled upon traversing the time-reversed path back through the Soleil-Babinet and the linear polarizer. A perfect null is achieved only when the light is perfectly circularly polarized at the end of the fiber. An iris (to block other reflections), photodiode, chopper and oscilloscope make this back-reflected light easy to monitor. More broadly, this monitoring scheme effectively turns the back-reflected intensity into a polarization sensor. To switch from (say) RCP light to linear or LCP light at the sample, the Soleil-Babinet is then rotated by 45 or 90 degrees.

To pass the fiber into the SQUID, a few-centimeter section of the fiber was stripped of its acrylate jacket and was epoxied (Stycast 1266) into a small brass tube, which was then
passed through a standard quick-connect vacuum feedthrough. The feedthrough itself was epoxied to the top of a standard SQUID probe tube. The end of the fiber was positioned several centimeters above the sample, so that the pump light globally illuminated the sample. For all SQUID measurements shown here, we used <500 µW of light at the sample.

**FIG. S5.** SQUID measurements of the optically induced magnetic moment in SrTiO$_3$–δ and in as-received (unannealed) SrTiO$_3$. Pump polarization dependence of the magnetization of SrTiO$_3$–δ (upper panel) and SrTiO$_3$ (lower panel) shows that only SrTiO$_3$–δ exhibits optically induced magnetization. In a similar manner to the MCD results, the optically induced magnetization in SrTiO$_3$–δ persists long after the pump illumination is blocked.

The top panel of Fig. S5 demonstrates the ability to manipulate the induced magnetic moment in the sample with polarized light, just as the MCD results showed in Fig. 2a of the main text. As a control, we also tested an unannealed, as-received SrTiO$_3$ sample (lower panel). No optically induced magnetization was observed, in agreement with the MCD results presented in Fig. 1c of the main text. The small magnetization offset in this SQUID data is attributed to the diamagnetic response of SrTiO$_3$ created by the very small remnant field (<10$^{-4}$ T) present in the superconducting magnet of the SQUID magnetometer.
Pump Power Dependent Measurements

Fig. 2b of the main text shows that the equilibration rate of optically induced magnetization depends strongly on the intensity of the pump illumination, and that the induced magnetization saturates at approximately the same magnitude independent of pump intensity. This behavior is consistent with a material containing a fixed density of ground state levels in the gap that are optically polarizable and that have extremely long spin relaxation times. Fig. S6a shows that the MCD signals saturate not just at one wavelength, but over the entire MCD spectrum, independent of pump intensity. These data further support the scenario described in the main text: a manifold of (at least) three circularly polarized optical transitions are coupled to a common ground state, and the buildup of polarization in this ground state affects all three optical transitions simultaneously.

**FIG. S6.** Saturation of MCD spectra at different pump intensities. a, MCD spectra at $B=0$ T measured after optical pumping with 405 nm light of different power (5, 25, 50, and 500 µW). The spectra are approximately identical, indicating a saturation of the optically induced magnetization. (From each of these spectra the small, but non-zero, MCD spectrum acquired without optical pumping was subtracted.) b, The corresponding optical absorption spectra.

As discussed in the main text, even though the magnetization (MCD) is saturated, the MCD signals themselves are only of order $10^{-3}$. There is very little change in the total optical absorption in the 400-500 nm range, as shown in Fig. S6b. This observation is consistent with the absence of long-lived excited states, whose presence would likely create
more significant changes in the overall optical density.

**Slow Temporal Dynamics of Optically Induced Magnetism**

The extremely slow relaxation of optically induced magnetism in SrTiO$_{3-\delta}$ suggests a potential for magneto-optical information storage at low temperatures. However, the ability to induce and control magnetization with polarized pump light also means that optical probes of magnetization (such as MCD or Faraday rotation) can potentially perturb the magnetization. Thus, it is important to recognize and to minimize any influence of the probe light on the magnetization when measuring the relaxation dynamics of SrTiO$_{3-\delta}$. One way to accomplish this is to use very low intensities of probe light. As Fig. S7a shows, the act of continuously probing the MCD (here using $\lambda_{\text{probe}}=425$ nm) causes an optically induced magnetization to relax more quickly than if probed intermittently. Unsurprisingly, the relaxation rate is faster when using higher probe intensity, as the inset displays. Therefore, in both Figs. S7a and b, we used a very weak ($P_{\text{probe}} = 4$ nW) probe beam to measure the magnetization at discrete intervals. Each point shown in Figs. S7a-c is an average of data collected over tens of seconds with the error bars denoting the standard deviation (error bars are not shown in Fig. S7b for clarity). We investigated temperatures from 20 to 3 K, with 17.5 K being the fastest magnetization decay that we could reliably measure. From 3 to 14 K, probing was performed intermittently, while above those temperatures (as given in Fig. 2c in the main text) a continuous probe was employed.

Whether continuously or intermittently probed, each data trace was normalized to unity during the optically pumped portion of the curve (the first 100 seconds). A single exponential decay, $\exp(-t/\tau)$, fit every data trace quite well, allowing us to extract $\tau$ as a function of temperature (these values of $\tau$ are shown in Fig. 2d of the main text). $\tau$ approximately follows an activated (Arrhenius) behavior for temperatures between 13 K and 17 K, but deviates significantly from activated behavior below $\sim 10$ K. We note however that owing to the extremely long magnetization relaxation times in this low-temperature regime, even very tiny amounts of inadvertent light leaking on to the samples could account for this behavior.

