Reversible control of magnetic interactions by electric field in a single-phase material

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Intrinsic magnetoelectric coupling describes the interaction between magnetic and electric polarization through an inherent microscopic mechanism in a single-phase material. This phenomenon has the potential to control the magnetic state of a material with an electric field, an enticing prospect for device engineering. Here, we demonstrate ‘giant’ magnetoelectric cross-field control in a tetravalent titanate film. In bulk form, EuTiO$_3$ is antiferromagnetic. However, both antiferromagnetic interactions coexist between different nearest europium neighbours. In thin epitaxial films, strain was used to alter the relative strength of the magnetic exchange constants. We not only show that moderate biaxial compression precipitates local magnetic competition, but also demonstrate that the application of an electric field at this strain condition switches the magnetic ground state. Using first-principles density functional theory, we resolve the underlying microscopic mechanism resulting in G-type magnetic order and illustrate how it is responsible for the ‘giant’ magnetoelectric effect.
The magnetoelectric (ME) effect represents the coupling between the electric and magnetic parameters in matter. Multiferroic (MF) materials with coexisting ferromagnetism (FM) and ferroelectricity were thought to offer the best prospect of achieving a strong linear ME coupling coefficient owing to the combination of typically higher electric permittivity and magnetic permeability, both of which combine as an upper limit to any potential coupling strength. Unfortunately, ME–MF materials are rare as ferroelectric materials need to be robustly insulating while magnetic materials are typically conducting. Although uncommon, such compounds have been the subject of intense research over the past decade. The realization of this phenomenon may lead to the development of multistate logic, new memory or advanced sensor technologies. To integrate such characteristics into a functional device requires strong ME coupling between the ferroic properties, enabling the manipulation of magnetic order with an electric (E) field or electric polarity with a magnetic field. The intense search for materials exhibiting such functional ferroic combinations has centered upon a number of complex oxide systems with a pseudo-cubic perovskite structure. Within these systems, the electronic band structure of the central B-site cation generally determines the ferroic properties. A completely empty d band is required for ferroelectricity, while partial occupation is essential for the double and superexchange (SE) magnetic interactions, typical of these materials. One approach circumventing this obstacle has been to engineer spatially segregated two-phase systems, which take advantage of electronic or magnetostriction mediated through strain or proximity to generate ME coupling. However, finding an intrinsic single-phase mechanism would evade the inherent disadvantages and complexities of multiphase environments. In single-phase systems, the d band occupation issue is typically avoided through geometric (magnetic) frustration, where the ferroic properties arise from the Dzyaloshinski–Moriya interaction. In these cases, the ferroic properties are weak, relegating device application unlikely.

Suffice to say, a great deal has been accomplished regarding E-field-controlled magnetism. The popular MF pseudo-perovskite material BiFeO$_3$, which presents both G-AFM and ferroelectric order, has shown intrinsic single-phase ME character. The orientation of the AFM Fe spins are always perpendicular to its rhombohedral long axis, which derives from the ferroelectric distortion. As a result, the magnetic domain structure can be reoriented by E-field application. Equally important, the manganite family has had a significant role in our understanding of ME phenomena. Interest peaked with HoMnO$_3$, when FM, correlated with Ho$^{3+}$ spin ordering, was activated by a static E-field. Interestingly, the induced FM order originated from uncompensated magnetization at the AFM domain walls rather than from an intrinsic phenomenon. Similarily, cross-coupling effects were found in another single-crystal ferrite system, GdFeO$_3$, arising from domain wall interactions when weak MF–FM domains interfaced with ferroelectric regions. Designing epitaxial heterostructures have also generated several avenues creating coupled control parameters. Interfacing MF materials BiFeO$_3$ or YMnO$_3$ with a soft FM system provides opportunities for phase coupling to electrically control both magnetic exchange bias and spin reorientation. In addition, more direct methods have included altering the ferroelectric domain orientation of a BaTiO$_3$ single crystal demonstrating the ability to change the magnetic strength of a FM $\text{La}_0.66\text{Sr}_{0.33}\text{MnO}_3$ film, and active strain tuning through interfacing the same material to a piezoelectric single crystal presented the ability to change the magnetic transition temperature, $T_C$, with E-field.

