PHYSICAL REVIEW B **90**, 094420 (2014)

Spin-lattice coupling induced crossover from negative to positive magnetostriction in $EuTiO_3$

P. G. Reuvekamp, R. K. Kremer, J. Köhler, and A. Bussmann-Holder
Max Planck Institute for Solid State Research, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

(Received 11 August 2014; revised manuscript received 11 September 2014; published 29 September 2014)

Magnetostriction experiments have been performed at temperatures in and above the antiferromagnetic phase of $EuTiO_3$. For magnetic fields below the spin-flop transition the magnetostriction is large and negative and changes to small and positive for fields exceeding this threshold. At the antiferromagnetic phase transition temperature a steep anomaly in the thermal expansion is observed in zero field which broadens and moves to lower temperature with increasing field strength. A small but well resolved anisotropy in the longitudinal and transverse field configurations of the magnetostriction is observed at low temperatures, which rapidly vanishes with increasing temperature. The crossover field where the magnetostriction changes sign coincides with the field strength where the dielectric constant adopts normal quantum paraelectric behavior and signifies strong magnetoelectric coupling to be its origin.

DOI: 10.1103/PhysRevB.90.094420 PACS number(s): 75.30.Cr, 75.50.Ee, 75.80.+q

$EuTiO_3$ (ETO) has recently attracted renewed interest after Katsufuji and Takagi demonstrated that the dielectric constant exhibits an unusual drop at the antiferromagnetic transition temperature $T_N = 5.5\,\mathrm{K}$ [1]. The increasing dielectric constant with decreasing temperature has subsequently been shown to stem from a long-wavelength soft transverse optic mode reminiscent of a ferroelectric instability [2,3]. In spite of the fact that a polar catastrophe does not take place in ETO at finite temperature, the cross coupling between magnetism and dielectric constant is suggestive of strong magnetoelectric coupling important for the design of novel devices for applications. In addition, we have recently provided evidence that magnetic fluctuations persist well in the paramagnetic phase [4–7]. These are closely tied to the structural instability of ETO at $T_S = 282\,\mathrm{K}$ [8] and coupled to the related soft zone boundary acoustic mode [9,10], thus establishing that strong spin-lattice coupling is present also at high temperature. Further support of this notion has been obtained by showing that T_S is a function of magnetic field and increases nonlinearly with it [6].

The high-temperature phase transition has been confirmed in subsequent work [11–14]. The low-temperature phase has been investigated in detail by various experimental techniques. Measurements of the specific heat, the magnetization, and susceptibility and torque magnetometry as functions of temperature and magnetic field show that below T_N and at low fields a spin-flop transition takes place which is followed by a first-order phase transition from easy axis to easy plane antiferromagnetic (AFM) ordering around 3 K. [12]. In Ref. [12] an attempt has also been made to manipulate the magnetic properties by an electric field and to create an electric dipole via the cross coupling. This approach is rather intuitive in view of the above-mentioned fact that the dielectric constant can be influenced by a magnetic field. However, no conclusive data have been obtained and the only evidence for strong magnetoelectric coupling, so far, has been reported in Ref. [1].

Here we address this latter issue again by using magnetostriction measurements in and above the low-temperature AFM phase of ETO. Magnetostriction, viz., the lattice deformation which accompanies a change in the magnetization [15] is assigned to the dependence of the exchange energy on the elastic strain and as such is a versatile tool to explore spin-lattice interactions. Large magnetostriction and unconventional thermal expansion have been reported in the magnetic spinels [16], the antiferromagnetic manganite fluorides [15], chromium oxides [17], europium oxide [18], and many more AFM's. The magnetostriction can be positive as well as negative and has a broad range of technological applications [19]. Typically, it follows linearly the square of the applied magnetic field which is the combined response of the exchange constants and crystal field effects [18].

