

Dipole moment of a Pb-O vacancy pair in PbTiO₃

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The polarization of a nearest neighbor (nn) Pb-O vacancy pair ($(V_{Pb} - V_O)_{nn}$) in PbTiO₃ is calculated, using the modern theory of polarization, implemented in the density functional theory ultrasoft pseudopotential formalism. The dipole moment per divacancy, $\vec{\mu}_{(V_{Pb}-V_O)_{nn}}$, is about $2.28 e \vec{r}_{nn}$, where \vec{r}_{nn} is the vector from the V_{Pb} site to the V_O site. This value is slightly larger than the value of $2 e \vec{r}_{nn}$ for a purely ionic model of PbTiO₃. The dipole moment is about twice as large as typical polarizations per cell in Pb-based ferroelectrics, which indicates that V_{Pb} compensated by V_O can be an important source of local polarization and electric fields in Pb-containing perovskites.

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Pb-based perovskites are of industrial interest for applications ranging from multilayer ceramic capacitors to transducers to nonvolatile memories [1]. Single-crystal relaxor ferroelectric (RFE) based solid solutions such as PbMg_{1/3}Nb_{2/3}O₃-PbTiO₃ (PMN-PT) and PbZn_{1/3}Nb_{2/3}O₃-PbTiO₃ (PZN-PT), exhibit very large piezoelectric coefficients[2]. The properties and performance of these materials are expected to be strongly affected by defects such as lead vacancies (V_{Pb}). Studies of the RFE systems Pb(Sc_{1/2}Nb_{1/2})O₃ (PSN) and Pb(Sc_{1/2}Ta_{1/2})O₃ (PST) demonstrate that 2 % to 3 % V_{Pb} cause: 1) a significant reduction in the maximum, $\epsilon'_{max}(\nu)$, of the real part of the dielectric permittivity, $\epsilon'(T, \nu)$, which occurs at $T = T_{max}(\nu)$ [i.e. at $T = T_{max}(\nu)$, $\epsilon'(T, \nu)$ is maximized]; and 2) an enlarged T-range for RFE behavior at $T < T_{max}(\nu)$ [7, 8]. Also, oxygen vacancies, V_O , have been invoked as a source of domain-wall pinning, which leads to polarization fatigue in ferroelectrics[3-6].

In a fully or partly ionic compound, it is generally favorable for vacancies to be charge-balanced by other defects so that the system remains formally neutral (e.g. Schottky or Frenkel defects). Thus, Chu et al. reported stoichiometries of the form Pb_{1-x}Sc_{1/2}Nb_{1/2}O_{3-x} for PSN with V_{Pb} [7]. A vacancy compensated by a nearby substitutional defect, interstitial or vacancy, creates an electric dipole. Expansion of the RFE T-range in PSN and PST, when V_{Pb} are introduced, strongly suggests that local “*random fields*” (RF) from polar defects such as a nearest neighbor (nn) V_{Pb} - V_O divacancy, $(V_{Pb}-V_O)_{nn}$, may enhance RFE properties. Pöykkö and Chadi[9] showed that a nn substitutional-vacancy defect (Ti→Pt)-(V_O) is highly stable in PbTiO₃ and based a model for polarization fatigue on such dipolar defects. Keeble *et al.*[10] give evidence for the formation of V_{Pb} - V_O divacancies in (Pb,La)(Zr,Ti)O₃. To quantify the effects of dipolar defects on the properties and performance of materials, their dipole moments must be known.

Aside from the effects of dipolar defects on materials

properties, the dipole moments of defects in highly polarizable structures is of more fundamental interest. If PbTiO₃ were purely ionic, then the dipole moment of a $(V_{Pb}-V_O)_{nn}$ divacancy would be $\vec{\mu}_{(V_{Pb}-V_O)_{nn}} = 2 e \vec{r}_{nn}$, where \vec{r}_{nn} is the separation vector between V_{Pb} and V_O sites. Electronic structure models indicate that O ions in perovskite titanates are not completely ionized[11], which suggests that $|\vec{\mu}_{(V_{Pb}-V_O)_{nn}}|$ might be less than $|2 e \vec{r}_{nn}|$. However, the high polarizability and charge transfer effects in perovskite oxides that give rise to anomalously large ionic effective charges[12, 13] raise the intriguing possibility that $|\vec{\mu}_{(V_{Pb}-V_O)_{nn}}|$ might be *larger* than $|2 e \vec{r}_{nn}|$. In this Letter, we use first-principles calculations and the modern theory of polarization to properly calculate the dipole moment of a $(V_{Pb}-V_O)_{nn}$ divacancy in PbTiO₃, and demonstrate that it is indeed anomalously large.

