Spin-lattice coupling induced weak dynamical magnetism in $EuTiO_3$ at high temperatures

Z. Guguchia,[1,2] H. Keller,[1] R. K. Kremer,[3] J. Köhler,[3] H. Luetkens,[2] T. Goko,[2] A. Amato,[2] and A. Bussmann-Holder[3]
[1]*Physik-Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland*
[2]*Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland*
[3]*Max Planck Institute for Solid State Research, Heisenbergstraße 1, D-70569 Stuttgart, Germany*
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$EuTiO_3$, which is a G-type antiferromagnet below $T_N = 5.5$ K, has some fascinating properties at high temperatures, suggesting that macroscopically hidden dynamically fluctuating weak magnetism exists at high temperatures. This conjecture is substantiated by magnetic field dependent magnetization measurements, which exhibit pronounced anomalies below 200 K becoming more distinctive with increasing magnetic field strength. Additional results from muon spin rotation experiments provide evidence for weak fluctuating bulk magnetism induced by spin-lattice coupling which is strongly supported in increasing magnetic field.

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Perovskite oxides are well known for their rich ground states and the possibility of tuning these by doping, pressure, and temperature. In particular, their ferroelectric properties have attracted increased interest, since they offer a broad range of technological applications ([1], and references therein]. $EuTiO_3$ (ETO) was first synthesized in the early 1950s when a major boom in the search of ferroelectrics without hydrogen bonds took place [2]. Since ETO did not show any ferroelectric properties, but became antiferromagnetic (AFM) at low temperature with $T_N \approx 5.5$ K [3,4], it vanished from research activities and only regained substantial interest lately when it was demonstrated that strong magnetoelectric coupling is present in this material [5]. This was established by dielectric permittivity measurements, where an anomaly in the dielectric permittivity ε sets in at T_N. This anomaly vanishes upon the application of a magnetic field. The rather large and strongly temperature dependent dielectric permittivity has been related to a soft optic $q = 0$ mode, reminiscent of a ferroelectric soft mode [6,7]. However, its complete freezing is inhibited by quantum fluctuations quite analogous to $SrTiO_3$ (STO) [8]. In the search for new multiferroic materials ETO thus became a potential candidate and enormously enhanced the research in the ETO physical and chemical properties. The focus of the research was mainly the transition to the AFM phase [9,10] and its possible polar properties with novel spin arrangements together with electronic structure investigations [11].

The close analogy between ETO and STO, namely, the same lattice constants, the same ionic valency of the cation with almost equal ionic radii, and the tendency towards a polar instability, has recently been shown to be even closer, by establishing that ETO transforms from cubic to tetragonal caused by an oxygen octahedral rotation instability [12]. Amazingly, this takes place at $T_S = 282$ K in ETO, in contrast to STO with $T_S = 105$ K. This large spread in T_S between the two compounds can only be caused by the different atomic masses of Sr and Eu and also by the Eu $4f$ electrons with spin $S = 7/2$. In order to obtain a more clear picture of the origin of this difference in T_S, the mixed crystal series $Sr_xEu_{1-x}TiO_3$ has been studied as a function of x with focus on the development of T_S and T_N with x [13–15]. Interestingly, both transition temperatures vary nonlinearly with x, reflecting the dilution effect of the Eu $4f$ spins. In particular, the low temperature phase transition line indicates the stability of the AFM order which persists up to $x \sim 0.25$, in contrast to recent theoretical arguments which predict a transition from AFM via ferrimagnetic to ferromagnetic order with increasing x [16,17]. The high temperature phase transition line has been obtained by different experimental techniques, namely, electron paramagnetic resonance (EPR), muon spin rotation (μSR), electrical resistivity, and specific heat measurements [13]. The spectacular aspect stems from EPR and μSR data which test magnetic properties. In particular, a finite μSR relaxation rate signals the presence of some kind of exotic magnetism being present in the bulk sample, and indicates that dynamic magnetic order must be present in spatially confined regions of the ceramics. This conclusion is further supported by the fact that T_S depends on an applied external magnetic field which is amazing, since T_S lies 275 K above T_N [18], i.e., deeply in the paramagnetic region. From both results it must be concluded that the oxygen octahedral rotations influence the Eu $4f$ spin-spin interactions still at high temperatures and contribute to an effective second nearest neighbor ferromagnetic spin exchange which is otherwise small or vanishing.

