Complexity in the structural and magnetic properties of almost multiferroic EuTiO_3

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In a number of recent publications hidden magnetic properties at high temperatures have been reported for EuTiO_3 (ETO), which orders antiferromagnetically below $T_N = 5.7$ K. In addition, structural phase transitions have been discovered which correlate with the magnetic responses and can be tuned by a magnetic field. In order to identify the magnetic properties of ETO at temperatures well above T_N , low-energy muon-spin rotation (μSR) experiments have been performed on thin films of ETO which exhibit all properties observed in bulk materials and are thus well suited to conclude about the magnetic order of the bulk. The μSR data reveal anomalies at 282 and 200 K related to the structural phase transitions in accordance with birefringence results. In addition, a transition to some kind of magnetic order below 100 K was observed as previously indirectly deduced from conductivity and dielectric constant measurements.

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EuTiO_3 (ETO) was discovered early on [1] and was rapidly confirmed to undergo a transition to G -type antiferromagnetic order below $T_N = 5.7$ K [2]. Interest in this compound came up only in the early 21st century when strong magnetodielectric coupling below T_N was reported [3]. The abrupt decrease of the temperature-dependent dielectric constant related to a soft optic mode below T_N [4] has been taken as a signature for possible multiferroic properties. These have subsequently been confirmed indirectly in strained thin films, where a peak in the dielectric constant around 240 K, together with ferromagnetic properties below 4.5 K, support this viewpoint [5]. These data, however, have to be taken with care, since the subsequently discovered structural phase transition at 282 K [6,7] was unknown then. In addition, leakage problems hindered the observation of a hysteresis loop and conclusions about true ferroelectricity remain elusive.

In a variety of recent publications it has been shown that the antiferromagnetic phase of ETO is much more complex than anticipated [8–11]. Also, magnetic field effects have been observed for temperatures well above T_N [12], and signatures of hidden magnetism have been detected in bulk materials of ETO by μSR [13], conductivity, and dielectric constant measurements [14]. From the latter experiments two temperature scales have been reported, namely, around $T^* = 190$ K and around $T' = 100$ K. Both of these data did not yet permit one to draw conclusions about either another structural phase transition or magnetic order. Very recent birefringence measurements on transparent thin films of ETO unambiguously evidence a structural phase transition from tetragonal to monoclinic at T^* which can be influenced by a magnetic field [15]. This conclusion is supported by the fact that the axes [100], [010] and [110], [1 $\bar{1}$ 0] are no longer equivalent. The data, unfortunately, do not allow one to conclude about any magnetic order below 200 K. However, correlating these with low-field μSR data enables us to identify the magnetic order below T^* and T' .

Thin films of ETO of 1000 nm thickness have been grown on a SrTiO_3 substrate and characterized by magnetic

susceptibility measurements, ellipsometry, x-ray diffraction (XRD), and birefringence. The samples are highly transparent with a large band gap [15], much larger than reported before, exhibit no leakage currents (a problem encountered in previously investigated films [5,16,17]), and are strain free and single crystalline. They become antiferromagnetic below $T_N = 5.2$ K, and undergo a structural instability from cubic to tetragonal at $T_S = 282$ K, as found for bulk ETO. However, for the ETO films, two additional structural phase transitions have been observed by birefringence at $T^* = 190$ K and $T' = 100$ K (Fig. 1) [15] which have already been suspected from previous μSR data [13]. This observation evidences that the phase diagram of ETO is much more complex than anticipated.

Since the birefringence at T_S and T^* can be tuned by a small magnetic field, some ordering of the large Eu $4f^7$ spins takes place at both temperatures. In order to identify its origin, low-energy μSR experiments were performed at the μE4 beamline at the Paul Scherrer Institut (PSI, Switzerland). For the ETO thin-film measurements a mosaic of four $1 \times 1 \text{ cm}^2$ large thin-film samples on the SrTiO_3 substrate was glued with silver paint onto a nickel-coated aluminum plate. The measurements have been carried out in ultrahigh vacuum (about 10^{-9} mbar). To investigate the ETO films, the muons were slowed down using a solid Ar/N_2 moderator, so that they stopped on a nm scale in condensed matter. At the μE4 beamline the low-energy muons were produced at a rate of about 10^4 s^{-1} with 100% spin polarization [18,19]. The muons were implanted into the sample where they thermalized within a few picoseconds without a noticeable loss of polarization. The muon stopping distributions $n(z)$ (see Fig. 2) were simulated for energies in the range 4–25 keV using the Monte Carlo code TRIM.SP [20]. The reliability of these simulations has been studied in various thin films [21,22]. The mean stopping depth $z = \int n(z)zdz$ of the muons in ETO is in the range 20–120 nm. This ensures that our measurements are not contaminated by contributions from the substrate, which is especially important near T' of ETO where SrTiO_3 undergoes a structural phase transition from cubic to tetragonal [23–26].

FIG. 1. Birefringence Δn of the ETO film, calculated for a region of $130 \mu\text{m} \times 180 \mu\text{m}$, as a function of temperature and in a magnetic field of $B = 0.1 \text{ T}$. The transition temperatures T' , T^* , and T_S are marked by vertical dashed lines. The straight red line corresponds to the temperature dependence of the birefringence as expected from Landau theory.