The rare earth tetravalent titanate, EuTiO$_3$ (ETO), is an emerging multication ferroic prototype, whereby magnetic spins are carried by the half-occupied Eu 4f$^3$ spins, and the unoccupied Ti 3d$^0$ band lends itself to potential ferroelectricity. Moreover, the anomalous response of the dielectric constant to spin alignment indicates an inherent ME coupling mechanism in ETO (ref. 23). It was this effect that impelled Fennie and Rabe to calculate that, through strain engineering, one could create strong multiferroicity and additionally predicted the exceptional strain-boundary state, allowing cross-field control capability. Indeed, epitaxial films of tensile-strained ETO showed multiferroicity with a large ferromagnetic moment ($7 \mu_B$/Eu) alongside spontaneous electric polarization ($\sim 10 \mu C/m^2$) (ref. 25). Furthermore, ETO demonstrates a third-order biquadratic ME coupling response ($E^2H^2$) allowing for circumvention of the linear ME susceptibility boundary condition.

In this article, we present E-field control of the full magnetic moment in the single-phase ETO system. However, our findings do not match initial predictions. Instead, we find that the dramatic ME effect does not require the proposed polar instability. Rather, the combination of tuning the relative strengths of the intrinsic competing magnetic interactions under a moderate compressive strain state with the inherent paraelectric nature of the system is sufficient to generate complete ME control. X-ray resonant magnetic scattering (XRMS) was used to confirm the magnetic structure of the contrasted strained ETO film series and reveal the emergence of competition between coexisting magnetic interactions in a moderately ($\sim 0.9\%$) compressed state. First-principles density functional theory (DFT) calculations identified the third nearest neighbour (NN) Eu interaction central to the G-AFM structure of ETO. Finally, using in situ (E-field) XRMS, we demonstrate cross-field ME control by eliminating long-range AFM order and inducing a magnetic state of nanometre-sized FM clusters. The underlying intrinsic mechanism is illustrated through simulations replicating the effect of E-field application by calculating the energy difference between the AFM and FM spin configurations.

Results

X-ray resonant magnetic scattering. X-ray scattering is sensitive to both charge and magnetic distributions. Typically, the magnetic component is about six orders of magnitude lower than conventional charge scattering. However, an enhanced magnetic response is achieved through resonance, in the present case at the Eu L$_{II}$ edge, whereby, mediated by the Eu 4f-5d exchange interaction, the Eu sublattice magnetic structure is probed with E1 ($2p_{1/2} \rightarrow 5d_{3/2}$) electronic excitations. In addition, owing to the polarization dependence of magnetic scattering a post-sample analyser can be used to preferentially suppress charge scattering as illustrated in Fig. 1a. Unstrained, compressive and tensile strain states were accomplished with 22 nm of epitaxial cubic on cubic-layered growth by ozone-assisted molecular beam epitaxy on SrTiO$_3$(STO), (LaAlO$_3$)$_{0.29}$(LSAT) and DyScO$_3$(DSO) single-crystal substrates, respectively.

Both ETO and STO share the same lattice parameter, thus when grown on the (001) surface, the film is nominally unstrained and exhibits bulk like G-AFM order with the emergence of magnetic scattering intensity at $1/2 1/2 5/2$ ETO below $T_N$ at 5.25 K shown in Fig. 1a. A $\sim 0.9\%$ compressive strain is then imposed by the LSAT (001) substrate and as shown in Fig. 1b, both ETO and STO remain the same lattice parameter, however strain the ETO film grown on DSO(110) is, however, ferromagnetic, confirmed both by the absence of a resonant magnetic signature at the $1/2$
half-order reflections typical of LSAT. The inset shows the resonant response with an energy scan at 1.5 K through the Eu LII edge. The error bars present s.d. data set for the compressively (polarization selection analysis (inset) used to suppress charge and optimize the magnetic/charge scattering ratio. (contribution was about 9% of the total intensity. The results of statistical error propagation is presented for the difference signal.

shown with the increase of scattered intensity through the edge and indicates the spontaneous (zero field) FM long-range order. The magnetic scattering through the Eu LII edge above and below C mark of 4.05 K. Some charge-scattered leakage is detected; however, an energy scan through the Eu LII edge is presented in the inset showing no resonant (magnetic) response. The finding demonstrates absence of long-range G-AFM order of the Eu ions in the FM phase. The leaked charge amplitude derives from the octahedral tilting pattern, (a ~ c5) (ref. 32). (b) Presents contrasting energy scans through the Eu LII edge above and below Tc at the integer (001)ETO reflection. Inset plots an L-scan through the same reflection. Owing to the overlap of both charge and magnetic scattering at this reflection, complete suppression of the former is constrained. The onset of magnetic scattering below Tc is shown with the increase of scattered intensity through the edge and indicates the spontaneous (zero field) FM long-range order. The magnetic scattering contribution was about 9% of the total intensity. The results of statistical error propagation is presented for the difference signal.

