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Finite-Temperature Properties of Ba(Zr, Ti)O$_3$ Relaxors from First Principles

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A first-principles-based technique is developed to investigate the properties of Ba(Zr, Ti)O$_3$ relaxor ferroelectrics as a function of temperature. The use of this scheme provides answers to important, unresolved and/or controversial questions such as the following. What do the different critical temperatures usually found in relaxors correspond to? Do polar nanoregions really exist in relaxors? If yes, do they only form inside chemically ordered regions? Is it necessary that antiferroelectricity develop in order for the relaxor behavior to occur? Are random fields and random strains really the mechanisms responsible for relaxor behavior? If not, what are these mechanisms? These ab initio based calculations also lead to deep microscopic insight into relaxors.

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Relaxor ferroelectrics are characterized by some striking anomalous properties (see, e.g., Refs. [1–21] and references therein). For instance, they adopt a peak in their ac dielectric response versus temperature function while they remain macroscopically paraelectric and cubic down to the lowest temperatures [1]. Furthermore, this dielectric response deviates from the “traditional” Curie-Weiss law [22] for temperatures lower than the so-called Burns temperature [2]. Other examples of anomalous properties include the plateau observed in their static dc dielectric susceptibilities in typical ferroelectrics, Fig. 1(a) for temperatures lower than the so-called Burns temperature [1]. Furthermore, this dielectric response deviates from the “traditional” Curie-Weiss law for temperatures lower than the so-called Burns temperature [1], which is consistent with measurements [40]. We also computed the dielectric susceptibility, at different temperatures by progressively cooling down the system, from our MC simulations via two different approaches: (i) a “direct” method for which the resulting dielectric susceptibility is denoted as $\chi^{\text{direct}}$ and is calculated as the change in polarization with respect to an applied electric field (with this field practically being oriented along the [111] pseudocubic direction and having a magnitude of $10^3$ V/m); and (ii) the “correlation-function” approaches of Refs. [41,42] for which the resulting dielectric susceptibility is referred to as $\chi^{\text{CF}}$ and is provided by the fluctuation-dissipation theorem via $\chi^{\text{CF}}_{\alpha\beta} = \frac{(Nz)^2}{\epsilon_s k_B T} [\langle u_\alpha u_\beta \rangle - \langle u_\alpha \rangle \langle u_\beta \rangle]$, where $\langle u_\alpha u_\beta \rangle$ denotes the statistical average of the product between the $\alpha$ and $\beta$ components of the supercell average of the local mode vectors, and where $\langle u_\alpha \rangle$ (respectively, $\langle u_\beta \rangle$) is the statistical average of the $\alpha$ (respectively, $\beta$) component of the supercell average of the local mode vectors. $N$ is the number of sites in the supercell while $V$ is its volume. $k_B$ is Boltzmann’s constant, and $\epsilon_s$ is the permittivity of the vacuum. Strikingly, while previous work (see, e.g., Ref. [42]) found that these two different methods provide nearly identical dielectric susceptibilities in typical ferroelectrics, Fig. 1(a)
ac electric fields having frequencies ranging between
neighbor),
a freezing temperature ranging between 100 and 140 K has
susceptibility arising from the fit of
saturates to a plateau for lower temperature. Both the
temperature behavior of
takes place for temperatures (in Region I); (2) it is large and also increases
remains nearly linearly with decreasing temperature at high tem-
relaxor [16]. For instance, (1) it is small and increases
Curie temperature has also been experimentally
can be nicely fitted by the Curie-Weiss formula [22];
for which neither
and
is nearly constant there. T$_f$ can be assigned to be the
Burns temperature [2] while $T^*$ can be thought of as being
the novel critical temperature recently found in relaxors
[11,12]. The facts that $\chi^{CF}$ follows the Curie-Weiss law
only for temperatures above the Burns temperature and that
this Burns temperature is of the order of 450 K have both
been observed in Ba(Zr$_{0.5}$Ti$_{0.5}$)O$_3$ [40]. Similarly, a nega-
tive $T_0$ Curie temperature has also been experimentally
extracted in BZT samples [40].

