Critical Behavior in Ferroelectrics from First Principles

Emad Almahmoud,[1] Igor Kornev,[2,3] and L. Bellaiche[2]

[1]*Physics Department, Al al-Bayt University, Mafraq 25113, Jordan*
[2]*Physics Department, University of Arkansas, Fayetteville, Arkansas 72701, USA*
[3]*Laboratoire SPMS, UMR 8580 du CNRS, Ecole Centrale Paris, 92295 Chatenay-Malabry, France*

(Received 9 July 2008; revised manuscript received 22 January 2009; published 12 March 2009)

We report first-principles-based calculations, combined with an efficient Monte Carlo technique, that undoubtedly show that $Pb(Zr_{0.5}Ti_{0.5})O_3$, one of the most important ferroelectrics to date, adopts critical behavior that strongly deviates from the classical mean-field approach while being, in fact, consistent with the 3D-random Ising universality class.

DOI: 10.1103/PhysRevLett.102.105701 PACS numbers: 64.60.F−, 77.80.Bh, 77.84.Dy

Ferromagnetic systems form an important class of materials that possess a spontaneous (magnetic) dipole for temperatures below their Curie temperature, T_C [1]. They are known for around 50 years [2] to exhibit, around T_C, critical behaviors that are governed by specific exponents. Examples of such critical behaviors and exponents are [3]:

$$\xi \propto (T - T_c)^{-\nu}, \qquad \chi \propto (T - T_c)^{-\gamma}, \qquad M \propto (T - T_c)^{\beta}, \tag{1}$$

where ξ, χ, and M are the correlation length, susceptibility and spontaneous magnetization, respectively. The exact value of the exponents (ν, γ, β) solely depend on the so-called universality class to which the ferromagnetic system belongs. For instance, a large number of ferromagnets are associated with Ising or Heisenberg universality classes (see Refs. [4,5] and references therein), whose critical exponents are indicated in Table I.

Interestingly, while critical behaviors in ferromagnetics are undoubtedly established and have been the focus of a flurry of studies (see, e.g., Refs. [4,5,10] and references therein), a great controversy surrounds another type of dipolar systems that are of large technological and fundamental interest since World War II because of their fascinating physical properties [11,12]. This second type is formed by ferroelectrics, which are compounds possessing a spontaneous (electric) polarization below their Curie temperature. As a matter of fact, two schools of thought ''oppose'' each other regarding critical behaviors in ferroelectrics. One school emphasizes that ferroelectrics can also adopt critical behaviors associated with universality classes typically found in magnets, and therefore can show deviation from classical mean-field, Landau, behavior (see, e.g., Refs. [13–15] and references therein). This, despite the fact that long-range dipolar interactions are much more important in ferroelectrics than in ferromagnets, and that such long-range effects tend to suppress the short-range-induced large fluctuations that are responsible for the deviation of properties with respect to the mean-field behavior [16] (which is related to the so-called Levanyuk-Ginzburg criterion [17,18]). On the other hand, the other school of thought asserts that the only possible critical exponents in ferroelectrics are those given by the mean-field approach [19–22] (based on the hypothetical full suppression of the short-range-induced fluctuations), and that the non-mean-field critical exponents previously reported in the literature for ferroelectrics either result from an unreliable fit of data or from the existence of defects in the studied ferroelectric samples. Such long-standing controversy in such important materials has motivated us to use a first-principles-based approach within Monte Carlo simulations to determine critical behaviors (if any) in the defect-free $Pb(Zr_{0.5}Ti_{0.5})O_3$ (PZT) system, which is one of the most used ferroelectric materials in applications (such as actuators, transducers, ferroelectric random access memories, etc. [23]). The use of this *ab initio* technique enables us to undoubtedly reveal that PZT adopts critical behaviors that (1) strongly deviate from those given by the mean-field model, and (2) are, in fact, consistent with those associated with the 3D-random-Ising universality class.