1/2 5/2)ETO reflection shown in Fig. 2a and with the emergence of a resonant enhancement of the magnetic scattering at the (001)ETO reflection at 1.6 K below the Tc mark of 4.05 K. Some charge-scattered leakage is detected; however, an energy scan through the Eu LII edge is presented in the inset showing no resonant (magnetic) response. The finding demonstrates absence of long-range G-AFM order of the Eu ions in the FM phase. The leaked charge amplitude derives from the octahedral tilting pattern, (a ~ c5) (ref. 32). (b) Presents contrasting energy scans through the Eu LII edge above and below Tc at the integer (001)ETO reflection. Inset plots an L-scan through the same reflection. Owing to the overlap of both charge and magnetic scattering at this reflection, complete suppression of the former is constrained. The onset of magnetic scattering below Tc is shown with the increase of scattered intensity through the edge and indicates the spontaneous (zero field) FM long-range order. The magnetic scattering contribution was about 9% of the total intensity. The results of statistical error propagation is presented for the difference signal.

Contrasting with the unstrained (STO) and tensile strain (DSO) conditions, the temperature dependence of the magnetic scattering intensity of the compressive state (LSAT) shows a significantly dissimiliar and suppressed critical behaviour, presented in Fig. 3a. This character is found in systems owing to local competition between FM and AFM interactions exemplified by the mixed-magnetic crystal system Gd0.1Eu0.9S (ref. 28). The temperature-dependent magnetic scattering intensity is fit to the critical behaviour \( \langle m^2 \rangle \sim I = I_0 (1 - T/T_C)^{2\beta} \), where \( \langle m \rangle \) is the magnetic moment, T is the magnetic transition temperature and \( \beta \) is the critical order exponent. The AFM order of the ETO on STO film is best described by the three-dimensional Heisenberg model owing to the isotropic (rotational degree of freedom) character of half-filled Eu 4f spin states. The measured critical order exponent, \( \beta = 0.385 \) of the same film follows ‘universally’ within the framework of statistical mechanics. However, a larger exponent, 0.496, is found in the compressively strained ETO film on LSAT (001). The substantial magnetic suppression demonstrates significant local magnetic competition. Similar to the unstrained G-AFM state, the tensile-strained ETO–DSO film in the FM phase also indicates three-dimensional Heisenberg behaviour where the local FM exchange dominates the AFM interactions without evidence of competing magnetic interactions.

DFT calculations. Clearly both local AFM and FM interactions coexist within the ETO. In order to describe the underlying mechanism determining the G-AFM Eu spin structure, previous
Figure 3 | Magnetic critical behaviour of the three strain states and XRD of the oxygen octahedral rotations in the ETO on LSAT. (a) The temperature dependence of the XRMS Eu LII amplitudes for all three strain states, STO—unstrained, LSAT—0.9% compressive and DSO—1.1% tensile. The solid lines are fits of the critical behaviour \( \langle m \rangle^2 \sim J = J_0(1 - T/T_c)^{2\beta} \), where \( \langle m \rangle \) is the magnetic moment, \( J \) is the magnetic scattered intensity, \( T \) is the sample temperature, \( T_c \) is the magnetic transition temperature and \( \beta \) is the critical order exponent. Both the G-AFM order in the unstrained (STO) and FM order of tensile (DSO) films show typical three-dimensional Heisenberg behaviour while the compressively strained (LSAT) film shows significant suppression, a classic indicator of local magnetic competition. Inset—top, presents a log-log plot showing the near transition region. Inset bottom illustrates the magnetic interactions between the first, second and third NN Eu ions. (b) The symmetry response of the ETO film to the biaxial compressive tetragonal distortion imposed by the LSAT (001) substrate. Both the (1/2 1/2 5/2)ETO and (1/2 1/2 5/2)ETO reflections at 300 K are presented. The occurrence of half-order Bragg peaks show the presence of long-range AFD rotations in the film. The combination of \( H = L \) allowed and \( H = K \) forbidden reflections indicate I4/mcm symmetry with the oxygen octahedral pattern \((a^0a^0c^-)\) in Glazer notation \(^{32}\), illustrated in the bottom inset. Again the LSAT substrate generates substantial background from the anti-phase boundary half-order reflections. The top inset indicates the relative position of the (002)\(_{\text{ETO}}\) reciprocal position with respect to the substrate (002)\(_{\text{LSAT}}\).