To substantiate these conclusions, we have recently proposed an approach to test strong spin-lattice couplings by magnetization measurements [19]. If a coupling between the spins and the lattice is present in the form of a quadratic interaction $E_{SL} \sim \alpha \sum_{n,i,j} w^2 S_i S_j$, where w is the polarizability coordinate of the TiO_6 cluster and S_i,S_j are second nearest neighbor spins along the diagonal via the intermediate oxygen ions, with α being the coupling strength, then the magnetic susceptibility attains an extra temperature dependent component in the paramagnetic phase according to $\chi = N\mu_0 g^2 \mu_B^2 S(S+1)(1+\alpha\langle w\rangle_T^2)/(3k_BT)$ with N, μ_B, and g being the number of magnetic moments per volume, the Bohr magneton, and the g factor, respectively. The polarizability coordinate refers to the relative displacement coordinate between core and shell of the nonlinearly polarizable cluster mass at the TiO_3 lattice site and its role in phase transitions has been discussed in detail in Refs. [20–22]. Since $\langle w\rangle_T^2$ is the thermal average over the polarizability coordinate into which all dynamical information enters, the temperature dependence of the soft transverse acoustic zone boundary

mode contributes essentially to its temperature dependence. Above T_S the squared soft mode frequency decreases linearly with decreasing temperature to become zero at T_S. Below T_S the mode recovers to increase in a Curie-Weiss-type manner linearly with twice the gradient as compared to the para phase. This scenario has the consequence that the product of susceptibility and temperature is not a constant far above T_N but follows the T dependence of the soft mode which we indeed were able to demonstrate recently [18]. However, in addition another consequence results, since the increasing size of $\langle w \rangle_T^2$ below T_S, respectively the increasing rotation angle, leads to an increasing strength in the ferromagnetic second nearest neighbor exchange. This supports the formation of growing dynamical magnetic clusters which can be tested by applying a magnetic field. Indirectly cluster formation has already been seen in the bare magnetic susceptibility data where an upturn was detected approximately 100 K below T_S [18].

In order to substantiate this scenario, we have performed magnetization measurements in applied magnetic fields up to $\mu_0 H = 7$ T on ceramic samples of ETO which have been prepared as described in Ref. [12]. The magnetic moment m as a function of temperature and at various magnetic fields is shown in Fig. 1(a). While the data in Fig. 1(a) appear to be typical for a paramagnetic system, a detailed analysis of the data in terms of the product mT normalized by the magnetic field $\mu_0 H$ versus T reveals striking anomalies which—for the smallest field $\mu_0 H = 0.002$ T—are related to the structural instability as already reported before. With increasing field strength a second temperature scale emerges from the data appearing around $T_0 \simeq 210$ K which does not depend on the field strength [Fig. 1(b)]. In the following we denote T_0 as the magnetic crossover temperature. The normalization of the data with respect to H has the advantage that data for all field strengths can be shown in a single graph. However, this methodology obscures important details which are striking when mT is plotted as a function of temperature. The details are shown in Fig. 2 for three representative field strengths. Apparently, in Fig. 2 a change in slope (in the temperature range between 150 and 210 K) of mT versus T takes place with increasing field strength which is shown in detail and for all field strengths in Fig. 3. With increasing field strength the slope increases nonlinearly with the magnetic field, evidencing

