Configuration Dependence of Physical Properties of a Ferroelectric Solid Solution

Eric Cockayne and Karin M. Rabe

Department of Applied Physics, Yale University, P.O. Box 208284, New Haven, CT 06520-8284

Abstract. In this article, we motivate the detailed comparison of the physical properties of individual configurations of a ferroelectric solid solution as a means toward developing first principles models for these systems. We compare energies, dielectric constants $\varepsilon_\infty$, mode effective charges of local polar distortions, and the zero temperature piezoelectric behavior of several ordered Pb$_3$GeTe$_4$ supercells. Cluster expansions of these properties show the importance of second-neighbor effects, which can be related to symmetry-preserving relaxation and its effect on the symmetry breaking polar instabilities.

INTRODUCTION

Ferroelectric solid solutions are of great technological importance. For example, the largest piezoelectric response are found in mixed ferroelectrics, such as Pb(Zr$_{1-x}$Ti$_x$)$_3$O$_3$. Recently, giant piezoelectricity was discovered in the relaxor ferroelectric systems Pb(A$_{1/3}$Nb$_{2/3}$)$_3$O$_3$–PbTiO$_3$, (A = Zn, Mg). [1] Understanding the physics of ferroelectric solid solutions on the microscopic level would be of great theoretical interest and could also point to new ways to tune their piezoelectric response and other properties.

Ab initio calculations have proved successful in relating properties of stoichiometric ferroelectrics to phenomena on the atomic level [2]. Structural parameters [2,3], dielectric constants, effective charges, phonon dispersion relations [4,5], and polarizations [6] have been calculated from first principles. To predict the behavior at finite temperature, first-principles models have been constructed. [7–11]. Generally, these models are based on a vector representation of the local polar distortions responsible for the ferroelectric phase transition. An electric dipole moment is associated with each local distortion. At long distance, the interaction between local

---

1) To be published in the proceedings of the Fifth Williamsburg Workshop on First-Principles Calculations for Ferroelectrics, February 1998.
distortions is dipole-dipole; significant corrections appear at short range. Anharmonic terms, elastic constants and strain coupling to local distortion also appear, determining the ground state and the nature of the phase transitions in the models. [12] The models obtained allow for simulation of ferroelectric phase transitions, where the Curie point is generally in good agreement with experiment. The models also allow piezoelectricity and dielectric functions to be computed [13,14]. In the following, we discuss the modeling of ferroelectric and piezoelectric behavior in solid solutions, and lay part of the groundwork for a Pb$_{1-x}$Ge$_x$Te model by exploring the configuration dependence of certain quantities essential for constructing the model.

WHY COMPARE CONFIGURATIONS?

Consider a ferroelectric solid solution. The physical properties of this solid solution are the ensemble averages of the properties of the individual ensemble members. Thus one needs to be able to compute these physical properties for individual ensemble members. A given ensemble member (configuration) can be treated as if it were an actual crystal structure and modeled in the same manner as for a stoichiometric ferroelectric.

While models for a few chosen small unit cell configurations are obtained using this approach, some model for the general configuration is necessary in order to properly take ensemble averages. Given the nature of the model described in the Introduction, we expect that in a model for the general configuration, there will again be polar instabilities, a local basis for these distortions, and interactions between the local distortions. However, now the local polar distortions themselves and their interactions will be site-dependent. In principle, the site-dependence of any quantity can be described by a cluster expansion. The models obtained for the series of individual small unit cell configurations can be used to obtain the cluster expansions for a model that is valid for all configurations.

In modeling stoichiometric ferroelectrics, two kinds of truncation in the models are necessary to prevent an explosion of terms: the order of the expansion of the energy in powers of the local distortion variable and the range of the local interactions. The cluster expansion approach necessitates a third kind of physically motivated truncation: the range of the cluster expansion. Where possible, terms should be found whose configuration dependence is unimportant and then kept constant for all configurations. For those terms where a cluster expansion is necessary, it should be truncated at the shortest possible range. Toward this end, it is thus very important to establish and understand the configuration dependence of those quantities that determine the model parameters.