Table 1 | Calculated magnetic exchange constants.

| ETO—LSAT          | \( J_{1\text{st}} \) | \( J_{2\text{nd}} \) | \( J_{3\text{rd}} \) | \( J_{2\text{nd}} \) | \( J_{3\text{rd}} \) |
|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| /K_{0f}(K)—bulk   | +0.075          | -0.114          | +0.062          | +0.083          | -0.031          |
| # Neighbours      | 4               | 2               | 4               | 8               | 8               |
| /K_{0f}(K)—LSAT   | +0.086          | -0.147          | +0.06           | +0.087          | -0.034          |

Shown are the exchange constants (\( J \)) calculated between the Eu ions within the unconstrained bulk I4/mcm ETO and the ETO film on LSAT with \((a^0a^0c^-)\) structure under \(-0.9\%\) compressive strain, including the first, second and third NN Eu ions describing both the in-plane \((xy)\) and out-of-plane \((z)\) interactions. Positive indicates FM and negative AFM coupling. The second row indicates the number of neighbours for each particular interaction. The first and second NN interactions are mostly FM bar the first NN out-of-plane \( J_4 \) exchange constant. The calculations indicate the importance of \( J_3 \) in determining the G-AFM structure in ETO.

first-principles DFT focused on the first and second NN Eu ion interactions, illustrated in Fig. 3a—inset\(^{29,30}\). Without significant volume (lattice) expansion, the calculations found FM order preferential. However, to investigate the underlying factor leading to the G-AFM magnetic structure, the issue of symmetry needed to be addressed, in order to best know the structure at hand. This is preferred under compressive strain. XRD confirmed the I4/mcm symmetry in the compressed ETO film on LSAT(001). The competition between \( J \) and rotational structural instabilities leads to the calculated suppression of the phonon instability state \(^{34}\). The biaxial compression drives the AFD in-plane rotation in an attempt to maintain the Ti–O bond lengths, consequently preventing the T01 phonon from ‘freezing’ out of the film plane by providing a mechanism to minimize bond length changes. While the previous calculations without rotations (pm-3m) indicated a \(~ -0.9\%\) strain generating the polar instability, our current calculations, including the AFD rotations, require \(~ -2.5\%\) compressive strain beyond what is currently achievable.

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- **ETO—LSAT**
  - \( J_{1\text{st}} \) = +0.075, \( J_{2\text{nd}} \) = -0.114, \( J_{3\text{rd}} \) = +0.062, \( J_{2\text{nd}} \) = +0.083, \( J_{3\text{rd}} \) = -0.031
  - \# Neighbours = 4 (4), 2 (2), 4 (4), 8 (8), 8 (8)
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**Notes:**
- These exchange constants \( J \) are calculated between the Eu ions within the unconstrained bulk I4/mcm ETO and the ETO film on LSAT with \((a^0a^0c^-)\) structure under \(-0.9\%\) compressive strain, including the first, second and third NN Eu ions describing both the in-plane \((xy)\) and out-of-plane \((z)\) interactions. Positive indicates FM and negative AFM coupling. The second row indicates the number of neighbours for each particular interaction. The first and second NN interactions are mostly FM but the first NN out-of-plane \( J_4 \) exchange constant. The calculations indicate the importance of \( J_3 \) in determining the G-AFM structure in ETO.
The calculation replicates the suppression of the AFM state in agreement with the experimental observation. The central Ti 3d 0 band coupled to the Eu 4f 7 spins however, is AFM coupled. This diagonal exchange is most likely interact in aggregate, with FM order. The third NN interaction, respectively. We find that both the first and second NN Eu atoms configurations as a function of polarization modelled upon the ETO on LSAT with a compressive strain state of xy

In Table 1, we present the calculated results of the magnetic exchange interactions (J) for the first, second and third NN Eu ions for the ETO I4/mcm structure for both bulk (zero boundary conditions) and under ~0.9% compressive strain, simulating epitaxial growth on the LSAT substrate. The exchange constants are broken down further into in-plane (xy) and out-of-plane (z), with positive and negative values indicating FM and AFM, respectively. We find that both the first and second NN Eu atoms interact in aggregate, with FM order. The third NN interaction, however, is AFM coupled. This diagonal exchange is most likely facilitated by the central Ti 3d0 band coupled to the Eu 4f0 spins through a 180° SE mechanism mediated by the intra-atomic-hybridized 4f-5d orbitals, similar to the previously proposed 90° SE mechanism between the first NN Eu ions.