Ceramic polycrystalline samples of ETO were prepared as described in Ref. [8]. The purity and quality of the samples were checked by high-resolution x-ray diffraction. The samples were characterized by specific heat, magnetic susceptibility, and magnetization measurements from which $T_N = 5.7\,\mathrm{K}$ was determined. The structural phase transition temperature was determined by specific heat as $T_S = 282\,\mathrm{K}$, in accordance with previous samples and measurements. For both temperatures clear peaks in the specific heat were observed. The magnetization and specific heat measurements were performed with Quantum Design's Magnetic Property Measurements System (MPMS-XL7) and Physical Property Measurements System (PPMS). The thermal expansion versus temperature and magnetic field was measured using a high-resolution miniature dilatometer hosted in the PPMS system [20].

As has already been demonstrated in Ref. [12], a magnetic field rapidly shifts T_N to lower temperatures and leads to a complete suppression of AFM order for fields above 1 T. The magnetization as a function of the magnetic field and temperature is shown in Fig. 1. It increases linearly with the field to saturate at 1.05 T with a moment of $m_{\mathrm{sat}} = 6.7(1)\,\mu_B$ at $T = 2\,\mathrm{K}$, slightly below the expected moment of $7\mu_B$ at 0 K and in agreement with our previously derived data [21] where magnetic fields up to 3 T have been employed. With increasing temperature m_{sat} decreases and a linear-in-T dependence without any saturation [corresponding to paramagnetic (PM) behavior] is seen already below 5.5 K. This is especially well seen when the field derivative of the data is used. From these data the field-dependent PM AFM phase diagram can be constructed (Fig. 2) by differentiating the data of Fig. 1 and by using the maxima of the thermal expansion coefficient shown

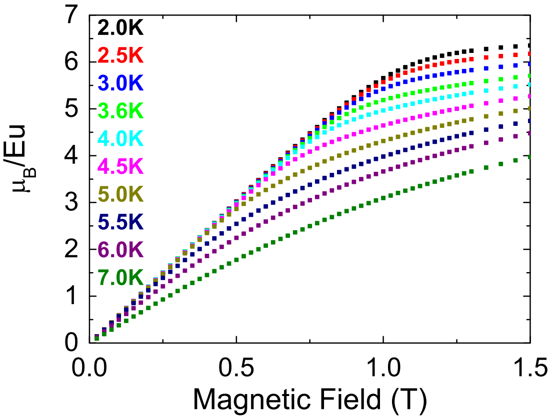

FIG. 1. (Color online) Temperature and magnetic field dependence of the magnetization of ETO.

in Fig. 4 for the low-field data. The insets to this figure refer to the specific heat (upper inset) and the magnetic susceptibility (lower inset) which compare very well with Ref. [12] and our previously obtained data on another sample [8].

The above-described experiments have been used to characterize our sample and demonstrate its quality. Further characterizations for ETO are obtained by magnetostriction together with thermal expansion experiments in the temperature range between 1.3 and 12 K. The magnetic field has been varied between 0 and 6 T. The raw data of these experiments are shown in Fig. 3 where the length change of the sample in the presence of a magnetic field $\frac{[L(T_0)-L(B)]}{L(T_0)} = \frac{\Delta L}{L(T_0)}$ is plotted as a function of temperature and magnetic field with the reference length, $L(T_0)$, taken at $T_0 = 10\,\mathrm{K}$, well above T_N. In zero field (taken before and after the field has been applied) a strong drop in $\Delta L/L$ is observed at T_N which is comparable to the one reported, e.g., for $\mathrm{ZnCr_2Se_4}$ [16]. With increasing field this anomaly shifts to lower temperatures and changes its character. For fields >0.625 T the magnetostriction becomes positive with a well resolved peak at 1 T where the Néel state is completely suppressed. For fields exceeding this threshold value $\Delta L/L$ continuously increases with decreasing temperature and increasing field. This behavior is very much reminiscent of the dielectric constant ε of ETO at low temperature which shows a rapid suppression at T_N followed by a peak up to 1 T to steadily increase with increasing field [1]. Since ε is inversely proportional to the squared soft optic mode frequency, this hardens at T_N and becomes softer with increasing magnetic field [8]. In relation to the data of Fig. 3 this implies that the field induced lattice expansion above 1 T together with the loss of AFM order supports the mode softening and is counteracting true multiferroic order [22].