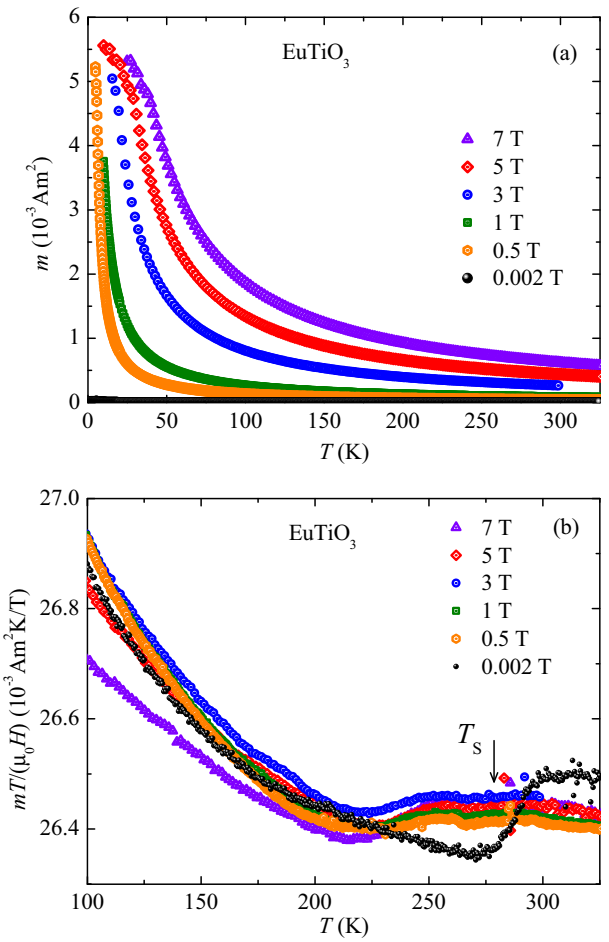

FIG. 1. (Color online) (a) The magnetic moment m of $EuTiO_3$ as a function of temperature and magnetic field. (b) The quantity $mT/(\mu_0 H)$ as a function of temperature and magnetic field. The arrows indicate the structural phase transition temperature T_S and the magnetic crossover temperature T_0.

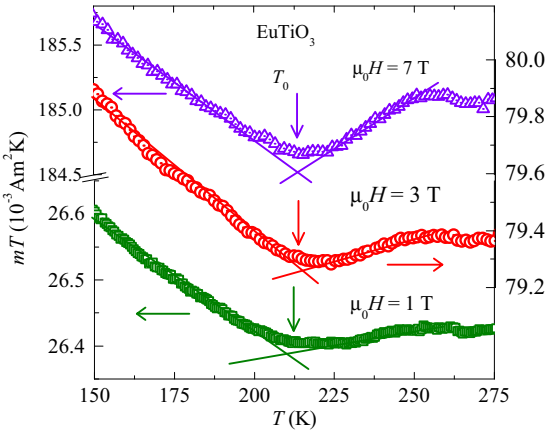

FIG. 2. (Color online) Magnetic moment m multiplied by temperature T of $EuTiO_3$ for $\mu_0 H = 1$, 3, and 7 T. The arrows indicate the magnetic crossover temperature T_0.

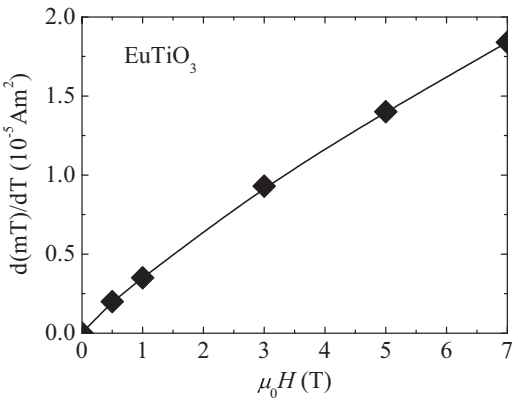

FIG. 3. The slope of the magnetic moment times temperature data mT (Fig. 2) as a function of the applied magnetic field $\mu_0 H$ for $EuTiO_3$ as obtained in the temperature range between 150 and 200 K. The full line in the figure is a guide to the eye. The size of the symbols exceeds the experimental error bars.

that some kind of correlated magnetism is present. Since the oxygen octahedral rotations modify the second nearest neighbor ferromagnetic exchange interaction only and have no influence on the direct nearest neighbor AFM exchange, we suggest that weak ferromagnetism appears below 210 K. Note, that this finding has nothing to do with structural modulations as reported in Refs. [10] and [23], since the x-ray tested temperature dependent structural data are only in accordance with tetragonal symmetry and show no superlattice reflections. It is also important to note that the data in [10] report a T_S around 245 K, much lower than our value, which has been corrected in a subsequent publication to arrive at the same value as ours. In Ref. [23] single crystals have been investigated with T_N being substantially smaller than our and other literature values, which might stem from impurities or defects and thus can give rise to the reported structural modulations. In addition, a recent detailed structural study confirmed our results and arrived at the conclusion that the unmodulated case corresponds to the bulk structure of pure material [24]. The weak magnetism has been tested by bulk sensitive local probe experiments as provided by the μSR technique. As has already been demonstrated in Ref. [12], a finite μSR relaxation rate is seen above the structural phase transition temperature and persists in the tetragonal phase.