As a result, the G-AFM structure is dependent upon this third NN interaction. Moreover, the strength of this SE coupling is reliant upon the Eu–Ti–Eu bond alignment and the degree of interatomic orbital overlap, thus sufficient angular distortion could significantly alter the magnetic structure of the entire system.

Applying electric fields. Upon this premise, the paraelectric nature of the ETO film becomes central to the feasibility of ME control. In Fig. 4a, the cartoon illustrates how the third NN interaction bond angle alignment is distorted by the Ti displacement from its central position under an applied E-field, reducing the efficacy of the interaction. Under biaxial compression, the system is expected to have a preferential uniaxial polar anisotropy with the Ti displacement out of the film plane. Thus in order to examine the capability of ME cross-field control, we measured the magnetic signature of the strained ETO–LSAT film where the competition between the magnetic interactions is prevalent and applied an E-field across the film to further alter the magnetic balance, as illustrated in the sample schematic in Fig. 4b.

A series of reciprocal space scans through the G-AFM (1/2 1/2 5/2) ETO magnetic reflection at 1.9 K versus E-field strength is presented in Fig. 4c. The suppression of the XRMS intensity with E-field is clearly displayed and is ostensibly eliminated by 1.0 × 105 V cm−1. The transition lacks hysteresis, is continuous and reproducible. In Fig. 4d, the resonant magnetic scattering amplitude at the fixed film Q position is plotted with decreasing E-field strength and on the return the data are extracted from a series of L scans through the magnetic reflection at each field point. This plot exemplifies the reversibility and demonstrates the stability of the transition with each data point separated by 30 min on the return.

To further establish the proposed underlying ME microscopic mechanism, we performed first-principles DFT calculations to replicate the response of the applied E-field on the strained film. In Fig. 4d, the calculated enthalpy difference between the G-AFM and FM spin configurations is plotted against the effective electric field strength reducing the third NN exchange coupling. This shift affects the relative strength of the local magnetic interactions reducing the third NN exchange coupling.

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The charge–magnetic interference phenomenon is eliminated with the external magnetic field direction result in charge–magnetic interference of the magnetic moments uniformly canting towards an external H-field. Naturally, the G-AFM-ordered Eu spins coherently cant towards the external H-field direction; however, with applied E-field, the near magnetic degenerate states likely induce a collinear mixed AFM–FM phase devoid of long-range magnetic ordering. While the FM regions produce insufficient coherency themselves, by pining neighbouring AFM spin orientations along the applied H-field direction they inhibit spin canting and in effect mute the interference effect. S.d. errors are propagated for the difference measurements.

**X-ray resonant interference scattering.** To explore the ensuing magnetic state by E-field, we employed X-ray resonant interference scattering (XRIS)\(^{36}\). XRIS is sensitive to the magnetic moment aligned along one direction by either an internal FM interaction or an external magnetic field. Even in the AFM state, the magnetic moments uniformly canting towards an external magnetic field direction result in charge–magnetic interference of the scattered intensity illustrated in Fig. 5a. Here, contrasting energy scans through the Eu L\(_{\text{II}}\) edge at the (003\(_{\text{ETO}}\) reflection with \(\pm 1.2\) T showing the maximum interference effect at full saturation between the magnetic and charge scattering amplitudes. The sign of the magnetic amplitude switches with the H-field direction altering the interference effect. Similarly, if the electric field induced a true AFM–FM degenerate state, such magnetically frustrated moments would nevertheless align along the applied magnetic field direction resulting in an interference effect. Similarly, if the E-field caused a paramagnetic state, 0.1 T is sufficient to align the magnetic moments producing an interference effect owing to small thermal fluctuations at this temperature, 1.9 K. Consequently, the magnetic state induced by the E-field is neither frustrated nor paramagnetic. However, to adequately explain both the XRIS and AFM order suppression would require the emergence of short-range-ordered nanometre-sized FM clustering. This model disrupts the long-range spin coherence of the AFM order while the emergence of FM interactions in short-range cluster formation remains insufficiently large to significantly contribute to the charge–magnetic interference.