We consider here a disordered solid solution made of $Pb(Zr_{0.5}Ti_{0.5})O_3$, as mimicked by a $L \times L \times L$ supercell that is periodic along any Cartesian direction. Practically, we use $L = 12$, 14, 16, 18, and 20, which corresponds to a relatively large number of atoms (namely, from 8640 to 40 000). The total energy of this bulk, E_{tot}, is provided by an *ab initio* effective Hamiltonian method (that is technically valid for Ti compositions close to 50%). More precisely, the expression and first-principle-derived parameters of E_{tot} are those of Ref. [24]. As a result, its degrees of freedom are the local soft modes in all the unit cells i of the supercell, $\{\boldsymbol{u}(i)\}$ (which are directly proportional to the electrical dipole moments centered on those sites), and the $\{\eta\}$ strain tensor (that gathers the homogeneous and inhomogeneous parts [24]). E_{tot} has seven different energetic parts [24,25]: a local-mode self-energy (quartic in $\{\boldsymbol{u}(i)\}$); a long-range electric dipole-dipole interaction [quadratic in $\boldsymbol{u}(i)$, and that is computed via an Ewald construction in the 3D-reciprocal space [25]]; a short-range interaction between local soft modes [qua-

 © 2009 The American Physical Society

TABLE I. Critical exponents for different universality classes and in PZT.

Exponent	PZT Bulk	3D-Heisenberg model [6]	3D-Ising model [7]	3D-random-Ising model [8,9]
ν	0.6723 ± 0.0053	0.7048 ± 0.0030	0.6270 ± 0.0020	0.7100 ± 0.0300 0.683
γ	1.4946 ± 0.0838	1.3873 ± 0.0085	1.2470 ± 0.0070	1.4600 ± 0.0700 1.341
β	0.33 ± 0.02	0.3639 ± 0.0035	0.3258 ± 0.0044	0.3400 ± 0.0200 0.354

dratic in $\boldsymbol{u}(i)$]; an elastic energy (quadratic in η); an interaction between the local soft modes and strains [quadratic in $\boldsymbol{u}(i)$ and linear in η]; an on site effect of alloying on local modes [quartic in $\boldsymbol{u}(i)$]; and an intersite contribution of alloying to local soft modes [linear in $\boldsymbol{u}(i)$] and to strain (linear in η). It is important to realize that the analytical expression of E_{tot} results from a Taylor development around the cubic paraelectric phase, and does not contain any *a priori* hypothesis about the universality class that PZT may belong to (if any). In other words, the analytical expression of E_{bulk} is rather general for ferroelectric solid solutions, and does not assume, or guarantee in advance, that PZT belongs to a specific universality class.

Technically, E_{tot} is used in Monte Carlo (MC) simulations within the so-called Wang-Landau algorithm, which is an efficient and accurate method for the study of phase transitions and that calculates the density of states, $g(E)$, by carrying out a random walk in energy space with an acceptance probability proportional to $1/g(E)$ (instead of the usual Boltzmann weight used in conventional MC simulations) [26]. The density of states is the key quantity for calculating thermodynamic observables at all temperatures. The local soft modes and strains of bulk PZT are collected at each MC sweep. Note that the use of the effective Hamiltonian approaches in MC simulations has been shown to be rather accurate in PZT systems, by, e.g., confirming the existence of a monoclinic phase in the phase diagram of bulk PZT [24] and of periodic nanostripe domains in PZT thin films [27]. The presently used effective Hamiltonian predicts, below the Curie temperature and in agreement with experiments [28], a $P4mm$ tetragonal ferroelectric state with a polarization lying along a $\langle 100 \rangle$ pseudocubic direction for the investigated Ti composition of 50% [24].

