

Change from 3D-Ising to Random Field-Ising-Model Criticality in a Uniaxial Relaxor Ferroelectric

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(Received 24 June 2003; published 10 February 2004)

Pyroelectric measurements of polarization have been used to determine the temperature dependence of the polarization in strontium barium niobate, SBN:Ce, close to its phase transition temperature $T_c \approx 317$ K. A gradual increase of the critical exponent from $\beta \approx 0.13$ to $\beta \approx 0.30$ is observed when decreasing the initial polarization from 100% to 0.8% of the saturation value. A change from three-dimensional random-field Ising to pure Ising model behavior is conjectured and explained by a gradual compensation of quenched random electric fields by those emerging from charged fractal nanodomain walls.

DOI: 10.1103/PhysRevLett.92.065701

PACS numbers: 64.60.Fr, 77.70.+a, 77.80.Bh

Ever since its discovery by Smolenskii *et al.* in the late 1950s [1,2], the nature of ferroelectric relaxor transitions has been under intense discussion. Special attention was given to the question of whether they are indeed phase transitions which can be described with critical exponents, or if they are more correctly described by non-critical approaches such as glasslike freezing of electric dipoles, a question which will be addressed in this Letter. The interest in the nature of the relaxor transition has increased since relaxor ferroelectrics have found a multitude of technical applications ranging from piezoelectric sensors or actuators, where ceramics of lead zirconate titanate (PZT) or lead lanthanum zirconate titanate (PLZT) are extensively used [3], to optical applications like phase conjugated mirrors, where strontium barium niobate (SBN) is the material of choice [4,5]. At low temperatures relaxor ferroelectrics are polar with glassy or domain state properties, respectively [6], while at high temperatures they are nonpolar paraelectrics. For most applications it is favorable to work as close to the transition temperature as possible without exceeding it, since most physical effects reach a maximum at the transition from the ferroelectric into the paraelectric state. This transition is characterized by three features which set relaxor systems apart from “normal” ferroelectrics [7]: A broad maximum of the temperature dependence of the dielectric permittivity $\chi'(T)$, strong frequency dependence of its position, and the existence of polar properties at temperatures well above this maximum. To explain this behavior, a three-dimensional random-field Ising model (RFIM) [8] has been proposed [6,9]. This model is based on the assumption that the dynamics of the system are determined not only by the mutual interaction between electric dipoles, but also by the interaction of the dipoles

with immobile electric monopoles. The fields generated by these monopoles stabilize local polar clusters at high temperatures, leading locally to a nonzero value of the spontaneous polarization. Since the Ising model is usually applied to ferromagnetic systems and since there are no magnetic monopoles, it has hitherto not been possible to examine a ferromagnetic RFIM system experimentally. However, many experimental clues were recently found to support the validity of the RFIM to apply to the uniaxial ferroelectric relaxor strontium barium niobate ($\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$, SBN), which is regarded as the first actual realization of the ferroic RFIM [6]. The postulated existence of internal fields and their interaction with domain walls has been demonstrated [10–12]. As a remarkable benefit of the inherent disorder, RFIM criticality of the relaxor transition has been evidenced despite the long-range interaction involved [6]. Furthermore, a distinct change in the dynamic behavior of polar areas under external electric fields has been shown when the phase transition (Curie-) temperature T_c is exceeded [13,14]. For $T < T_c$, local dipoles interact to form stable ferroelectric domains, while at $T > T_c$ they are only loosely correlated into polar clusters, which are thermodynamically unstable at infinite times. The dynamics of the relaxing ferroelectric domains have been successfully described with a stretched exponential function, while the thermally activated clusters follow a generalized power law. Based on the RFIM, predictions about critical exponents were possible. According to thermodynamic theories, a phase transition can be described by a constant set of critical exponents, which are well determined and unchangeable in a single system. This critical behavior is an inherent property caused by the interaction of the system's constituent parts. In this context, the behavior

of the order parameter, i.e., the spontaneous polarization P , over the temperature T is of special interest. In the vicinity of the phase transition it is described by the equation

$$P(T) = P_0(1 - T/T_c)^\beta \quad (1)$$

with the critical exponent β . Most theoretical calculations predict very small values of $\beta \approx 0$ for RFIM systems [15]. However, experimental attempts to determine β in SBN were not conclusive: Measurements of the linear birefringence resulted in $\beta \approx 0.35$ [16], which rather points to a pure 3D-Ising model ($\beta = 0.325$) or a “random bond” Ising model ($\beta = 0.349$). NMR measurements yielded $\beta = 0.14$ [17], a value which deviates from theoretical predictions, but is still reconcilable with the RFIM.

