Magnetic field enhanced structural instability in $EuTiO_3$

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$EuTiO_3$ (ETO) undergoes a structural phase transition from cubic to tetragonal at T_S=282K which is not accompanied by any long range magnetic order but related to the oxygen octahedra rotation driven by a zone boundary acoustic mode softening [1]. High resolution laboratory X-ray powder diffraction evidences superlattice reflections at low temperatures connetcted to a cubic to tetragonal phase transition in ETO with a multiplication of the unit cell to $\sqrt{2}a\times\sqrt{2}a\times 2a$, with a being the cubic lattice parameter [2]. The room temperature structure could be refined in *Pm3m* with a = 3.908(1) Å and at 100 K the refinement in the tetragonal space group *I4/mcm* resulted in a = 5.519(1) and c = 7.816(1) Å. A schematic representation of the low temperature structure is presented in Fig. 1 where for clarity the oxygen octahedral rotation angle has been enlarged.

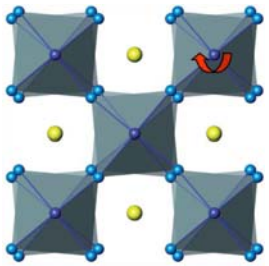

Figure 1: The schematic crystal structure of $EuTiO_3$ at -180°C in a projection along the *b*-axis, exhibiting TiO_6 polyhedra (blue shaded). The oxygen ions are displayed in blue, the Eu ions in yellow. For clarity the corresponding rotation angle indicated by an arrow has been enlarged by a factor of 2.

In order to compare the structural refinement of $EuTiO_3$ (ETO) with the one of $SrTiO_3$ (STO), the cubic c/a ratio is readily obtained from the above data. While this ratio is 1.00062 in STO at 4.2K, i.e. 100 K below the transition temperature, it is 1.0014 in ETO at 93 K, almost 200 K below the phase transition. This ratio can be combined with the angle of rotation φ of the oxygen octahedron via the relation $c/a = 1/\cos\varphi$ [2]. While in STO φ =2.1° at 4.2 K, in ETO it is φ =3.03° at 93 K. Since φ is the order parameter of the phase transition, its squared value varies linearly with $t=T/T_S$ as long as T is not too close to T_S. By using this relation and comparing the value of φ of ETO at 93K with data of STO, the extrapolated zero temperature value of the rotation angle is estimated to be 3.37 which is rather large as compared to STO, but a consequence of the fact that T_S of ETO (T_S=282K) is much larger than T_S in STO (T_S=105K).

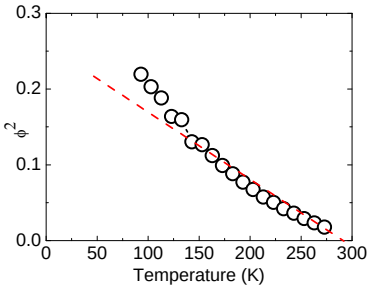

Figure 2: The temperature dependence of the square of the deviation angle φ from cubic symmetry (open circles). The dashed line is a guide to the eye [2].

The temperature dependence of the square of the deviation angle φ from the cubic symmetry is shown in Fig. 2. Analogous to STO it decreases almost linearly with increasing temperature and extrapolates to zero at T_S=282K. Opposite to this observation the lattice constant splitting is not observable at T_S but only at substantially lower temperatures substantiating the smallness of the tetragonal distortion [2].

Here we show that this displacive second order structural phase transition can be shifted to higher temperatures by the application of an external magnetic field (ΔT_S~4K for $\mu_0 H$=9T). This observed field dependence is in agreement with theoretical predictions based on a coupled spin-anharmonic-phonon interaction model [1,3].
A recent new result for ETO was obtained from μSR experiments where a finite relaxation rate λ_{para} could be detected in the paramagnetic phase of ETO up to temperatures well exceeding T_S [4]. Its temperature dependence follows the one of the soft zone boundary mode as well as the one of the

inverse EPR line width. This finding not only proves that the spin-lattice coupling is strong, but also demonstrates that correlated fluctuating spins are present already above T_S. Theoretically, this observation has been modeled within a spin-lattice coupled model Hamiltonian from which a hybrid paramagnon phonon coupled mode has been predicted to appear far above T_N [1,4,5]. Another consequence of this approach is that a magnetic field has a substantial influence on the eigenfrequencies of the system and thus possibly also on T_S. This suggests that strong a magneto-elastic coupling is present which should be detectable by resonant ultrasound spectroscopy. Since this method is not available in our group, T_S has been measured by specific heat in the presence of a magnetic field [3].