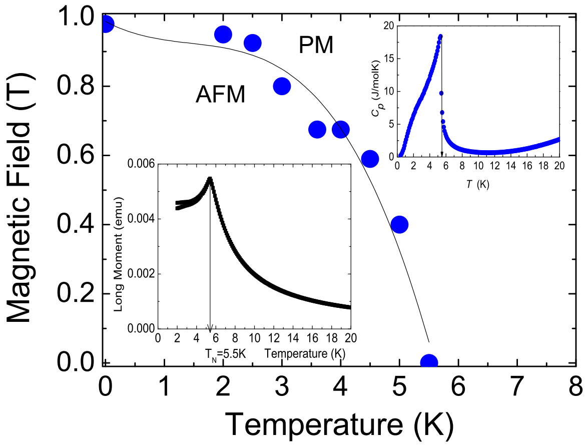

FIG. 2. (Color online) Phase diagram of ETO as a function of field and temperature. The full circles have been obtained from the field derivative of the data shown in Fig. 1 and the maximum in the thermal expansion coefficient shown in Fig. 4. The inset in the lower left corner shows the magnetic susceptibility of ETO and the inset in the upper right corner displays the low-temperature specific heat of ETO.

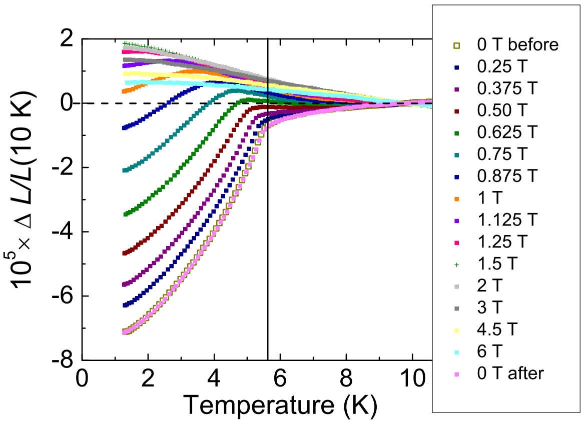

FIG. 3. (Color online) Relative length change as a function of temperature at different magnetic fields for ETO.

The data are further analyzed by deriving the thermal coefficient $\alpha = \frac{1}{L} dL/dT$ which is shown in Fig. 4 as a function of magnetic field $H \leqslant 1.25\,\mathrm{T}$ and temperature $1.3 < T < 12\,\mathrm{K}$. In zero field a sharp cusplike anomaly of α appears very similar to the specific heat jump, which moves to lower temperatures with increasing field and simultaneously broadens and decreases. The anomaly has almost completely

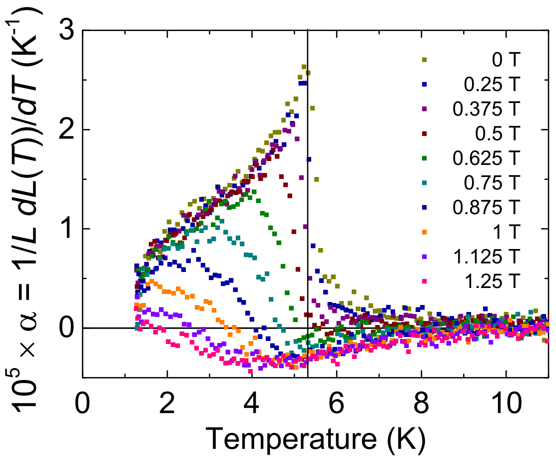

FIG. 4. (Color online) Magnetic field dependence of the average linear coefficient of thermal expansion.

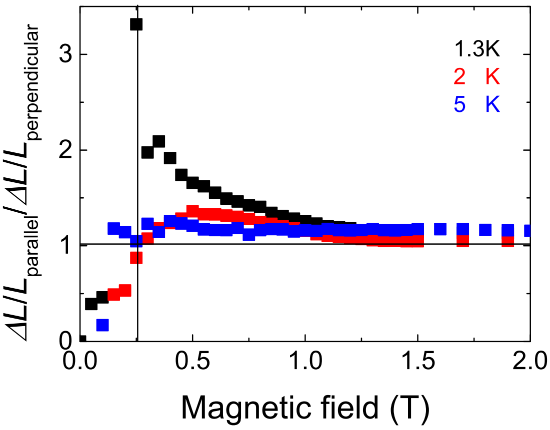

FIG. 5. (Color online) Anisotropy ratio γ of ETO as a function of magnetic field for representative temperatures.

vanished at $H = 1$ T and changes its sign for fields larger than the threshold field.