These former data are here complemented by measurements of the μSR relaxation rate as a function of temperature and magnetic field. Transverse-field μSR experiments were performed at the πE3 beamline of the Paul Scherrer Institute (Villigen, Switzerland), using the HAL-9500 μSR spectrometer. The specimen was mounted in a He gas-flow cryostat with the largest face perpendicular to the muon beam direction, along which the external field was applied. Magnetic fields between 10 mT and 5 T were applied, and the temperatures were varied between 100 and 300 K. The μSR time spectra were analyzed using the free software package MUSRFIT [25].

For all fields and in the whole investigated temperature range, two-component signals were observed: a signal with fast exponential relaxation (broad signal) and another one with a slow exponential relaxation (narrow one). As an example, the Fourier transform (FT) of the μSR asymmetry at 100 K and for 0.5 and 3 T is shown in Fig. 4. The μSR time spectra were analyzed by using the following functional form:

$$A(t) = A_1 \exp(-\lambda_1 t)\cos(\gamma_\mu B_{\mu 1} t + \varphi) + A_2 \exp(-\lambda_2 t)\cos(\gamma_\mu B_{\mu 2} t + \varphi), \quad (1)$$

where A_1 (A_2), $B_{\mu 1}$ ($B_{\mu 2}$), and λ_1 (λ_2) denote the assymmetry, the local magnetic field at muon site, and the relaxation rate of the fast (slow) component. $\gamma/(2\pi) \simeq 135.5$ MHz/T is the muon gyromagnetic ratio, and φ is the initial phase of the muon-spin ensemble. Regarding the two-component signals of $EuTiO_3$, the signal with the fast (slow) relaxation is associated with the volume fraction with (without or only very weak) magnetic order. Since the major fraction ($\simeq$80%) of the μSR signal comes from the muons stopping in the part of the sample with fast relaxation, we discuss here only the temperature and field dependence of the relaxation rate λ_1 of the fast (magnetic) component.

The temperature dependence of λ_1 for various applied fields is shown in Fig. 5. It is evident that $\lambda_1(T)$ exhibits a pronounced

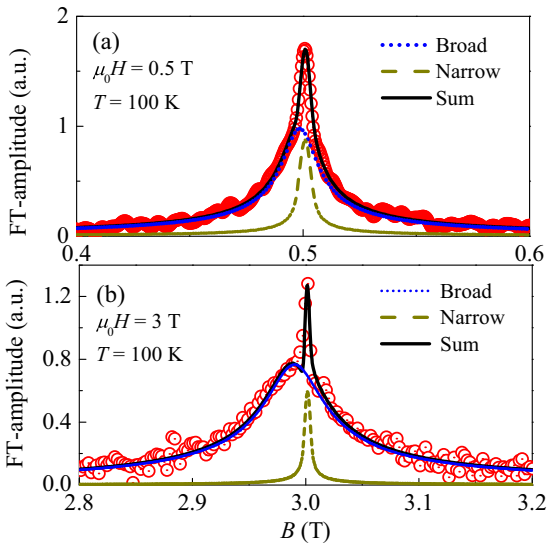

FIG. 4. (Color online) Fourier transform for the μSR asymmetry spectra of $EuTiO_3$ at 100 K for two magnetic fields: (a) $\mu_0 H$ = 0.5 T and (b) 3 T. The solid lines are the FTs of the corresponding theoretical $A(t)$ given by Eq. (1).

kink at the magnetic crossover temperature $T_0 \simeq 200$ K for all measured fields. Note that this value of T_0 is smaller than $T_0 \simeq 210$ K derived from magnetization measurements (see Fig. 2). This is likely due to the different experimental techniques (magnetization and μSR) used to determine T_0. Between 300 and 200 K $\lambda_1(T)$ increases with decreasing temperature. For $T < T_0$, an additional significant increase of $\lambda_1(T)$ is observed. Moreover, a strong enhancement of λ_1 with increasing field was found at all investigated temperatures