Figure 1(b) reports the temperature evolution of the so-
called Edwards-Anderson parameter [25], $q_{EA}$, that is cal-
culated as $q_{EA} = (\langle Z^2 \mathbf{u}_i^2 \rangle)$, where the inner averaging is
made over the $t$ Monte Carlo sweeps while the outer averaging is made over the $i$ lattice sites. The behavior of the simulated $q_{EA}$ of BZT bulk versus temperature bears some striking resemblance with those predicted by the spherical random bond–random field model and measured from nuclear magnetic resonance for the PbMg$_{1/3}$Nb$_{2/3}$O$_3$ relaxor [16]. For instance, (1) it is small and increases
nearby linearly with decreasing temperature at high tem-
peratures (in Region I); (2) it is large and also increases
linearly with decreasing temperature at low temperatures
(in Region IV); and (3) the $q_{EA}$-$versus-T$ function is curved
upward in between (in Regions II and III). Figure 1(b) also
reveals that the temperature behavior and values of the overall Edward-Anderson parameter (for any tem-
perature) almost entirely originate from the electric dipoles
centered on Ti ions. Consequently, the contribution of the
dipoles belonging to BaZrO$_3$ unit cells to the total

\[ \chi^{CF}(T) = \frac{C}{T - T_0} \]

\[ \chi^{direct}(T) = \frac{C}{T - T_f} \]

\[ \chi^{0.5}(T) = \frac{C}{T - T_0} \]

\[ \chi^{3}(T) = \frac{C}{T - T_f} \]

\[ \chi^{max}(T) = \frac{C}{T - T_0} \]

\[ \chi^{Total}(T) = \frac{C}{T - T_0} \]

\[ \chi^{Max}(T) = \frac{C}{T - T_f} \]

\[ \chi^{Direct}(T) = \frac{C}{T - T_0} \]

\[ \chi^{Total}(T) = \frac{C}{T - T_f} \]

\[ \chi^{Max}(T) = \frac{C}{T - T_0} \]

\[ \chi^{Direct}(T) = \frac{C}{T - T_f} \]

\[ \chi^{Total}(T) = \frac{C}{T - T_0} \]

\[ \chi^{Max}(T) = \frac{C}{T - T_f} \]

\[ \chi^{Direct}(T) = \frac{C}{T - T_0} \]

\[ \chi^{Total}(T) = \frac{C}{T - T_f} \]

\[ \chi^{Max}(T) = \frac{C}{T - T_0} \]

\[ \chi^{Direct}(T) = \frac{C}{T - T_f} \]

\[ \chi^{Total}(T) = \frac{C}{T - T_0} \]

\[ \chi^{Max}(T) = \frac{C}{T - T_f} \]

\[ \chi^{Direct}(T) = \frac{C}{T - T_0} \]

\[ \chi^{Total}(T) = \frac{C}{T - T_f} \]

\[ \chi^{Max}(T) = \frac{C}{T - T_0} \]

\[ \chi^{Direct}(T) = \frac{C}{T - T_f} \]
Edwards-Anderson parameter nearly vanishes. Other dramatic differences between local properties associated with Zr versus Ti atoms are revealed in Fig. 1(c), which shows that not only is the average magnitude of the local dipoles centered on Zr ions much smaller than those centered on Ti ions, but its temperature behavior is also strikingly different: the dipoles belonging to BaZrO₃ unit cells continuously shrink on average as the temperature is reduced, while the dipoles located inside BaTiO₃ cells suddenly become enlarged with decreasing temperature below 7°C. Electric diffraction measurements [39] and a model emphasizing the importance of the BaTiO₃ soft mode on the relaxor behavior of BZT [45] are also consistent with our prediction that the Ti sites carry much larger dipoles than the Zr sites. Moreover, the results from Fig. 1(c) imply that, at the lowest temperatures, the Ti atoms displace on average about 0.16 Å, while the Zr atoms move by 0.03 Å from their cubic, equilibrium positions. Such numbers are in remarkable agreement with the values of 0.17 and 0.03 Å, respectively, obtained by the first-principles calculations of Ref. [46] for a BZT supercell containing 135 atoms [47].