Pb$_{1-x}$Ge$_x$Te provides an excellent prototype system for investigating the form of first-principles models in solid solutions using the approach just outlined. For all compositions above a critical composition $x \approx 0.005$ [15], Pb$_{1-x}$Ge$_x$Te undergoes a transition from a cubic phase for $T > T_c(x)$ to a rhombohedral phase at $T < T_c(x)$ [16]. Because the endmembers of the solid solution series have the
rocksalt structure with only 2 atoms per primitive cell, a large number of different mixed configurations can be investigated without the need for excessively large supercells. To simplify the problem further, we focus on configuration dependence at a fixed composition, Pb$_{0.75}$Ge$_{0.25}$Te. This composition was chosen to be near the low Ge concentration regime of physical interest, while allowing for a variety of supercells with only 8 atoms. We present results on the five 8-atom supercells of highest symmetry, shown in Figure 1. In each configuration studied, all Ge ions are translationally equivalent and therefore have the same environment, greatly simplifying the analysis.

**FIRST PRINCIPLES METHODS**

In our study of the structural phase transition in the cP8 configuration [10], we give full details of the first principles calculations. Briefly, we performed all calculations using density functional theory within the local density approximation (LDA). Ab initio pseudopotentials were used for the ions and a plane wave basis set with cutoff energy 300 eV was used for the Kohn-Sham eigenfunctions. Total energies were calculated via conjugate gradients optimization using the CASTEP 2.1 package [17]. The CASTEP 2.1 package was modified [18] to do variational linear response [5] calculations of force constants, Born effective charges and dielectric constants. Brillouin zone averages for the cP8 configuration were performed using a $4 \times 4 \times 4$ Monkhorst-Pack set. For the other configurations, the same $k$ point grid was used, folded into the corresponding Brillouin zone.

**FIGURE 1.** Pb$_3$GeTe$_4$ configurations investigated. Each has 8 atoms per primitive unit cell. (The Pearson symbols specify the number of atoms in the conventional unit cell.)
SYMMETRY PRESERVING RELAXATION

We found two distinct ways in which the total energies of the configurations that we studied could be lowered with respect to the energy of the structures with all atoms fixed on rocksalt positions: symmetry-preserving relaxation and symmetry-breaking polar instabilities. The existence of symmetry-preserving relaxation follows from group theory. Except for the cP8 configuration, all of the configurations have one or more identity irreducible representations (irreps) among its normal modes. An identity irrep implies an energy term that is linear in the corresponding mode and thus a lowering of the energy by relaxation in the ionic displacement subspace spanned by these modes. This relaxation neither lowers the symmetry nor causes net polarization in the configurations studied. The other normal modes in the systems have non-identity irreps; thus to lowest order, the total energy is quadratic in these modes. The existence of instabilities (normal modes whose harmonic coefficient is negative) with their concurrent symmetry breaking is a system-specific phenomenon, as is the polar nature of these instabilities. This section focuses on symmetry-preserving relaxation; the next section focuses on symmetry-breaking polar instabilities.

Before investigating symmetry-preserving relaxation, we relaxed each configuration of Figure 1 with respect to strain, holding all ions fixed at ideal rocksalt positions. At this point, the total energies all differed by less than 10 meV/(8 atom cell) and the (pseudocubic) lattice parameters all differed by less than 0.06%. Had all subsequent calculations been performed with respect to the same pseudocubic lattice parameters, e.g. the cP8 value of \(a = 6.275\ \text{Å}\), the strain energies involved would been negligible.

Each configuration was allowed to undergo symmetry preserving relaxation, with its strain held fixed. The relaxed atomic coordinates can be simply described (to within 0.03 Å) by displacement of the Te ions in each Pb-Te-Ge chain segment 0.12 Å toward to the Ge ion, with all other ions held fixed. [19] Qualitatively, relaxation in Pb\(_{1-x}\)Ge\(_x\)Te can be regarded as the result of the size mismatch between the smaller Ge and the larger Pb ions. The energy of the cP8 configuration, for which no symmetry-preserving relaxation occurs, was 171 meV/cell higher than for the relaxed oC16 configuration, in which every Te is displaced.

The energies of the relaxed configurations were fit to a pair-only cluster expansion out to fourth cation-cation neighbors. In meV/cell, the total energy of the configurations tested is given by:

\[
E = E_0 - 2.9\overline{N}_1 + 26.4\overline{N}_2 - 1.5\overline{N}_3 + 1.3\overline{N}_4, \tag{1}
\]

where \(\overline{N}_i\) is the average number of \(i\)’th neighbor Ge ions per Ge ion. The cation sublattice in Pb\(_{1-x}\)Ge\(_x\)Te is fcc; each cation has 12 first neighbors cations at \((a/2, a/2, 0)\), etc., 6 second neighbors at \((0, 0, a)\), etc., 24 third neighbors at \((a/2, a/2, a)\), etc., and 12 fourth neighbors at \((a, a, 0)\), etc., where \(a\) is the conventional fcc lattice parameter. The sensitivity of energy to \(\overline{N}_2\) is an order of magnitude
larger than for the other terms, illustrating the importance of the above-mentioned relaxation. The Ge and the Pb in a linear Ge-Te-Pb segment where the Te undergoes significant relaxation are second neighbors; the more Ge-Te-Pb segments, the fewer Ge-Te-Ge segments, the lower $N_2$, and the lower the relaxed energy.