In a different set of experiments, a SrTiO$_{3-\delta}$ sample ($n = 1 \times 10^{17}$ cm$^{-3}$) was magnetized in a 6 T magnetic field. The field was then ramped to zero, and a MCD spectrum was then acquired using a 0.4 nW probe. Over the next $\approx 9$ hours, the sample magnetization was
FIG. S7. **Temporal dynamics of magnetization relaxation in SrTiO$_{3-\delta}$.**

**a,** Continuous probing (red trace) and intermittent probing (green points) of the MCD signal after optical pumping with RCP light ($\lambda_{\text{pump}}=405$ nm, $\lambda_{\text{probe}}=425$ nm). The faster decay with continuous probing shows that the MCD measurement itself can accelerate the relaxation of the optically induced magnetization. Inset: MCD signal as a function of time after optical pumping, using 40 nW and 4 nW of probe power. The higher probe power clearly produces a faster decay of the magnetization.

**b,** Intermittent probing of the 425 nm MCD signal after 405 nm optical excitation, for several temperatures. The black lines indicate single-exponential fits to the data.

**c,** Measuring the relaxation of optically induced magnetization at 3 K over the course of $\approx 9$ hours. Only a small decay of approximately 4% is observed over that time span. A probe power of 0.4 nW was used in order to minimize probe-induced relaxation.

**d,** The full MCD spectrum measured just after magnetizing the sample (black line) and 9.2 hours later (red dashed line) shows that the induced magnetization at 3 K has barely changed. As with **c,** 0.4 nW of probe power was used to minimize probe-induced relaxation.
intermittently probed by MCD (at 425 nm) for tens of seconds at a time, after which another full MCD spectrum was acquired. Figure S7c shows the averaged results of the intermittent probing, in units of relative decay from a starting normalized value of 1. Remarkably, the MCD decays by less than 4% over the course of 9 hours, demonstrating the persistence of the induced magnetization at $B = 0$ T. A comparison of the full MCD spectra at $t = 0$ and at $t = 9.2$ hours is given in Fig. S7d; the spectra are essentially identical. This ability to induce a long-lived magnetization using either circularly polarized light or a magnetic field is consistent with a scenario in which magnetization in SrTiO$_{3-\delta}$ originates from polarizable ground state levels with an extremely long relaxation time.

**FIG. S8. MCD versus applied magnetic field, at different temperatures.** MCD signal using a fixed probe wavelength (425 nm) for SrTiO$_{3-\delta}$, taken as the applied magnetic field was swept. Data at the lowest temperatures exhibit open hysteresis loops due to the extremely slow magnetization relaxation dynamics.

The slow relaxation dynamics at the lowest temperatures manifest themselves as open hysteresis loops when MCD is measured at a fixed wavelength as a function of swept magnetic field. As seen in Fig. S8, these loops open as $T$ decreases, due to the increasingly slow magnetization equilibration dynamics discussed in the main paper. When the sweep rate of the magnetic field is lowered, the MCD($B$) loops become narrower, especially at higher $T$. At no point did we see ramp-rate-independent hysteresis loops associated with ferromagnetism. These MCD($B$) data at different temperatures suggest magnetization of paramagnetic moments, consistent with the interpretation of the data as discussed in the main text.
Photoluminescence Measurements

FIG. S9. **Photoluminescence (PL) from SrTiO$_{3-\delta}$ using above- and below-bandgap excitation.** a, Using weak above-bandgap excitation (325 nm), normalized PL spectra from substrates with different $V_O$ densities shows that the PL remains largely unaffected by oxygen removal from the lattice. b, Comparison of PL from an unannealed, as-received sample and an oxygen-deficient sample, for weak excitation both above-bandgap (374 nm) and below-bandgap (390 nm). Below-bandgap excitation generates negligible PL relative to above-bandgap excitation. Regardless of excitation, the PL from unannealed and from reduced SrTiO$_3$ looks qualitatively similar.

Photoluminescence (PL) was excited using either a He-Cd laser (325 nm) or a frequency-doubled Ti:sapphire laser (tunable wavelengths from 360-490 nm). The latter permits either above-bandgap or below-bandgap excitation. A series of oxygen-deficient SrTiO$_{3-\delta}$ samples and an unannealed (as-received) SrTiO$_3$ sample was measured. For the case of 325 nm (above-gap) excitation, all samples showed a very broad and very similar PL band peaked well below the band-edge (see Fig. S9a), consistent with prior results [5, 6] and likely due to self-trapped excitons or defects. No significant differences between oxygen-deficient and as-received samples was observed in the PL.

Figure S9b shows the marked difference in PL between above- and below-bandgap excitation, for both as-received SrTiO$_3$ (top) and for SrTiO$_{3-\delta}$ (bottom). Here, the PL intensities for each sample were scaled by the integration time and then normalized to the PL peak of the unannealed SrTiO$_3$ substrate. For both samples, the below-bandgap PL is negligi-
ble when compared to above-bandgap excitation, and no significant differences between the samples are observed.

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