An additional proof that strains from the substrate below T' are not affecting the ETO film properties has been obtained from birefringence measurements of the substrate [15] only, which is more than one order of magnitude smaller than the one of the film. Furthermore, previous μSR measurements have been carried out on ceramic bulk samples of ETO [13] showing this transition as well.

In zero field and in the temperature range 4.5–320 K, two-component signals were observed, as shown in Fig. 3(a), a signal with very fast exponential relaxation and one with slow relaxation. Thus, the μSR data were analyzed by using the following functional form,

$$A(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t), \quad (1)$$

FIG. 2. The normalized stopping distribution for positively charged muons at different implantation energies for ETO was simulated with TRIM.SP. The lines are guides to the eye.

FIG. 3. (a) Zero-field (ZF) μSR spectra of $A_{\text{ZF}}(t)$ of ETO film, recorded at various temperatures. (b) Longitudinal field (LF) μSR time spectra $A_{\text{LF}}(t)$ of ETO film recorded at $T = 4.5 \text{ K}$ with different magnetic fields applied along the initial direction of the muon-spin polarization.

where A_1 and A_2 denote the asymmetries of the fast and the slow components, respectively. The relaxation rates λ_1 and λ_2 characterize the exponential damping of the two components. Regarding the two-component signals in EuTiO_3 , the signal with fast (slow) relaxation is due to the volume fraction of strongly (weakly) magnetic regions in the sample. The weakly magnetic regions are caused by the magnetic field influence of the strongly magnetic regions on these paramagnetic areas. One can visualize the sample as a two-component system where strongly magnetic regions coexist with paramagnetic ones and polarizing those by their net magnetic field.

Figure 3(b) shows the results of the μSR experiments in longitudinal fields (LFs) (magnetic fields are applied along the initial direction of the muon-spin polarization) up to 150 mT at $T = 4.5 \text{ K}$. These experiments showed that at modest external fields between 10 and 150 mT, the muon-spin relaxation of the slow component is substantially suppressed. This means that the muon spins are fully decoupled from the internal magnetic fields, demonstrating that the weak internal fields are static

FIG. 4. (a) The temperature dependencies of A_1 (black circles) and A_2 (red squares), corresponding to the ZF asymmetries of the fast and the slow components, respectively. (b) The temperature dependence of the relaxation rate λ_1 of the slow component and (c) the λ_2 of the fast component.

rather than dynamic, supporting the quasistatic origin of the slow muon-spin depolarization.

The temperature dependences of the above described parameters are shown in Fig. 4. $A_2(A_1)$, which is proportional to the volume of the strongly (weakly) magnetic regions, increases (decreases) [see Fig. 3(a)] below $T_S \approx 280$ K and reaches a saturation value of $\approx 0.115(0.12)$ at $T' \approx 100$ K. Below T' , strong and weak magnetic regions acquire 20% and 80% magnetic volume fractions, respectively. There is an intermediate regime between $T^* \approx 190$ and 100 K where both A_1 and A_2 show a continuous increase (decrease) with temperature. Since T^* has been unambiguously assigned to a structural transition from tetragonal to monoclinic and

shown to be strongly magnetic field dependent [15], the data of Fig. 4(a) are interpreted as magnetic fluctuation enhanced regions with possible ferromagnetic correlations. The relaxation rate λ_1 starts to increase below the structural phase transition temperature $T_S \approx 282$ K, which is consistent with our previous results on the bulk ETO sample [12]. Around T^* a smooth increase takes place with an abrupt increase below T' . λ_2 also shows a peaklike anomaly at $T_S \approx 280$ K. The sensitivity of the relaxation rates λ_1 and λ_2 to the structural phase transition can be understood as a consequence of strong spin-lattice coupling in ETO, as discussed in our previous reports [12,13,27,28]. Below $T' \approx 100$ K, λ_1 shows an additional increase, suggesting the transition to some kind of magnetic phase.

In order to gain deeper insight into this magnetic transition in ETO films, μ SR experiments under weak transverse magnetic field (WTF) μ SR, applied perpendicularly to the initial direction of the muon-spin polarization, were carried out. WTF- μ SR spectra were fitted in the time domain with a combination of a slowly relaxing signal with a precession frequency corresponding to the applied field of $\mu_0 H = 5$ and 10 mT (due to muons in a paramagnetic environment) and a fast relaxing signal due to muons stopped in the strongly magnetic regions,

$$A(t) = A'_S \exp(-\lambda'_t) \cos(\gamma_\mu B' t) + A''_S \exp(-\lambda''_t) \cos(\gamma_\mu B'' t), \quad (2)$$

where $\gamma_\mu/(2\pi) \approx 135.54$ MHz/T is the muon gyromagnetic ratio. A'_S and A''_S are the amplitudes of the slowly (paramagnetic) and fast relaxing sample signals, respectively. λ' is the relaxation rate of the paramagnetic region of the sample, caused by the paramagnetic spin fluctuations and/or nuclear dipolar moments. Moreover, since the paramagnetic areas are influenced by the magnetic regions (discussed above), λ' contains information about the magnetic areas of the sample. λ'' is the relaxation rate of the magnetic part of the sample. B' and B'' are the magnetic fields, probed by the muons stopped in the paramagnetic and magnetic parts of the sample, respectively.