The expression 1 is a fit of 5 relaxed cell energies to five parameters. It is also important to get an estimate of the predictive power of a cluster expansion truncated at a smaller number of terms. We did a series of cluster expansions in terms of $N_1$, $N_2$ and $N_3$ to each subset of 4 configurations [20] in Figure 1, and used the resulting expression to calculate the energy of the configuration that was left out. The rms error was 16 meV/cell and the maximum error was 20 meV/cell. This compares with the root mean square variance of 57 meV/cell for the relaxed energies of the set of configurations studied, showing modest but not excellent predictability for a cluster expansion out to third neighbor. In what follows, we present results based on three or fewer configurations and the cluster expansions are truncated where the number of parameters matches the number of unknowns. Calculations on additional configurations would be necessary to make any meaningful test of predictability.

SYMMETRY BREAKING INSTABILITIES

Next, we looked at energy lowering via symmetry-breaking distortions. For each configuration, we then calculated the normal modes at the zone center. We performed linear response force constant calculations at $q = 0$ for each relaxed configuration and then diagonalized the corresponding dynamical matrix to obtain the normal modes. For each configuration, there were symmetry-breaking polar instabilities, with a three-dimensional vector representation centered on the Ge ion. [21] Further $q \neq 0$ calculations on cP8 and tP8 showed that instabilities throughout the Brillouin zone could be well-represented by a local (lattice Wannier function [24]) basis with one vector on each Ge ion. This supports the Ge off-centering model for ferroelectricity in Pb$_{1-x}$Ge$_x$Te [22] and gives strong evidence that the correct form for a first-principles model for arbitrary configurations will have one vector per Ge ion.

In order to appropriately model the long-range physics within our models, both the electronic dielectric tensor $\epsilon_\infty$ and the polarization associated with the local instabilities must be determined. These are linear response functions of the relaxed high-symmetry structures. We have calculated the dielectric tensors $\epsilon_\infty$ and the Born effective charges for the cP8, tP8, and tI16 configurations. The Born effective charge tensors $Z_j^\star$ and the normal mode ionic displacement pattern $u_{j\beta}$ associated with the zone-center instability which transforms like the vector component $\alpha$ were used to calculate the so-called mode effective charge tensor through

$$Z_{\alpha\beta}^\star = \sum_{j\gamma} (Z_j^\star)_{\alpha\gamma} (u_{j\beta})_\gamma \tag{2}$$
The normal modes were all normalized such that $\sum_j |u_j\beta|^2$ was 1 Å$^2$.

The results for the $\epsilon_\infty$ and $Z^*$ tensors are shown in Table 1. Fitting to a pairwise cluster expansion out to second neighbor, we obtain:

$$(\epsilon_\infty)_{\alpha\alpha} = 42.5 - 0.175N_{1||} - 0.1N_{1\perp} + 1.7N_{2||} + 0.2N_{2\perp},$$

where $N_{i\perp}$ is the mean number of $i$’th neighbor Ge ions per Ge ion in a direction perpendicular to $\alpha$ and $N_{i||}$ is the mean number of $i$’th neighbor Ge ions per Ge ion in a direction having nonzero component along $\alpha$. Likewise, the mode effective charge is given (in units of eÅ) by

$$Z^*_{\alpha\alpha} = 17.31 - 0.14N_{1||} - 0.12N_{1\perp} - 2.17N_{2||} - 0.22N_{2\perp}. $$

The relative configuration dependence of $Z^*$ is larger than that of $\epsilon_\infty$. The three configurations all have diagonal dielectric and mode effective charge tensors; it should be noted that off-diagonal terms will be nonzero in the general (asymmetric) configuration. For the mode effective charge tensors, the more Ge-Te-Pb or Pb-Te-Ge segments along $z$, the lower $N_{2||}$ and the higher $Z^*_{zz}$. We have previously shown how this increase can be explained in terms of local bonding [23]. The differences in the Born effective charges of individual ions between configurations is relatively small; it is primarily the difference in the normal mode eigenvector between configurations that leads to the increase in $Z^*$. In particular, in Ge-Te-Pb chain segments, relaxation of the Te away from the Pb leads effectively to an off-centering instability of the Pb ion that does not occur when the Pb-Te distance is smaller. [23] The active participation of the Pb ion helps to increase $Z^*$.