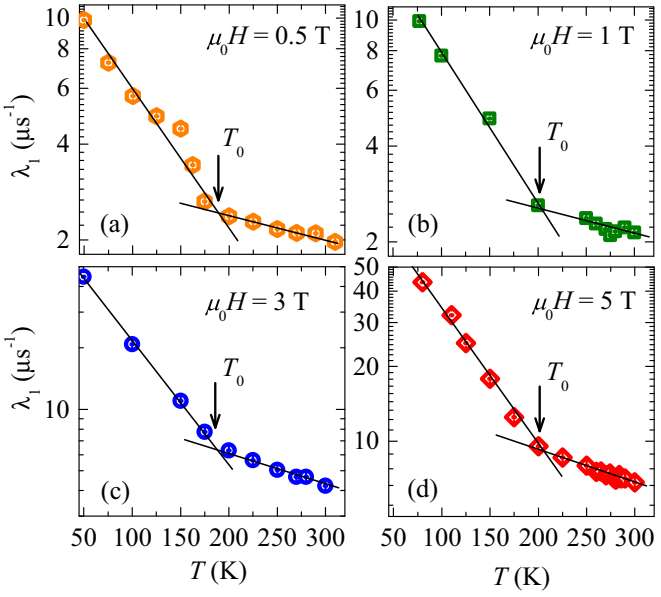

FIG. 5. (Color online) μSR relaxation rate λ_1 of $EuTiO_3$ as a function of temperature measured for various magnetic fields: (a) $\mu_0 H$ = 0.5 T, (b) $\mu_0 H$ = 1 T, (c) $\mu_0 H$ = 3 T, and (d) $\mu_0 H$ = 5 T. The thin lines are guides to the eyes. The arrow indicates the magnetic crossover temperature T_0 where the kink in λ_1 occurs. The experimental error bars are smaller than the size of the symbols.

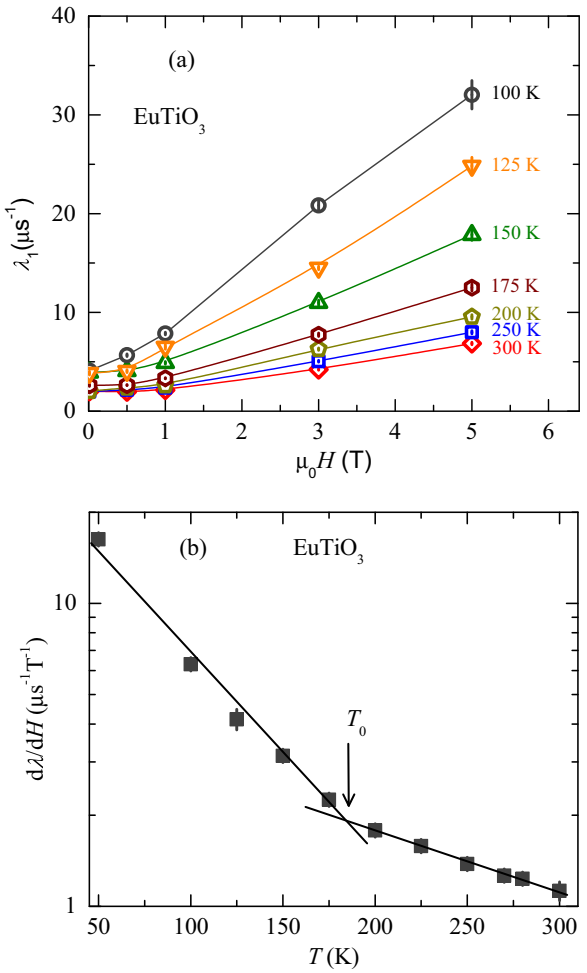

FIG. 6. (Color online) (a) μSR relaxation rate λ_1 of $EuTiO_3$ as a function of magnetic field for various temperatures. The solid lines are guides to the eyes. (b) The temperature dependence of the quantity $d\lambda/dH$. The arrow indicates the magnetic crossover temperature T_0.

[see Fig. 6(a)]. At low temperatures $\lambda_1(H)$ increases stronger than at high temperatures. For clarity, the quantity $d\lambda/dH$ determined from the linear part of $\lambda(H)$ is plotted in Fig. 6(b) as a function of temperature. A change in the slope of the temperature dependence of $d\lambda/dH$ can be clearly seen at $T_0 \simeq 200$ K. The pronounced increase and the stronger field dependence of λ_1 below T_0 suggests the appearance of some kind of magnetic correlations in the system. The formation of field induced magnetic clusters below T_0 may be a possible explanation as proposed in Ref. [19]. Unfortunately, our data do not admit to draw any definite conclusions on the type of magnetic correlations (AFM or ferromagnetic). However, we can figure out whether the fast depolarization of the μSR signal observed below T_0 in $EuTiO_3$ is either due to a broad distribution of static fields, and/or to strongly fluctuating magnetic moments. In order to discriminate between these two cases μSR experiments in longitudinal fields (LF) [26] are required. Therefore, we performed LF μSR experiments on ETO in fields up to 0.5 T below T_0. Since no recovery of the muon polarization was observed at long times we conclude that in $EuTiO_3$ dynamic magnetism is present.