Here, we present measurements of the polarization P in SBN in a temperature range that encompasses the relaxor transition. We describe $P(T)$ with a critical exponent β and demonstrate that the phase transition behavior depends on the degree of order of the ferroelectric domains: If the domains are not ordered, SBN behaves like an Ising system. When the degree of order is increased, the behavior shifts to that of a RFIM system. SBN is thus the first material that shows pronounced changes of the critical behavior in one and the same sample.

For our studies we used single crystals of SBN doped with 1.13 mol% cerium. The as-grown samples were cut along the crystallographic axes into cuboids with a thickness of 0.8 mm along the c axis. The two c faces of each sample were connected to a high voltage power supply and a charge amplifier, respectively. The sample was fixed in a temperature-controlled holder to measure the surface charge under varying external electric fields E and temperatures T . To increase the degree of order of the ferroelectric domains, an external field E was applied at $T = 293$ K in steps of 4 V/mm, with a duration of 5 sec for each step. P was measured during the application of E . After a preset level of P was reached, the external field was removed within 0.03 s. The final (meta)stable value of P of the domain state thus prepared was then established after relaxation by a few percent within a short time (<20 sec). Thus, samples with values between 0.8% and 100% of the maximum spontaneous polarization $P(T = 293 \text{ K}) = 24.6 \mu\text{C}/\text{cm}^2$ were prepared. The samples were then heated to 420 K with a heating rate of 0.01 K/s. During this process, $P(T)$ was recorded. Figure 1 exemplarily shows the resulting curves for the fully poled sample and a sample poled up to $0.37 \mu\text{C}/\text{cm}^2$, 1.5% of the maximum value. The data points have been thinned out to improve clarity. All measured curves could be described with Eq. (1) up to $T = T_c - 1.5$ K. For the data shown in Fig. 1, a fit of Eq. (1) to the data resulted in $T_c = (316.6 \pm 0.5)$ K and $\beta = 0.126 \pm 0.005$ for the fully poled sample. When the same sample was only partially poled, the transition temperature remained constant within the error margin at $T_c = (316.9 \pm 0.5)$ K.

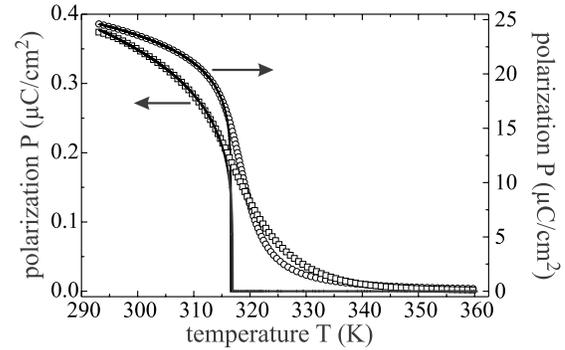


FIG. 1. Polarization versus temperature of SBN:Ce (1.13 mol%) for a fully poled sample (circles, right axis) and a sample poled to 1.5% of the maximum value (diamonds, left axis). In both curves the data points have been thinned out to allow better comparison. The solid lines represent fits of Eq. (1) to the measured data.

The critical exponent β , however, increased drastically to $\beta = 0.232 \pm 0.010$. The reproducibility of a measurement was chosen as a criterium for the errors given for the fitted values; both the error resulting from a single fit and the errors of the measurement setup were lower than those values. The resulting curves are displayed as continuous lines in the figure.

A description of $P(T)$ with Eq. (1) should be possible in the immediate vicinity of T_c , where the correlation length of the order parameter is expected to diverge. However, it is unusual that Eq. (1) appears to describe our measured data correctly up to 20 K and more below T_c , but similar observations have recently been reported on NMR experiments [17]. When the measurement range was extended to even lower temperatures, the quality of the fit quickly decreased, so we restricted ourselves to the temperature range shown above. In order to explain why the description of $P(T)$ with Eq. (1) fails above $T_c - 1.5$ K and to examine how reliable the resulting values of β are, we plotted P for three samples versus the reduced temperature $t = (1 - T/T_c)$ (Fig. 2). While curve A represents the fully poled sample, curves B and C were obtained from samples poled to $P = 3.9 \mu\text{C}/\text{cm}^2$ and $0.37 \mu\text{C}/\text{cm}^2$, i.e., 16 and 1.5% of the maximum value, respectively. All curves are normalized at $T = 293$ K to allow a comparison. Both axes have a logarithmic scale. In this plot, a graph of Eq. (1) is a straight line with slope β . The continuous lines are the results of a fit of Eq. (1) to each curve. One can clearly see that for a large temperature interval below T_c , the experimental data indeed follow straight lines for all three samples, showing that a description of the measured data with Eq. (1) is appropriate. The slope is strongly different for all three samples, so we can be sure that the differences in the values of β are real and not a result of some ambiguous fitting procedure. However, at a certain temperature all curves start to deviate from the straight line. The point of deviation depends on the initial polarization. For the