| Component | cP8 | tP8 | tI16 |
|-----------|-----|-----|------|
| $(\epsilon_\infty)_{xx}$ | 46.7 | 45.6 | 46.3 |
| $(\epsilon_\infty)_{yy}$ | 46.7 | 45.6 | 46.3 |
| $(\epsilon_\infty)_{zz}$ | 46.7 | 42.9 | 43.3 |
| $Z^*_{xx}$ | 12.10 | 11.97 | 12.54 |
| $Z^*_{yy}$ | 12.10 | 11.97 | 12.54 |
| $Z^*_{zz}$ | 12.10 | 15.95 | 16.44 |

PIEZOELECTRICITY AT ZERO TEMPERATURE

The above calculations were for relaxed high symmetry states. We now turn our attention to properties of the fully distorted LDA ground states. We have previously reported the piezoelectric tensors at zero temperature for the cP8 and tP8...
configurations [23]. In this section, we give further results for the tI16 configuration, write a simple cluster expansion for the zero-temperature piezoelectricity in Pb$_{0.75}$Ge$_{0.25}$Te, and use this expansion to estimate the piezoelectric tensor of the disordered system.

**TABLE 2.** LDA ground state of Pb$_3$GeTe$_4$-tI16. Monoclinic, space group Cm, $a = 8.984$ Å, $b = 8.876$ Å, $c = 7.738$ Å, $\beta = 54.08^\circ$.

| Atom | Wyckoff position | x    | y    | z    |
|------|------------------|------|------|------|
| Pb   | 2(a)             | 0.5034 | 0    | 0.0061 |
| Pb   | 4(b)             | 0.5020 | 0.2489 | 0.5000 |
| Ge   | 2(a)             | 0.0291 | 0    | 0.0069 |
| Te   | 2(a)             | 0.2355 | 0    | 0.5158 |
| Te   | 2(a)             | 0.7578 | 0    | 0.4753 |
| Te   | 4(b)             | 0.2391 | 0.2383 | 0.9976 |

The LDA ground state for the tI16 configuration is given in Table 2. In Table 3, we give the full piezoelectric tensors for the LDA ground states of the cP8, tP8 and tI16 configurations. In each case, the orientation is with respect to the axes of Figure 1, and the symmetry has been broken such that the Ge displacement and the polarization lie in the $+\{111\}$ quadrant.

**TABLE 3.** Comparison of piezoelectric strain tensors for the ground states of three Pb$_3$GeTe$_4$ configurations (in C/m$^2$). Components in parentheses are equal to other components via symmetry. Components which do not appear in the table are related by symmetry to those that do; e.g. $e_{22} = e_{11}$ for each configuration.

| Component | cP8 | tP8 | tI16 |
|-----------|-----|-----|------|
| $e_{11}$  | 1.8 | 2.5 | 2.4  |
| $e_{12}$  | -0.6 | -1.2 | -1.2 |
| $e_{13}$  | (-0.6) | -0.9 | -0.6 |
| $e_{14}$  | -0.2 | -0.6 | -0.5 |
| $e_{15}$  | 1.0 | 1.2 | 0.2  |
| $e_{16}$  | (1.0) | 1.1 | 1.1  |
| $e_{31}$  | (-0.6) | -0.3 | -0.5 |
| $e_{33}$  | (1.8) | 5.1 | 6.5  |
| $e_{34}$  | (1.0) | 2.2 | 6.4  |
| $e_{36}$  | (-0.2) | -0.5 | -0.7 |

If only pair terms are included in the cluster expansion for piezoelectricity, then the piezoelectric tensor is given by

$$
e = e_0 + \sum_d N_d e_d,$$

(5)
where $\mathbf{e}$ is the piezoelectric tensor, $\mathbf{e}_0$ is a configuration-independent term, $\{\mathbf{d}\}$ is the set of cation-cation separations, $\overline{N_d}$ is the average number of Ge neighbors per Ge ion at separation $\mathbf{d}$, and $\mathbf{e}_d$ is the correction to the piezoelectric tensor due to neighbors at separation $\mathbf{d}$. We are now dealing with a property of Pb$_{0.75}$Ge$_{0.25}$Te at zero temperature; the discussion of piezoelectric tensor in this section only applies to the subensemble of zero temperature structures that have been poled by a field in the +111 direction. The subensemble has rhombohedral symmetry; the average piezoelectric tensor has only four independent components: $e_{11}$, $e_{12}$, $e_{14}$ and $e_{15}$.