In order to determine if PZT bulk adopts a critical behavior, and to evaluate its critical exponents (if any), we follow the well-established finite-size scaling scheme of Refs. [6,7]. Such a scheme, e.g., (i) involves the maximum values of $-T^2 \frac{d\ln\langle p\rangle}{dT}$, $-T^2 \frac{d\ln\langle p^2\rangle}{dT}$, and $-T^2 \frac{d\ln\langle p^4\rangle}{dT}$ for a given supercell dimension, L (with these maximum values being denoted by $-T^2 \frac{d\ln\langle p\rangle}{dT}|_{\max}$, $-T^2 \frac{d\ln\langle p^2\rangle}{dT}|_{\max}$, and $-T^2 \frac{d\ln\langle p^4\rangle}{dT}|_{\max}$, respectively, in the following) with T, p, and $\langle\rangle$ representing the temperature, dipole, and statistical average over the supercell sites and MC sweeps, respectively; and (ii) indicates that the log-log plots of $-T^2 \frac{d\ln\langle p\rangle}{dT}|_{\max}$, $-T^2 \frac{d\ln\langle p^2\rangle}{dT}|_{\max}$, and $-T^2 \frac{d\ln\langle p^4\rangle}{dT}|_{\max}$ versus the supercell dimension, L, should all be linear, with a slope equal to the inverse of the critical exponent ν if the studied system indeed exhibits a critical behavior. Figures 1(a)–1(c) display such log-log plots in the investigated PZT bulk, as resulting from our Monte Carlo simulations using the Wang-Landau algorithm. These three plots are not only all linear but also possess a very similar slope of 1.4874 ± 0.0118, which reveals that our presently studied PZT bulk adopts a critical behavior with an exponent ν of 0.6723 ± 0.0053 [29,30]. Such an exponent deviates from the well-known value of 0.5 provided by the classical Landau approach [3]. Such a finding therefore implies that ferroelectrics can indeed adopt non-mean-field critical exponents, as correctly guessed by Refs. [13–15] and unlike those advocated in Refs. [19–22]. Long-range dipolar interactions are therefore not sufficient enough to fully eliminate short-range-induced fluctuations in ferroelectrics [16–18].

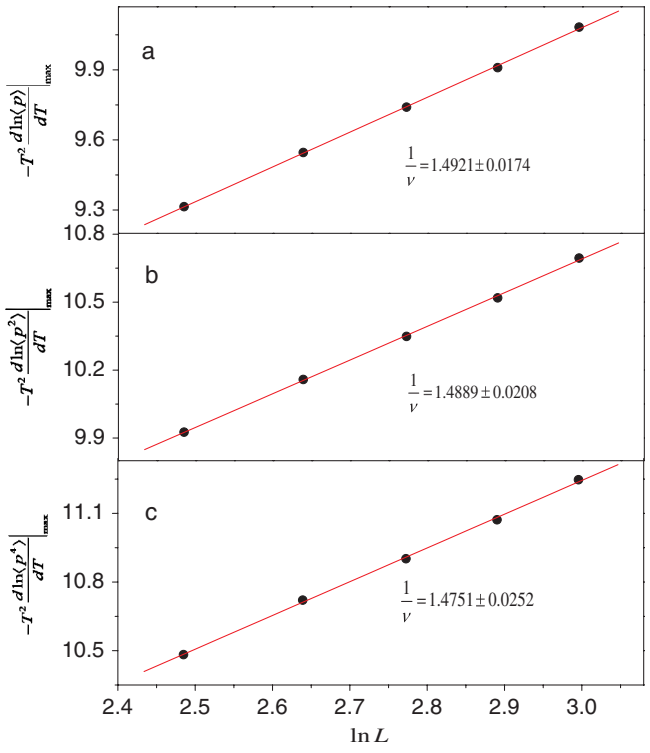

FIG. 1 (color online). Log-log plots of $-T^2 \frac{d\ln\langle p\rangle}{dT}|_{\max}$ (panel a), $-T^2 \frac{d\ln\langle p^2\rangle}{dT}|_{\max}$ (panel b) and $-T^2 \frac{d\ln\langle p^4\rangle}{dT}|_{\max}$ (panel c) in arbitrary units.