For $H > 1.25$ T the temperature dependence of α changes completely. It is negative and diminishes with increasing H (see Fig. 3) and is an order of magnitude smaller than in Fig. 4. In addition the data are rather scattered, nevertheless admitting to identify a minimum around T_N which is quite peculiar in view of the fact that at these field strengths the material is paramagnetic.

Finally we have investigated the magnetostriction for different field configurations, namely H parallel to the measured length and H perpendicular to it. The motivation for these measurements comes from the torque magnetometry results of Ref. [12], from which a first-order phase transition from c-axis to ab-plane AFM ordering has been deduced. The corresponding transition temperature T_{ab} and magnetic field H_{ab} have been determined to be $T_{\text{ab}} \sim 2.75 - 3$ K, $H_{\text{ab}} = 0.25$ T. These data have been taken on a single crystal whereas our data stem from ceramic samples. However, in a magnetic field a change in the spin alignment could yield an anisotropy in the magnetostriction and thus be detected in the experiments presented here. The results are shown in Fig. 5 where the anisotropy ratio $\gamma = (dL/L_{\text{parallel}})/(dL/L_{\text{perpendicular}})$ is plotted as a function of the magnetic field for three different temperatures: $T = 1.3, 2, 5$ K. While for 2 and 1.3 K an anomaly in γ is obvious around $H = 0.25$ T, this is absent for 5 K. At both low temperatures $T = 1.3, 2$ K, γ changes its sign from negative to positive and adopts large values at 1.3 K which are strongly reduced at 2 K. The data for $T = 5$ K exhibit an almost vanishingly small anisotropy. The data can be explained within the scenario developed in Ref. [18] where the AFM spin arrangement parallel to the magnetic field leads to a spontaneous striction. Upon changing the field direction the spins turn into the perpendicular direction thereby causing a dilation. Since the field at which the sign reversal of γ is observed coincides with H_{ab} and is seen only at $T = 2$ and 1.3 K, i.e., below T_{ab}, we conclude that our experiment is able to differentiate between the different spin configurations as deduced from the torque magnetometry experiment.

In conclusion, we have carried out magnetostriction experiments on ETO samples at low temperatures. The samples have been well characterized by specific heat, magnetization, and magnetic susceptibility measurements. The magnetostriction of ETO shows a peculiar behavior with a change of its sign with increasing magnetic field. A threshold is detected at fields where the AFM order vanishes and PM order sets in. In the PM phase the magnetostriction increases with increasing field and exhibits an astonishing similarity with the field dependence of the dielectric constant. This analogy suggests that soft mode dynamics is involved in this process which is characterized by a huge anharmonicity. The derivation of the mode Grüneisen parameter γ confirms this conclusion since this is temperature dependent and increases from $\gamma \sim 0.5$ to $\gamma \sim 2$ from low temperatures to $T = 300$ K. Similar conclusions have been drawn for rather analogous compounds, e.g., ZrW_2O_8 [23,24]. The thermal expansion coefficient exhibits a well resolved peak at T_N in zero field and follows the suppression of T_N with increasing field. The strong anisotropy of the thermal expansion observed for fields parallel and perpendicular to the length change traces the phase transition from a c-axis to an ab-plane spin configuration as described previously. What remains to be understood is the broad minimum in α at T_N for fields exceeding the threshold field, since here PM order is established.

---

[1] T. Katsufuji and H. Takagi, Phys. Rev. B **64**, 054415 (2001).

[2] S. Kamba, D. Nuzhnyy, P. Vaněk, M. Savinov, K. Knížek, Z. Shen, E. Šantavá, K. Maca, M. Sadowski, and J. Petzelt, Europhys. Lett. **80**, 27002 (2007).