This work is based on first-principles (FP) electronic structure calculations using the density functional theory (DFT) code VASP[14], with Vanderbilt-type ultrasoft pseudopotentials for each ion[15]. The local density approximation (LDA) was used for the exchange-correlation functional. A plane-wave basis set with an energy cutoff of 337 eV was used for the electronic wavefunctions, which is supplemented in the ultrasoft pseudopotential formulation by local augmentation charges to accommodate more rapid fluctuation of charge density in core regions[15].

In DFT calculations for periodic supercells that contain a defect, or defects, one must compromise between small supercells, in which the defect will interact more strongly with its periodic images, and large supercells, which are more computationally demanding. Here, a 38-atom Pb₇Ti₈O₂₃ supercell was first chosen, (Figure 1); i.e., a $2 \times 2 \times 2$ PbTiO₃ supercell with nn Pb- and O-atoms removed. Brillouin zone (BZ) integration for this supercell was performed by calculating electronic wavefunctions on a $4 \times 4 \times 4$ Monkhorst-Pack grid, except for LDA band gap calculations, in which a $4 \times 4 \times 4$ k-

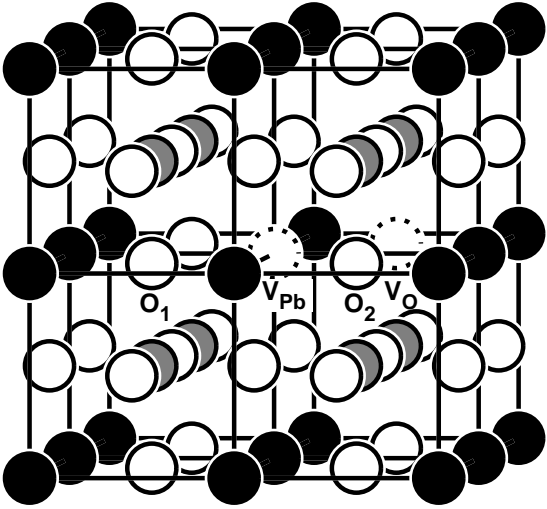


FIG. 1: $\text{Pb}_7\text{Ti}_8\text{O}_{23}$ supercell for which the vacancy pair polarization was calculated. Pb atoms black; Ti gray; O white. Dotted circles indicate the oxygen- (V_O) and Pb-vacancies (V_{Pb}). Oxygens O_1 and O_2 , which are involved in the adiabatic transformation, are also labeled.

point grid containing the BZ center was used, because band extrema are most likely to occur at zone center or high-symmetry zone boundary points.

Experimentally, the low-temperature state of PbTiO_3 is tetragonal, space group $P4mm$, with significant ferroelectric (FE) ionic displacements[16]; which is reproduced by FP calculations[20]. In PbTiO_3 with $(V_{\text{Pb}}-V_{\text{O}})_{nn}$ divacancies, one expects local contraction around the divacancy (*i.e.* significant inhomogeneous strain). Because the $(V_{\text{Pb}}-V_{\text{O}})_{nn}$ lacks an inversion center, the inhomogeneous strain will couple linearly with polarization. To isolate $\vec{\mu}_{(V_{\text{Pb}}-V_{\text{O}})_{nn}}$ from polarization due to FE distortion, inhomogeneous strain, etc., the polarization is calculated for a nonequilibrium $\text{Pb}_7\text{Ti}_8\text{O}_{23}$ supercell, space group $Amm2$, in which all ions are fixed in ideal perovskite positions (Fig. 1).

The reference structure lattice parameter was obtained as follows. First, the LDA stress was found for undistorted cubic PbTiO_3 at the experimental cell volume[16]. Then $\text{Pb}_7\text{Ti}_8\text{O}_{23}$ was relaxed under the same stress, subject to the constraints $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$; which yields $a_0 = 3.968 \text{ \AA}$.