Let us now focus on Fig. 2, which displays dipolar snapshots within a given (y, z) plane at different temperatures, in order to gain a microscopic understanding of relaxors. Figure 2(a) reveals that Region I consists of randomly oriented dipoles that are centered on Ti ions and that are surrounded by much smaller dipoles located inside BaZrO₃ cells. As indicated in Fig. 2(b), some of these Ti sites act as nuclei to the formation of small clusters inside which the dipoles begin to parallel each other in Region II. We numerically found that the polarization of these small clusters in Region II does not automatically lie along a (111) direction. For instance, the average direction of the local modes inside the bottom cluster of Fig. 2(b) is close to neither the center nor the boundary of the cubic zone—namely, it is close to [011]. Interestingly, some of these clusters do not even possess a polarization that is parallel to a high symmetry direction in Region II, such as the top cluster of Fig. 2(b) for which the vector resulting from the average of the local modes is equal to (−0.012, −0.052, −0.021) in the (x, y, z) basis—that is, a triclinic direction. It is interesting to realize that thermal strain measurements [40] strongly suggest that polar nanoclusters can exist in BZT up to ~440 K, which is consistent with our finding of small polar clusters in Region II (that extend up to 450 K).

As the system enters Region III, two novel features occur that can be inferred from Fig. 2(c). First, more (small) polar clusters form as the temperature is decreased, which makes the average magnitude of the Ti dipoles increase [see Fig. 1(c)]. Second, some of these clusters now possess a polarization close to the (111) direction, such as the left and right clusters displayed in Fig. 2(c) for which the average local modes are equal to (0.043, −0.048, 0.043) and (0.034, 0.037, 0.045), respectively. Note that, while the clusters are always formed at Ti sites, they do not necessarily stay at the same sites for different temperatures, or even for different MC sweeps at the same temperature, in Regions II and III. In that sense, they can be thought of as being of dynamical nature rather than being static.

Below T_f, some of these clusters have considerably grown in size, like the one located at the bottom right corners in Figs. 2(d)–2(f). Novel clusters can still form when decreasing the temperature in Region IV, such as the one near the bottom left corner of Fig. 2(f) at 10 K. On the other hand, other clusters are frozen in the sense that they are always located at the same region of space and have a polarization that lies along the same direction, independently of the temperature and MC sweep in Region IV (see the central and bottom right clusters in Fig. 2(d)–2(f)).

While the different clusters possess different numbers of Ti sites and have different overall shapes, they share a common feature in Region IV: they all have a polarization close to one of the eight equivalent (111) directions, consistent with the experimental finding that Raman spectra indicate a rhombohedral structure for the polar regions at liquid nitrogen temperature in BZT relaxors [48]. As the temperature is reduced in Region IV, the matrix possesses Zr-centered dipoles that are significantly shrinking in magnitude. This matrix in Regions II, III, and IV also possesses individual Ti dipoles that are oriented along many different directions, as in Region I.

To gain further insight into the relaxor behavior, let us denote as k_{max} the vector of the first Brillouin zone possessing the largest magnitude of the Fourier transform of the local dipoles configuration [49]. k_{max} is numerically found to be slightly dependent on the choice of the supercell used, but is always a nonhighly symmetric vector that is close to neither the center nor the boundary of the cubic first Brillouin zone. For instance, in case of a 12 × 12 × 12
supercell, \( \mathbf{k}_{\text{max}} = \frac{2\pi}{\text{lat}}(\mathbf{y} + \mathbf{z}) \), where \( \text{lat} \) is the lattice constant of the five-atom primitive cell and where \( \mathbf{y} \) and \( \mathbf{z} \) are unit vectors along the \( y \)- and \( z \)-axes, respectively. Figure 1(d) shows the temperature evolution of the square of the Fourier transform of the local dipoles configuration at \( \mathbf{k}_{\text{max}} \). One can clearly see that, in Regions I and II, this quantity is nearly zero. On the other hand, it increases when the temperature decreases below \( T^* \) while still remaining fairly small (around 1.5% of the total spectra gathering the Fourier transforms at all possible \( k \)-points, at 5 K). We interpret such latter results as indicative that the different nanopolar regions slightly interact in Regions III and IV in an antiferroelectric-like (or incommensurate [50] or dipolar-wave-like) fashion. Interestingly, antiferroelectricity has been previously reported in some relaxor systems [14,15].