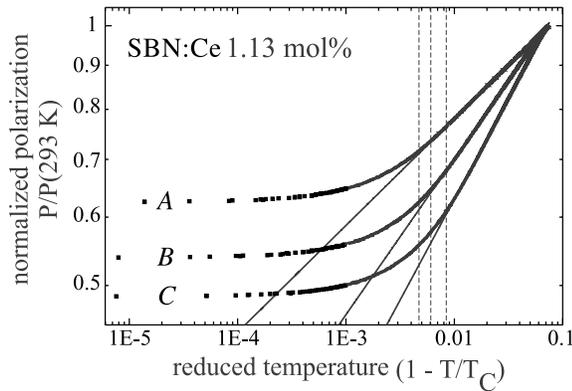


FIG. 2. Normalized polarization $P/P(293\text{ K})$ of SBN:Ce (1.13 mol%) versus reduced temperature $[1 - (T/T_c)]$ for a fully poled sample [curve A], a sample poled to 16% [curve B], and a sample poled to 1.5% [curve C] of the maximum spontaneous polarization. The straight lines represent the results of a fit of Eq. (1) to each curve.

measurement with the fully poled crystal [curve A], the fitted curves coincides with an accuracy of 1% with the measured curve up to $T_c - 1.5\text{ K}$, i.e., for $t < 4.7 \times 10^{-3}$, curve B deviates already at $T_c - 1.9\text{ K}$ ($t < 5.9 \times 10^{-3}$) from the fitted curve, and the sample with the lowest polarization is no longer accurately described by Eq. (1) when T exceeds $T_c - 2.4\text{ K}$ ($t < 7.5 \times 10^{-3}$). This observation can be explained by dynamical critical rounding, which is well known from related RFIM systems, namely, dilute uniaxial antiferromagnets in an axial field (DAFF) [18]. In the present case the ferroelectric domains are slowly transforming into slowly fluctuating dynamic polar clusters in the vicinity of T_c , which retain the memory of the polarization longer than anticipated by the critical power law, Eq. (1). While the dynamical critical rounding in the case of a transforming single domain [Fig. 2, curve A] solely depends on the time scale of the experiment, an initial domain structure as encountered in curves B and C is self-stabilizing by virtue of the random-field distribution, which is actually at its origin. This is why the reduced rounding temperature (see above) increases with decreasing initial polarization. We verified this by examining the dynamic behavior of the polarization both above and below T_c by the method described in detail in [14]. In these measurements, an external electric field was applied to the sample and then rapidly turned off. The following decay of P versus time was measured. Up to a temperature 3 K below T_c , it followed a stretched exponential function, while from a temperature 3 K above T_c upward it could be described by a generalized power law. In a temperature interval of 2 K around T_c , we observed a dynamic behavior that could not be unambiguously assigned to either of the two temperature ranges. The existence of this intermediate range, where the transition from nonactivated to activated dynamics takes place, causes the observed deviation of $P(T)$ from the theoretical predictions.

It should be stressed that the above effective exponents have been reproduced, within errors, independently of the heating rate ranging within $0.001\text{ K/s} < dT/dt < 0.1\text{ K/s}$. Hence, the data are obviously not subject to nonequilibrium thermodynamics while sweeping the sample continuously to higher temperatures. Thus the decrease of P versus T is believed to reflect true criticality of the system as long as no domain wall motion affects the variation of $P(T)$. This holds outside the dynamical rounding regime, $t \leq 10^{-2}$. In particular, in this temperature regime equilibrium properties are also obtained for the metastable domain states, which have purposely been prepared by depolarization to $P < P_s$. Similarly as in ferromagnetic systems, where criticality can reliably be tested on metastable multidomain state samples by microscopic methods such as NMR, Mössbauer effect or neutron diffraction, we are convinced that our pyroelectric method provides correct data of the intrinsic $P(T)$ as long as the mesoscopic domain structure is invariant, i.e., at $t \leq 10^{-2}$.

The critical exponent β showed a systematic dependence on the starting polarization $P(293\text{ K})$ in all samples, decreasing from $\beta = 0.297$ for the sample with the lowest starting polarization to $\beta = 0.126$ for the fully poled sample. Figure 3 shows β as a function of $P(293\text{ K})$. The transition temperature T_c did not show a systematic dependence on the degree of poling. From 12 measurements we obtained an average value of $T_c = (316.5 \pm 0.6)\text{ K}$. Similar measurements performed with five samples with different doping concentrations between 0.0 and 2.07 mol% cerium showed no systematic dependence of β on the doping concentration.