Symmetry constrains the form of the individual $\mathbf{e}_d$. Consider for example the effect of adding one Ge-Ge pair separated by $\left(\frac{a}{2}, \frac{a}{2}, 0\right)$ to a perfectly rhombohedral configuration. The global symmetry is broken to monoclinic. By writing the appropriate symmetrized form of the piezoelectric tensor for a monoclinic system and subtracting that for a rhombohedral system, the correct symmetry for $\mathbf{e}_{(a/2,a/2,0)}$ is obtained. It is straightforward to show that the tensors $\mathbf{e}_d$ for two different $\mathbf{d}$ are related if and only if the two $\mathbf{d}$ are equivalent by symmetry under the rhombohedral group. In the cation sublattice, the 12 first neighbors break under rhombohedral distortion into 2 groups of 6, while the 6 second neighbors are all equivalent.

The cP8, tP8 and tI16 configurations are sufficient to separate the first neighbor and second neighbor contributions to the piezoelectric tensor, but insufficient for determining the independent contributions of the two kinds of first neighbor. In Table 4, we give $\mathbf{e}_0$ and the contributions $\mathbf{e}_{(a/2,a/2,0)} + \mathbf{e}_{(a/2,-a/2,0)}$ and $\mathbf{e}_{(0,0,a)}$. Both the tensors $\mathbf{e}_{(a/2,a/2,0)} + \mathbf{e}_{(a/2,-a/2,0)}$ and $\mathbf{e}_{(0,0,a)}$ have the same symmetry as that for the tP8 and tI16 ground state piezoelectric tensors.

The dominant terms reflect the piezoelectric components that change the most from configuration to configuration. The lack of second neighbor Ge pairs along $(0,0,a)$ tends to increase the value of $e_{33}$, while the lack of Ge pairs separated by $(\pm a/2, \pm a/2, 0)$ and $(0,0,a)$ both increase the value of $e_{34}$. The physics of the $(0,0,a)$ pairs is clear: the presence of a Ge-Te-Pb chain segment means that there is relaxation of the Te atom joining them and thus a weakening of the instability that transforms like $z$. A weak instability implies large response [23,14]. The $e_{33}$ and $e_{34}$ components are the ones enhanced because the instability along $\hat{z}$ is effectively coupled most strongly to these components. [10]. The exact source of the large influence of first neighbor pairs on $e_{34}$ has yet to be determined.

Given the data in Table 4, it is possible to estimate the piezoelectric tensor of disordered Pb$_{0.75}$Ge$_{0.25}$Te. We assume for present purposes that all members of the poled subensemble are equiprobable. Then there are no spatial correlations and $\overline{N_d} = 0.25$ for all $\mathbf{d}$. Using the values in Table 4 and Eq. 5, we estimate for disordered Pb$_{0.75}$Ge$_{0.25}$Te that $e_{11} = 5.9$, $e_{12} = -0.9$, $e_{14} = -1.0$, and $e_{15} = 3.7$, reproducing the tensor form expected for rhombohedral symmetry. The estimated values of the components suggest that the piezoelectric response of the cP8 configuration is particularly unrepresentative for the disordered system. Because of the strong dependence of piezoelectric response on the magnitude of instability in a system and the configuration dependence of the magnitude of local instabil-
TABLE 4. Terms in cluster expansion of Pb$_{0.75}$Ge$_{0.25}$Te piezoelectric tensor (in C/m$^2$)

| Component | $e_9$ | $e_{(a/2,0/2,0)} + e_{(a/2,-a/2,0)}$ | $e_{(0,0,a)}$ |
|-----------|-------|-----------------------------------|---------------|
| $e_{11}$  | 7.7   | 0.1                               | -0.3          |
| $e_{12}$  | -1.0  | 0.2                               | 0.3           |
| $e_{13}$  | (-1.0)| -0.1                              | 0.0           |
| $e_{14}$  | -1.2  | 0.0                               | 0.1           |
| $e_{15}$  | 5.6   | 0.5                               | 0.4           |
| $e_{16}$  | (5.6) | 0.0                               | 0.0           |
| $e_{31}$  | (-1.0)| 0.1                               | -0.1          |
| $e_{33}$  | (7.7) | -0.7                              | -2.4          |
| $e_{34}$  | (5.6) | -2.2                              | -2.7          |
| $e_{36}$  | (-1.2)| 0.1                               | 0.2           |

ity, piezoelectric results on single high symmetry supercells of mixed ferroelectrics should be treated with caution.