To conclude, magnetization measurements and μSR data as functions of temperature and magnetic field provide evidence for dynamic weak magnetic clusters forming below $T_0 \simeq 200$ K. While from magnetization an anomalous upturn in the product mT appears around T_0 in a magnetic field, μSR data directly prove magnetic correlations which are field dependent. Our finding has important consequences for possible spintronic applications of $EuTiO_3$, since the magnetism far above T_N should considerably influence transport properties and also cause magnetic field induced changes or anomalies in the dielectric constant at high temperatures which—until now—has not been measured.

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[1] J. F. Scott, Science **315**, 954 (2007).
[2] J. Brous, I. Frankuchen, and E. Banks, Acta Crystallogr. **6**, 67 (1953).
[3] T. R. McGuire, M. W. Shafer, R. J. Joenk, H. A. Halperin, and S. J. Pickart, J. Appl. Phys. **37**, 981 (1966).
[4] L. Chien, S. DeBenedetti, and F. De. S. Barros, Phys. Rev. B **10**, 3913 (1974).
[5] T. Katsufuji and H. Takagi, Phys. Rev. B **64**, 054415 (2001).
[6] 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).
[7] V. Goian, S. Kamba, J. Hlinka, P. Vaněk, A. A. Belik, T. Kolodiazhnyi, and J. Petzelt, Eur. Phys. J. B **71**, 429 (2009).
[8] K. A. Müller and H. Burkard, Phys. Rev. B **19**, 3593 (1979).
[9] V. Scagnoli, M. Allieta, H. Walker, M. Scavini, T. Katsufuji, L. Sagarna, O. Zaharko, and C. Mazzoli, Phys. Rev. B **86**, 094432 (2012).
[10] 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).
[11] J. L. Bettis, M.-H. Whangbo, J. Köhler, A. Bussmann-Holder, and A. R. Bishop, Phys. Rev. B **84**, 184114 (2011).
[12] A. Bussmann-Holder, J. Köhler, R. K. Kremer, and J. M. Law, Phys. Rev. B **83**, 212102 (2011).
[13] A. Bussmann-Holder, Z. Guguchia, J. Köhler, H. Keller, A. Shengelaya, and A. R. Bishop, New J. Phys. **14**, 093013 (2012).
[14] Z. Guguchia, A. Shengelaya, H. Keller, J. Köhler, and A. Bussmann-Holder, Phys. Rev. B **85**, 134113 (2012).
[15] Z. Guguchia, H. Keller, A. Bussmann-Holder, J. Köhler, and R. K. Kremer, Eur. Phys. J. B **86**, 409 (2013).
[16] A. N. Morozovska, Y. Gu, V. V. Khist, M. D. Glinchuk, L.-Q. Chen, V. Gopalan, and E. A. Eliseev, Phys. Rev. B **87**, 134102 (2013).
[17] E. A. Eliseev, M. D. Glinchuk, V. V. Khist, C.-W. Lee, C. S. Deo, R. K. Behera, and A. N. Morozovska, J. Appl. Phys. **113**, 024107 (2013).
[18] Z. Guguchia, H. Keller, J. Köhler, and A. Bussmann-Holder, J. Phys.: Condens. Matter **24**, 492201 (2012).

[19] K. Caslin, R. K. Kremer, Z. Guguchia, H. Keller, J. Köhler, and A. Bussmann-Holder, J. Phys.: Condens. Matter **26**, 022202 (2014).
[20] A. Bussmann-Holder, J. Phys.: Condens. Matter **24**, 273202 (2012).
[21] R. Migoni, H. Bilz, and D. Bäuerle, Phys. Rev. Lett. **37**, 1155 (1976).
[22] H. Bilz, G. Benedek, and A. Bussmann-Holder, Phys. Rev. B **35**, 4840 (1987).
[23] 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).
[24] D. S. Ellis, H. Uchiyama, S. Tsutsui, K. Sugimoto, K. Kato, and A. Q. R. Baron, Physica B **442**, 34 (2014).
[25] A. Suter and B. M. Wojek, Phys. Procedia **30**, 69 (2012).
[26] A. Yaouanc and P. Dalmas de Réotier, J. Phys.: Condens. Matter **9**, 9113 (1997).