Finite-size scaling laws [6,7,31] further indicate that the value of the critical exponent γ and β can be extracted from the knowledge of the maximum value of the dielectric susceptibility, $\chi_{\max}$, and of the value of the average dipole at the critical temperature, $\langle p(T_c)\rangle$, for several supercell dimensions, once having determined ν. More precisely, the log-log plot of $\chi_{\max}$ versus L should be a linear function with a slope equal to γ/ν, while the log-log plot of $\langle p(T_c)\rangle$ as a function of L should also be linear but with a slope now given by β/ν. Figure 2 displays these log-log plots, as resulting from the use of our *ab initio*-based method in our investigated PZT bulk (note that its Curie temperature was practically determined by linearly interpolating the temperature associated with the maximum of the derivative of p with respect to T down to a zero value of $L^{-1/\nu}$ [7]). Such plots are indeed linear, thus further confirming that the studied PZT bulk possesses critical behaviors. Their slopes provide critical exponents γ of 1.4946 ± 0.0838 and β of 0.33 ± 0.02, when adopting the value 0.6723 ± 0.0053 determined from Fig. 1 for ν. Interestingly, our value for β agrees with the measurement of Ref. [14] yielding $\beta = 0.33 \pm 0.04$ in a $Pb(Zr_{0.9}Ti_{0.1})O_3$ sample near its Curie temperature, while we are not aware of any previous (theoretical or experimental) determination of ν and γ in disordered PZT solid solutions. Moreover, our determined values for both γ and β strongly differ from those associated with the mean-field approach (that are 1 and 0.5, respectively [3]), which further emphasizes that fluctuations are important to describe properties of ferroelectrics near their paraelectric-to-ferroelectric phase transition (note that we further performed simulations on disordered PZT solid solutions having other Ti compositions, namely, 40% and 55%, which corresponds to a rhombohedral and tetragonal phase below T_C, respectively [28], and also found that such PZT compounds possess critical behaviors that strongly deviate from those predicted by the mean-field approach).

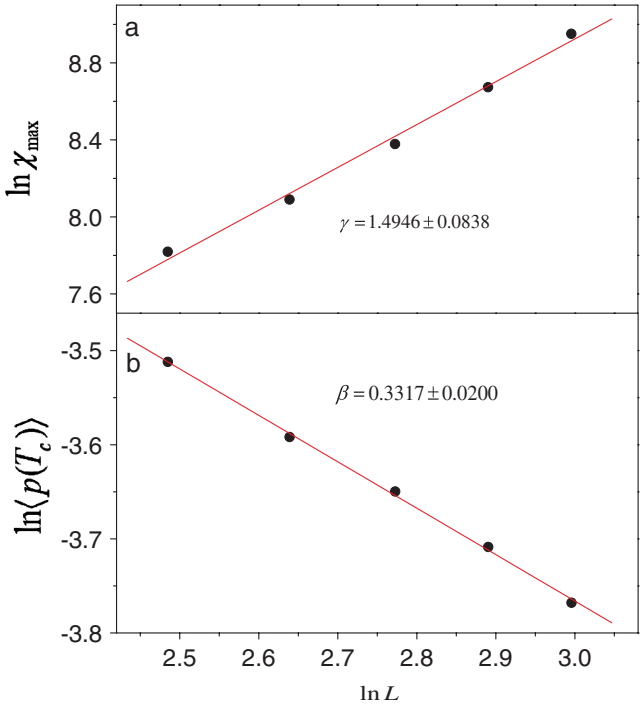

FIG. 2 (color online). Log-log plot of (a) the maximum value of the dielectric susceptibility and (b) $\langle p(T_c)\rangle$ (in arbitrary units), as a function of the supercell dimensional, L.