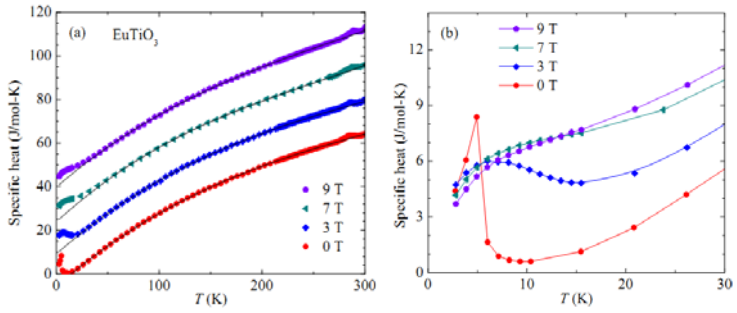

Figure 3 Specific heat of ETO as a function of temperature at $\mu_0 H$ = 0 T, 3 T, 7T, and 9T. For clarity the data are shifted by 15 J/mol-K relative to each other with increasing magnetic field. **b)** Specific heat of ETO at low temperatures showing the anomaly at T_N = 5.5 K (same data as in a).

The specific heat measurements were first performed in zero field and then repeated in fields of 3, 7, and 9T, see Fig. 3. Importantly, the zero field data (Fig. 3a) are in excellent agreement with our previously reported data [1]. For the field dependent data it is obvious from Figs. 3a and 3b that the low temperature specific heat anomaly caused by the antiferromagnetic phase transition diminishes with increasing field. At high temperatures the anomaly stemming from the structural phase transition is visible as a distinct peak (Fig. 4a). By concentrating on a limited temperature range around T_S the anomaly is enlarged and better visible as shown in Fig. 4a. Obviously a shift of T_S to higher temperatures takes place with increasing magnetic H which is shown in Fig. 4b. While the data of 0T and 3T are almost identical, a nonlinear enhancement of T_S is observed for larger magnetic fields. This observation has no analogies to other incipient ferroelectric perovskites, where the oxygen octahedra rotation instability is insensitive to a magnetic field. The consequences are multifold since a tuning of piezoelectric and pyroelectric effects in amorphous ETO is possible by a magnetic field and novel functionalities can be expected.

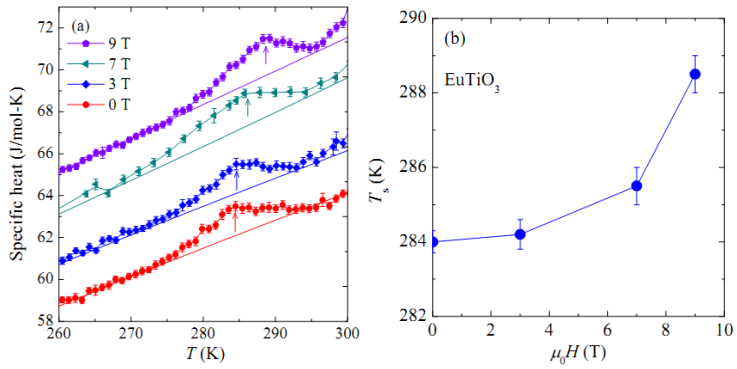

Figure 4 Specific heat of ETO as a function of temperature at $\mu_0 H$ = 0 T, 3 T, 7T, and 9T. For clarity the data are shifted by 15 J/mol-K relative to each other with increasing magnetic field. **b)** Specific heat of ETO at low temperatures showing the anomaly at T_N = 5.5 K (same data as in a).

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