[3] V. Goian, S. Kamba, J. Hlinka, P. Vaněk, A. A. Belik, T. Kolodiazhnyi, and T. Petzelt, Eur. Phys. J. B **71**, 429 (2009).

[4] Z. Guguchia, H. Keller, J. Köhler, and A. Bussmann-Holder, J. Phys.: Condens. Matter **24**, 492201 (2012).

[5] K. Caslin, R. K. Kremer, Z. Guguchia, H. Keller, J. K. Köhler, and A. Bussmann-Holder J. Phys.: Condens. Matter **26**, 022202 (2014).

[6] Z. Guguchia, K. Caslin, R. K. Kremer, H. Keller, A. Shengelaya, A. Maisuradze, J. L. Bettis, J. Köhler, A. Bussmann-Holder, and M.-H. Whangbo, J. Phys.: Condens. Matter **25**, 376002 (2013).

[7] Z. Guguchia, H. Keller, R. K. Kremer, J. Köhler, H. Luetkens, T. Goko, A. Amato, and A. Bussmann-Holder, Phys. Rev. B **90**, 064413 (2014).

[8] A. Bussmann-Holder, J. Köhler, R. K. Kremer, and J. M. Law, Phys. Rev. B **83**, 212102 (2011).

[9] D. S. Ellis, H. Uchiyama, S. Tsutsui, K. Sugimoto, K. Kato, D. Ishikawa, and A. Q. R. Baron, Phys. Rev. B **86**, 220301 (2012).

[10] D. S. Ellis, H. Uchiyama, S. Tsutsui, K. Sugimoto, K. Kato, and A. Q. R. Baron, Physica B **442**, 34 (2014).

[11] M. Allieta, M. Scavini, L. J. Spalek, V. Scagnoli, H. C. Walker, C. Panagopoulos, S. S. Saxena, T. Katsufuji, and C. Mazzoli, Phys. Rev. B **85**, 184107 (2012).

[12] A. P. Petrovic, Y. Kato, S. S. Sunku, T. Ito, P. Sengupta, L. Spalek, M. Shimuta, T. Katsufuji, C. D. Batista, S. S. Saxena, and C. Panagopoulos, Phys. Rev. B **87**, 064103 (2013).

[13] J.-W. Kim, P. Thompson, S. Brown, P. S. Normile, J. A. Schlueter, A. Shkabko, A. Weidenkaff, and P. J. Ryan, Phys. Rev. Lett. **110**, 027201 (2013).

[14] V. Goian, S. Kamba, O. Pacherova, J. Drahokoupil, L. Palatinus, M. Dušek, J. Rohlíček, M. Savinov, F. Laufek, W. Schranz, A. Fuith, M. Kachlik, K. Maca, A. Shkabko, L. Sagarna, A. Weidenkaff, and A. A. Belik, Phys. Rev. B **86**, 054112 (2012).

[15] Y. Shapira and N. F. Oliveira, Jr., Phys. Rev. B **18**, 1425 (1978).

[16] J. Hemberger, H.-A. Krug von Nidda, V. Tsurkan, and A. Loidl, Phys. Rev. Lett. **98**, 147203 (2007).

[17] K. L. Dudko, V. V. Eremenko, and L. M. Semenenko, Physica Status Solidi (b) **43**, 471 (1971).

[18] M. Doerr, M. Rotter, and A. Lindbaum, Adv. Phys. **54**, 1 (2005).

[19] T. Koshi, Sci. Technol. Adv. Mater. **13**, 013001 (2012).

[20] M. Rotter, H. Müller, E. Gratz, M. Doerr, and M. Loewenhaupt, Rev. Sci. Instrum. **69**, 2742 (1998).

[21] Z. Guguchi, H. Keller, A. Bussmann-Holder, J. Köhler, and R. K. Kremer, Eur. Phys. J. B **86**, 409 (2013).

[22] A. Bussmann-Holder and J. Köhler, J. Phys. Chem. Solids (unpublished).

[23] G. Ernst, C. Broholm, G. R. Kowach, and A. P. Ramirez, Nature **396**, 147 (1998).

[24] A. Sanson, Chem. Mater. **26**, 3716 (2014).