Let us now reveal if our values for ν, γ, and β for $Pb(Zr_{0.5}Ti_{0.5})O_3$ are associated with a well-known universality class. For that, we report them in Table I, along with the critical exponents corresponding to the 3D-Heisenberg [6], 3D-Ising [7], and 3D-random-Ising [8,9] models. Our extracted value for ν (and its small uncertainty) rules out both the 3D-Ising and 3D-Heisenberg models as the universality class that the disordered $Pb(Zr_{0.5}Ti_{0.5})O_3$ solid solutions belong too, while it is very close to the one of the 3D-random-Ising universality class. In fact, Table I indicates that our three numerically-determined exponents for disordered $Pb(Zr_{0.5}Ti_{0.5})O_3$ solid solutions are all close to those provided by the 3D-random-Ising universality class. The inherent reason for which these critical exponents are close to those of the 3D-random-Ising universality class rather than of the "pure" 3D-Ising model originates from the (random) alloying distribution of the Ti and Zr atoms in the system. As a matter of fact, we numerically found that switching off the alloying effects in the total energy of our effective Hamiltonian (such as to create an hypothetical simple system, known as the virtual crystal alloy and in which Ti and Zr atoms are all replaced by a virtual identical atom [32]) leads to critical exponents that are now rather close to those provided by the pure 3D-Ising model [33].

Finally, the temperature interval of the critical region in $Pb(Zr_{0.5}Ti_{0.5})O_3$ was estimated to range between the Curie temperature, T_C, and the so-called Ginzburg temperature [17,18], T_G, with $\varepsilon_{\text{crit}} = |T_G - T_C|/T_C = 4.5 \pm 3.5 \times 10^{-3}$, by focusing on $\langle p^2\rangle - \langle p\rangle^2$ and $\langle p\rangle^2$ (in the critical region, the order parameter's fluctuation should exceed the value of the order parameter). Interestingly, our estimated mean value of $\varepsilon_{\text{crit}}$ is in between the value of 10^{-4} estimated by Ginzburg in $BaTiO_3$ [18] and the value of 6×10^{-2} estimated by Clarke and Glazer from some experimental data on $Pb(Zr_{0.9}Ti_{0.1})O_3$ [14].

In conclusion, we investigated critical behaviors in disordered $Pb(Zr_{0.5}Ti_{0.5})O_3$ bulks by computing nontrivial statistical quantities from a first-principles-based scheme combined with a Monte Carlo technique. $Pb(Zr_{0.5}Ti_{0.5})O_3$ bulks exhibit critical behaviors with critical exponents all differing from those provided by the classical mean-field approach, while being consistent with those associated with the 3D-random-Ising universality class. Our study thus resolves a long-standing controversy: it undoubtedly proves that ferroelectrics can belong to universality classes typically found in ferromagnets, despite the fact that long-

range dipole-dipole interactions are much stronger than short-range interactions in ferroelectrics, unlike in ferromagnets. We are thus confident that our present work leads to a broad, general knowledge of phase transitions in dipolar systems, which is of fundamental and technological importance.

We acknowledge support from ONR grants N00014-04-1-0413 and N00014-08-1-0915; NSF grants DMR-0080054 (C-SPIN), DMR-0701558, and DMR-0404335; and DOE grant DE-FG02-05ER46188. Some computations were made possible thanks to MRI grants 0421099 and 0722625 from NSF.