Since $P(T)$ is accurately described by Eq. (1) in the low-temperature range, the relaxor transition in SBN is obviously exhibiting criticality. The observation that the critical exponent β decreases with increasing degree of poling and thus increasing degree of domain ordering is surprising at first: β is defined by the long-range order of the system and thus by the interaction of its component parts, which should not vary. In the following, we will propose a model to explain this unexpected phase transition behavior. In SBN, the local dipoles that form the

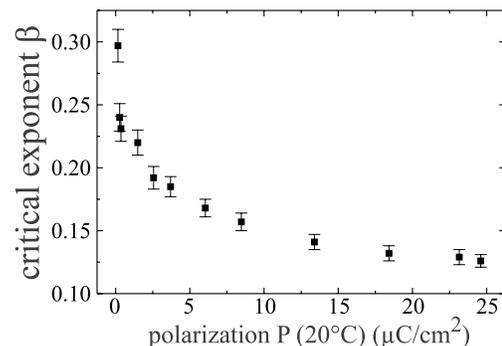


FIG. 3. Critical exponent β versus initial polarization at 293 K for SBN:Ce (1.13 mol%).

ferroelectric domains can only be oriented along the crystallographic c axis, i.e., there are only 180° domains in the crystal. Consequently, only variations of the Ising model need to be considered when discussing the phase transition. For the samples with small absolute values of the polarization the values of β approach that of a 3D-Ising system, where $\beta = 0.325$ is expected. For a fully poled sample we obtained values of $\beta = 0.126$, which is far away from the values of a pure 3D-Ising system, but close to the values of a 3D-RFIM system. Thus, the system apparently changes from random-field to pure Ising critical behavior when replacing the ferroelectric single domain by a multidomain state. Obviously the domain structure gives rise to suppression of the quenched local fields which are due to positive charges either in deficit at unoccupied Ba^{2+} and Sr^{2+} sites in the open tungsten bronze structure [19], or in excess at Ce^{3+} ions replacing Ba^{2+} or Sr^{2+} [20]. A natural source of charges, which might be able to suppress the electric fields emerging from the randomly distributed quenched defects is provided by 180° domain walls forming head-to-head or tail-to-tail configurations. Electrically charged interfaces are well known from needlelike “reciprocal” domains occurring in PbTiO_3 [21,22] and are also supposed to occur in SBN [23]. Recent piezoresponse force microscopical inspection of a [001] surface of SBN : Ce^{3+} [13] clearly confirmed highly entangled fractal nanodomains with diameters in the 10–100 nm range. Owing to their fractal structure in three dimensions, they are not supposed to form stripe domains with uncharged straight walls parallel to the polar c axis. Hence, uncompensated charges will decorate the domain walls. For energetic reasons they will partially compensate the quenched random fields. Very probably the domain walls may even try to absorb many of the charged defects in order to minimize the enhancement of the free energy. Similar mechanisms are known from the DAFF system [18], where the domain walls preferably intersect the magnetic vacancies for energetic reasons [24]. Obviously the compensation of the random fields by the charged domain walls is so effective that a complete “crossover” from pure to random-field Ising model behavior can be observed in our experiments. Here the term crossover is used as to describe the change of criticality when controlling the nonordering random fields. This mechanism can also explain some apparent discrepancies in the determination of the exponent β that have been reported in the literature. The measurements of the optical birefringence, which indicated values of $\beta \approx 0.3$, have been performed with unpoled crystals, while the NMR observations of $\beta = 0.14$ were obtained from fully poled crystals. It should be noted that $\beta \approx 0.14$ safely confirms that the phase transition encountered in the RFIM SBN is not first-order. The same exponent within errors was determined on the DAFF $\text{Fe}_{0.85}\text{Zn}_{0.15}\text{F}_2$ recently [25]. This coincidence does not seem to be fortuitous and—in the case of SBN—seems to exclude that different poling states may change a possible first-order

discontinuity of the order parameter and thus simulate a change in the critical exponents as those observed here.

In summary, the “relaxor” ferroelectric SBN clearly shows critical phase transition behavior and can therefore be considered a ferroelectric with long-range order between the local dipoles. The phase transition behavior is reflected by the critical exponent β which changes with increasing domain ordering from that of an undisturbed Ising system to that of a RFIM system. A possible explanation for this unusual behavior is the compensation of the quenched random fields by those emerging from charged fractal domain walls. Nearly perfect compensation arises in the limit of the fine-grained nearly spontaneous domain state, i.e., at minimal poling efficiency. By this mechanism an extrinsic control of the random fields, which has hitherto been considered as an exceptional advantage of the magnetic field controlled DAFF [18], has become available also in a ferroic RFIM system for the first time.

We are indebted to R. Pankrath from the crystal growth laboratory of the University of Osnabrück for supplying the samples. This work was supported by the Deutsche Forschungsgemeinschaft (Project No. SPP 1056/ WO618/3-4).

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