Let us now compute the correlation between Ti dipoles (we decided to focus on Ti-Ti dipolar correlations because Fig. 2 revealed that the polar clusters only contain Ti sites and because Fig. 1(b) shows that the overall Edwards-Anderson parameter mainly only originates from Ti dipoles). This correlation is practically defined by \( \theta(r) = \frac{1}{N_{Ti}} \sum_{i} \mathbf{u}_i \cdot \mathbf{u}_{i+r} \), where the index \( i \) runs over all the \( N_{Ti} \) Ti sites of the system and where \( \mathbf{u}_i \) and \( \mathbf{u}_{i+r} \) are the local modes in cell \( i \) and in the cell centered on the Ti atom (if any) distant from \( r \) from the cell \( i \), respectively [51]. A value of 1 (respectively, \(-1\)) for \( \theta(r) \) for a given \( r \) would indicate that Ti dipoles and their neighboring Ti dipoles distant from \( r \) are aligned along the same (respectively, opposite) direction. Figure 1(e) shows the value of \( \theta(r) \) for various representative \( r \)-vectors, as a function of temperature. One can see that, in Region I and on average, the Ti dipoles are only (and slightly) correlated with the Ti dipoles centered at their first nearest neighbor cells. Such a correlation further increases in strength when the polar nanoclusters form and become greater in size and in polarization, as the temperature is reduced in Regions II, III, and IV. Second- and third-nearest neighbors also begin to be more correlated on average as the temperature decreases in Regions III and IV. Interestingly, a significant anticorrelation (see the negative sign of the correlation) between Ti dipoles that are distant by three lattice constants along the \( z \)- (or \( x \)- or \( y \)-) axis also strongly develops in Regions III and IV, which reinforces the previous finding that antiferroelectric-like interactions exist within the BZT relaxor system. Note that the supplemental material [26] also provides and discusses the \( \theta(r) \) function for all the \( r \)-vectors lying in the \( (y, z) \) plane at 10 K.

A particularly important feature of our scheme is that we can switch on and off some interactions in order to determine their effect on physical properties. We numerically found that turning off random fields and random strains does not significantly affect the results shown in Fig. 1 and 2, which contrasts with a common belief on the microscopic origins of relaxors [4,16,17] while being more consistent with models proposed for the homovalent (K, Li)TaO\(_3\) relaxor [52,53]. On the other hand, our computations reveal that it is the difference in ferroelectric strength between Ti and Zr ions that leads to the relaxor behavior in BZT. As a matter of fact, annihilating such differences in the simulations leads to (1) \( \chi^{\text{direct}} \) and \( \chi^{\text{CF}} \) being equal to each other and continuously decreasing as the temperature decreases down to 0 K (with the system remaining cubic and nonpolar), (2) the Edwards-Anderson parameter being around 10 times smaller than the one depicted in Fig. 1(b) at low temperature, and (3) the polar nanoclusters disappearing. It should also be emphasized that our simulation results depicted in Figs. 1 and 2 imply that relaxor behavior can occur in BZT even if no large chemically ordered region exists in that system (since our computations were performed on disordered solid solutions). Such a finding seems to contrast with models recently proposed to explain the relaxor behavior of heterovalent Pb(Sc, Nb)O\(_3\) and Pb(Mg, Nb)O\(_3\) alloys [13], while agreeing with a study [39] downplaying the role of chemical short-range ordering on the formation of polar nanoregions in BZT. In fact, our simulations indicate that the relaxor behavior already occurs in disordered BZT solid solutions because some regions of space can be more Ti rich than others because of the random process of assigning sites in a disordered solid solution. Such a feature bears resemblance to the Anderson localization phenomenon for which electronic wave functions become localized in a region of space [of an overall disordered \((A', A'')\) solid solution] that is much richer in \( A' \) than in \( A'' \) [54]. Finally, we also increased the antiferroelectric-like interactions (by playing with the so-called \( j_3 \) short-range coefficient [27]). We found that such an increase leads to a shift towards higher temperatures of the peak of \( \chi^{\text{CF}} \), in addition to enhancing at low temperatures (i) the Edwards-Anderson parameter, (ii) the average magnitude of the local modes centered on Ti ions, (iii) the square of the Fourier transform of the local dipoles configuration at \( \mathbf{k}_{\text{max}} \), and (iv) the strength of the anticorrelation between Ti dipoles that are distant by three lattice constants along the \( z \)- (or \( x \)- or \( y \)-) axis. Such findings emphasize the importance of the antiferroelectric-like interactions between Ti-rich nanopolar clusters for the relaxor behavior.

We therefore hope that our study helps in achieving a better understanding of the fascinating relaxor ferroelectrics. In order to further enhance such understanding, future studies could examine the influence of static and dynamic (GHz–THz) electric fields [20,21] on the behaviors of BZT materials, and determine if the results found here also hold for heterovalent relaxors [such as Pb(Sc, Nb)O\(_3\) and Pb(Mg, Nb)O\(_3\)].

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