CONCLUSIONS

This work describes the necessity of cluster expansions in first principles models for piezoelectricity and ferroelectricity in solid solutions and the importance of comparing the properties of different configurations. In the specific example of Pb$_{0.75}$Ge$_{0.25}$Te, strong configuration dependence is found for relaxed energies, the nature of the local polar instabilities, and the polarization associated with these instabilities. A good model for ferroelectricity in a mixed system must be able to account for this variability. We show how results of the zero temperature piezoelectricity on several ordered supercells can be used to obtain an estimate of the zero temperature piezoelectricity of a completely disordered cell.

ACKNOWLEDGEMENTS

This work was supported by ONR N00014-97-J-0047.

REFERENCES

1. S.-E. Park and T. R. Strout, in 1996 IEEE Ultrasonics Symposium Proceedings (New York: IEEE, 1996), v.2, p. 935; J. Appl. Phys. 82, 1804 (1997), and references therein.
2. R. E. Cohen, Nature 358, 136 (1992).
3. D. J. Singh, Phys. Rev. B 52, 12559 (1995).
4. S. Baroni, P. Giannozzi and A. Testa, *Phys. Rev. Lett.* **58**, 1861 (1987).
5. X. Gonze, D. C. Allan and M. P. Teter, *Phys. Rev. Lett.* **68**, 3603 (1992).
6. R. D. King-Smith and D. Vanderbilt, *Phys. Rev. B* **47**, 1651 (1993).
7. K. M. Rabe and J. D. Joannopoulos, *Phys. Rev. Lett.* **59**, 570 (1987).
8. W. Zhong, D. Vanderbilt, and K. M. Rabe, *Phys. Rev. Lett.* **73**, 1861 (1994); *Phys. Rev. B* **52**, 6301 (1995).
9. K. M. Rabe and U. V. Waghmare, *Ferroelectrics* **164**, 15 (1995); U. V. Waghmare and K. M. Rabe, *Phys. Rev. B* **55**, 6161 (1997).
10. E. Cockayne and K. M. Rabe, *Phys. Rev. B* **56**, 7947 (1997).
11. H. Krakauer, R. Yu, C.-Z. Wang, K. M. Rabe and U. V. Waghmare, unpublished (cond-mat/9710088); H, Krakauer, R. Yu, C. Z. Wang, and C. Lasota, *Ferroelectrics* (to be published).
12. K. M. Rabe and U. V. Waghmare, *Phil. Trans. R. Soc. Lond. A* **354**, 2897 (1996).
13. A. Garcia and D. Vanderbilt, unpublished (cond-mat/9712312).
14. K. M. Rabe, these Proceedings.
15. S. Takaoka and K. Murase, *Phys. Rev. B* **20**, 2823 (1979).
16. D. K. Hohnke, H. Holloway and S. Kaiser, *J. Phys. Chem. Solids* **33**, 2053 (1972).
17. M. C. Payne et al., “CASTEP 2.1”, Cavendish Laboratory, University of Cambridge (1991).
18. U. Waghmare, Ph. D. thesis, Yale University (1996).
19. If a Te atom belongs to Pb-Te-Ge chain segments in more than one Cartesian direction, as for example the $z = 0$ Te atoms in the oP8 and oC16 configurations, then its relaxation is given approximately by the vector sum of the appropriate 0.12 Å relaxations for the individual chains.
20. For technical reasons, the subset of four configurations with cP8 missing could not be used in this analysis. The particular values of $N_1$, $N_2$, and $N_3$ for that set of four configurations gives an indeterminate set of linear equations.
21. The vector representation breaks into irreps according to the point group of the Ge site in the given configuration.
22. Yu. A. Logachev and B. Ya. Moizhes, *Sov. Phys. Solid State* **19**, 1635 (1977). (*Fiz. Tverd. Tela* (Leningrad) **19**, 2793 (1977)).
23. E. Cockayne and K. M. Rabe, unpublished (cond-mat/9712232).
24. K. M. Rabe and U. V. Waghmare, *Phys. Rev. B* **52**, 13236 (1995).