**Discussion**

Our findings present conclusive evidence for direct single-phase cross-field ME control in a compressively strained EuTiO\(_3\) film. Employing in situ X-ray scattering measurements, we present reversible electric switching of magnetic order using a strong intrinsic coupling phenomenon. We have directly measured the microscopic magnetic structure of EuTiO\(_3\) as G-AFM under low-strain states (0.0 and 0.9%) and FM under 1.1% tensile strain. The magnetic critical parameters show –0.9% compressive strain that alters the relative strengths of coexisting AFM and FM magnetic interactions bringing them into competition. First-principles DFT calculations indicate that the third NN Eu ion SE interaction, mediated through the central Ti ion, ultimately determines the G-AFM spin periodicity along the \(\langle 111\rangle\) direction. Moreover, by calculating the energy of the simulated ETO–LSAT film, we have replicated our experimental findings by modelling the field-induced polarization effect with controlled Ti displacements. As such, the energetic stability of the AFM order dissipates leading to the emergence of FM interactions.
The underlying mechanism relies on bond alignment distortion suppressing the efficacy of the third NN Eu–Ti–Eu interaction. This novel ‘giant’ ME coupling phenomenon will likely offer intriguing prospects to explore new types of ME functionality.

**Methods**

**X-ray resonant magnetic scattering.** XRMS measurements were performed on the 6-ID-B beamline at the Advanced Photon Source and the XMaS beamline at the European Synchrotron Radiation Facility. The sample was mounted on the cold finger of a Joule–Thomson stage closed cycle helium displex refrigerator. The 6-ID-B beamline is a bending magnet source, and the energy selection performed with a water-cooled double-crystal Si(111) monochromator. All samples were oriented with respect to the substrate crystalographic axis. The films are epitaxial to their substrates so that the film diffraction peaks are easily found with respect to the substrate reciprocal matrix. The incident X-ray is linearly polarized perpendicular to the scattering plane (σ polarization). The resonant magnetic scattering, arising from electric dipole transitions from the 2p- to 5d-states, rotates the polarization resulting in π-polarized photons (parallel to the scattering plane). A post-sample pyrolytic graphite analyser at the (0 0 6) PG reflection performed with a water-cooled double-crystal Si(111) monochromator. We used a 8 × 8 k-point grid for Brillouin zone integrals and a 500 eV plane-wave energy cutoff. This cutoff has been increased to 600 eV in certain parts of the volume. Exchange parameters for an Ising model are fitted to total energy calculations for greater accuracy. Geometric relaxations are done by keeping the in-plane lattice parameter ‘a’ fixed and relaxing the out-of-plane lattice parameter ‘c’. Residual force threshold was decreased to 0.5 eV Å$^{-1}$ where necessary in order to resolve differences between states close in energy. An external stress has been applied along the c axis in order to compensate for the overestimation of cell volume. Exchange parameters for an Ising model are fitted to total energy calculations done in a 2 × 2 × 2 perovskite supercell that consists of 40 atoms and 10 different magnetic configurations. S.d.s of these exchange parameters are not reported as they are of no qualitative significance.

EuTiO$_3$ is predicted to be near a magnetic phase transition as a function of the on-site Hubbard repulsion parameter U (ref. 30). In order to pick a best initial estimate of U, we calculate the Curie–Weiss constant and Neel temperature for bulk (under fixed stress boundary conditions) ETO, the results are presented in Table 2. It is not possible to reproduce the exact transition temperatures from first principles owing to limitations of the simple mean field theory we used, and also because of the very small energy differences under consideration. However, if we pick a U that gives a T$_C$/T$_N$ ratio close to experiment (T$_C$ is extracted from susceptibility measurements$^{28}$), then we can get a good sense of the competition between FM and AFM states. We see that U = 5.7 eV, which is the value that was used in previous studies works well when oxygen rotations were not taken into account$^{24}$. However, once the rotations are taken into account and calculations are repeated in the relevant structure (I4/mmc), a U = 5.7 eV overestimates the T$_C$/T$_N$ ratio. To better fix the deficiencies in DFT, we instead use U = 6.2 eV as standard. Also, an intra-atomic exchange parameter J = 1.0 eV is kept fixed.

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