The results of the WTF- μ SR experiments are summarized in Figs. 5(a)–5(c). Figure 5(a) shows A'_S as a function of temperature in EuTiO₃ films. Above T_S , A'_S exhibits a constant value, consistent with the fact that the sample is in the paramagnetic state, and all the muon spins precess in the applied magnetic field. A'_S starts to decrease with decreasing temperature below $T_S \approx 280$ K. A smooth decrease of A'_S takes place below $T^* \approx 190$ K, followed by an abrupt decrease below T' . The reduction of A'_S signals the appearance of magnetic order, where the muon spins experience a local magnetic field larger than the applied field. As a result, the fraction of muons in the paramagnetic state decreases. In Fig. 5(b) we plot the field shift $\mu_0 \Delta H = \mu_0(H_{\text{int}} - H_{\text{ext}})$ for a field of $\mu_0 H = 5$ and 10 mT. It is interesting to note that $\mu_0 \Delta H$ increases with decreasing temperature below $T_S \approx 280$ K. In a field of $\mu_0 H = 5$ mT, $\mu_0 \Delta H$ reaches the saturation value below $T' \approx 100$ K. In between T' and T^* again a smooth increase in $\mu_0 \Delta H$ takes place. With $\mu_0 H = 10$ mT, $\mu_0 \Delta H$ saturates at a slightly higher temperature. The increase of $\mu_0 \Delta H$ suggests the formation of ferromagnetic clusters which grow in size with decreasing temperature. These clusters are

FIG. 5. The temperature dependence of (a) the WTF asymmetry A' , (b) the field shift $\mu_0\Delta H$, and (c) the relaxation rate λ , for the 1000 nm ETO films in an applied field of $\mu_0H = 5$ and 10 mT.

most likely dynamic, as suggested by previous measurements of bulk samples [13]. λ' also shows a clear increase below $T' \approx 100$ K, supporting the above conclusion of the presence of magnetic order below this temperature, whereas T^* [Fig. 5(c)] is almost washed out. Figures 6(a) and 6(b) show the muon-energy dependence of λ' , and $\mu_0\Delta H$ in ETO films in a field of $\mu_0H = 5$ mT. As is obvious from Figs. 6(a), 6(b), and 2, within a depth range between about 20 and 120 nm, the magnetic properties of ETO are nearly unchanged, supporting our assumption that bulk properties are tested by the experiments and that the STO substrate is ineffective for the data.

To conclude, the above data provide convincing evidence for magnetic order far above the antiferromagnetic transition temperature $T_N = 5.4$ K. Specifically, they show that three temperature scales are relevant in ETO, namely, T_S, T^*, T' . While previous birefringence data, together with μ SR results [13], have already identified T_S and T^* , the lowest-temperature scale T' has only been speculated to exist from dielectric constant and capacitance experiments. At T_S magnetically fluctuating regions are formed, which is also supported from the magnetic field dependence of T_S [10]. Below T^* these regions increase smoothly in size to form almost static domains at T' which coexist with paramagnetic domains of approximately the same size.

Taking these results together with previous data, strong spin-lattice coupling is present in ETO already far above the antiferromagnetic phase transition at $T_N = 5.2$ K. Specifically, they show that three temperature ranges are relevant in ETO,

FIG. 6. (a) The relaxation rate λ , (b) the field shift $\mu_0\Delta H$, for the 1000 nm ETO films, measured in an applied field of $\mu_0H = 5$ mT as a function of the muon energy E .

namely, T_S, T^* , and T' which all coincide with a structural phase transition. While the cubic-to-tetragonal phase transition affects the second-nearest-neighbor spin exchange through changes in the Eu-O bond distance, the tetragonal-monoclinic transition at T^* modifies the direct exchange constant since two nearest-neighbor Eu ions approach each other along [100] and [010], whereby along [110] an elongation takes place, in contrast to [110], where the lattice contracts. Even though these changes are tiny, they lead to “ferromagnetic type” chains in alternation with “antiferromagnetic” ones along the main axis [100] or [010]. At T' another structural phase transition takes place where the above described pattern is modified through an additional c -axis contribution and the Eu ions are pairwise moving in and out of the ab plane. All three phase transitions have also clearly been identified by birefringence measurements [15], with the transition at T' being evidenced by an anomaly under the action of a magnetic field of 0.1 T (Fig. 1).

By considering the fact that the phase transition at T_S has remained elusive for almost 60 years, since the associated c/a ratio change is tiny, it is apparent that further transitions are hidden from XRD data, but are detectable by means of more sophisticated methods, such as birefringence and μ SR. The structural phases appearing below T^* and T' admit for polar properties and need additional investigations to confirm “ferroelectric” type properties, and thus true multiferroic behavior, however, absent on a macroscopic scale.

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