[1] P. Curie, Ann. Chim. Phys. **5**, 289 (1895).
[2] M. E. Fisher, Physica (Amsterdam) **25**, 521 (1959).
[3] M. E. Fisher, Rep. Prog. Phys. **30**, 615 (1967).
[4] F. Y. Yang., C. L. Chien, X. W. Li, G. Xiao, and A. Gupta, Phys. Rev. B **63**, 092403 (2001).
[5] E. Burzo *et al.*, J. Phys. F **13**, L89 (1983).
[6] K. Chen, A. M. Ferrenberg, and D. P. Landau, Phys. Rev. B **48**, 3249 (1993).
[7] A. M. Ferrenberg and D. P. Landau, Phys. Rev. B **44**, 5081 (1991).
[8] P. H. R. Barbosa, E. P. Raposo, and M. D. Coutinho-Filho, Phys. Rev. B **72**, 092401 (2005).
[9] M. Hasenbusch, F. Parisen Toldin, A. Pelissetto, and E. Vicari, J. Stat. Mech. (2007), P02016.
[10] P. Y. Lai and K. K. Mon, Phys. Rev. Lett. **62**, 2608 (1989).
[11] K. Uchino, *Piezoelectric Actuators and Ultrasonic Motors* (Kluwer Academic, Boston, 1996).
[12] N. Setter and R. Waser, Acta Mater. **48**, 151 (2000).
[13] W. Kleemann *et al.*, Europhys. Lett. **57**, 14 (2002).
[14] R. Clarke and A. M. Glazer, J. Phys. C **7**, 2147 (1974).
[15] K. Deguchi and E. Nakamura, Phys. Rev. Lett. **37**, 1642 (1976).
[16] A. Aharony and M. E. Fisher, Phys. Rev. B **8**, 3323 (1973).
[17] A. P. Levanyuk, Zh. Eksp. Teor. Fiz. **36**, 810 (1959) [Sov. Phys. JETP **9**, 571 (1959)].
[18] V. L. Ginzburg, Fiz. Tverd. Tela (Leningrad) **2**, 2031 (1960) [Sov. Phys. Solid State **2**, 1824 (1961)].
[19] J. F. Scott, Ferroelectrics **349**, 157 (2007).
[20] J. F. Scott, J. Phys. Condens. Matter **18**, 7123 (2006).
[21] M. A. Geday and A. M. Glazer, J. Phys. Condens. Matter **16**, 3303 (2004).
[22] J. A. Gonzalo, Phys. Rev. **144**, 662 (1966).
[23] V. G. M. Annamdas and C. K. Soh, Smart Materials and Structures **16**, 673 (2007).
[24] L. Bellaiche, A. Garcia, and D. Vanderbilt, Phys. Rev. Lett. **84**, 5427 (2000).
[25] W. Zhong, D. Vanderbilt, and K. M. Rabe, Phys. Rev. Lett. **73**, 1861 (1994); Phys. Rev. B **52**, 6301 (1995).
[26] F. Wang and D. P. Landau, Phys. Rev. Lett. **86**, 2050 (2001).
[27] I. Kornev, H. Fu, and L. Bellaiche, Phys. Rev. Lett. **93**, 196104 (2004).
[28] B. Noheda *et al.*, Phys. Rev. B **61**, 8687 (2000).
[29] Note that our effective Hamiltonian approach can accurately reproduce experimental temperature-dependent data if one rescales its temperature scale, that is if one multiplies the theoretical temperature by a constant coefficient [24]. Equations (1) indicate that such rescaling has no effect on the investigated critical exponents [we further numerically checked that the same critical exponents are obtained if one rescales (or not) our theoretical temperatures].
[30] We also perform calculations on PZT thin films under open-circuit electrical boundary conditions, using an effective Hamiltonian approach that mostly differs from the presently used approach by the long-range dipolar interactions [that are those of systems that are periodic in x and y directions but finite—and sandwiched by vacuum—along the z axis for the films; see I. Ponomareva *et al.* Phys. Rev. B **72**, 140102(R) (2005)]. These additional calculations yield a shift in Curie temperature that follows a critical law with the film's thickness, with this law being governed by the same ν parameter (within the uncertainty) as the one presently found in our calculations for PZT bulks. This finding is consistent with G. A. T. Allen, Phys. Rev. B **1**, 352 (1970), and further confirms the extracted value of the critical exponents for the bulk.
[31] D. P. Landau and K. A. Binder, *A Guide to Monte Carlo Simulations in Statistical Physics* (Cambridge University Press, Cambridge, England, 2000).
[32] L. Bellaiche and D. V. Vanderbilt, Phys. Rev. B **61**, 7877 (2000).
[33] For instance, ν and γ are found to be equal to 0.611 ± 0.004 and 1.290 ± 0.01, respectively, when using $L = 12$, 14, 16, and 18 for the virtual crystal alloy.