The same procedure was applied to calculate the total energy of unrelaxed $\text{Pb}_7\text{Ti}_8\text{O}_{23}$ with a next-nearest-neighbor (nnn) divacancy pair, $(V_{\text{Pb}} - V_{\text{O}})_{nnn}$ [17]. The total energy of $\text{Pb}_7\text{Ti}_8\text{O}_{23}$ with a $(V_{\text{Pb}} - V_{\text{O}})_{nnn}$ is 0.45 eV higher than that for $\text{Pb}_7\text{Ti}_8\text{O}_{23}$ with a $(V_{\text{Pb}} - V_{\text{O}})_{nn}$. Pöykkö and Chadi, however, compared nn and nnn divacancies in PbTiO_3 , via DFT calculations on a $2 \times 2 \times 4$ supercell, and found that nnn divacancies were more stable[18]. The main difference is that Pöykkö and Chadi included local relaxation around defects in their calculations. It is proper to include relaxation when computing

total energies from first principles. However, PbTiO_3 has a soft phonon mode associated with its FE \leftrightarrow paraelectric transition at 760K [19]. A dipolar defect will couple locally to the soft mode, greatly enhancing the dipole moment. This enhanced dipole interacts with image dipoles in a supercell calculation, overestimating relaxation energies relative to the relaxation energy of an isolated defect. Furthermore, the soft mode frequency in PT depends strongly on temperature; therefore the contribution of local soft mode coupling to the relaxation energy should also be temperature dependent. The equilibrium arrangement of V_{Pb} and V_{O} in PbTiO_3 at finite temperatures thus remains an unsolved problem. Whether $(V_{\text{Pb}}-V_{\text{O}})_{nn}$ are bound or not, the dipole moment of any $V_{\text{Pb}}-V_{\text{O}}$ at greater than nn-distance will be larger than $\vec{\mu}_{(V_{\text{Pb}}-V_{\text{O}})_{nn}}$. Therefore the conclusions in this Letter regarding the importance of divacancy induced local RF still hold.

The value of $\vec{\mu}_{(V_{\text{Pb}}-V_{\text{O}})_{nn}}$ was calculated using the modern theory of polarization[22], which states that only *changes* in total polarization \vec{P} have physical meaning. In an electronic structure calculation with norm-conserving pseudopotentials, there are two contributions to the change in dipole moment per unit cell $\vec{\mu}_{\text{cell}} = V_{\text{cell}}\vec{P}$ [21]: (1) an ionic contribution equal to the sum of the pseudopotential core charges multiplied by their displacements; and (2) an electronic contribution, related to the change in a particular Berry's phase, that is associated with the electronic wavefunctions. In an ultrasoft pseudopotential calculation, there is an additional contribution[23]: (3) the change in an “expectation value” term that is associated with augmentation charges. Software exists for calculating polarization within VASP[24].

In ferroelectrics, absolute polarizations of FE structures are generally determined from the change in polarization, relative to related centrosymmetric reference structure; e.g. an ideal centrosymmetric perovskite structure with polarization equal to zero. For the Pb-O divacancy problem, a centrosymmetric structure is obtained by moving O_1 to the V_{Pb} position. Electronic structure calculations indicate, however, that this centrosymmetric structure is *metallic*, even if all ions are further relaxed under symmetry-preserving constraints. Because polarization changes can only be calculated along a path that preserves an insulating structure[22], calculating the absolute dipole moment of a $(V_{\text{Pb}} - V_{\text{O}})_{nn}$ divacancy appears problematic, owing to the absence of a known, accessible, insulating, centrosymmetric structure.

The dipole moment, $\vec{\mu}_{(V_{\text{Pb}}-V_{\text{O}})_{nn}}$ can be calculated, however, by using the double O-shift shown in Figure 2, in which O_1 moves to the position of O_2 , and O_2 moves to the position of V_{O} . The double O-shift rotates $(\vec{\mu}_0)_{\text{cell}}$ into $-(\vec{\mu}_0)_{\text{cell}}$, so the change in polarization for the path shown in Fig. 2 is $\Delta\vec{\mu}_{\text{cell}} = -2\vec{\mu}_{(V_{\text{Pb}}-V_{\text{O}})_{nn}}$. Therefore, a centrosymmetric reference structure is avoided. (Note that the dipole moment of a charge neutral “object” is

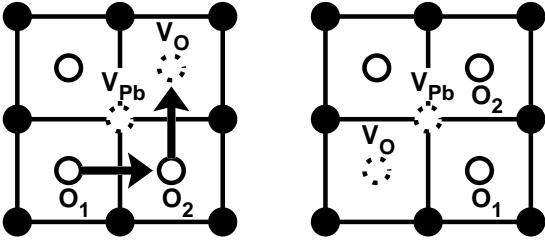


FIG. 2: Schematic of double oxygen shift that inverts the vacancy pair.

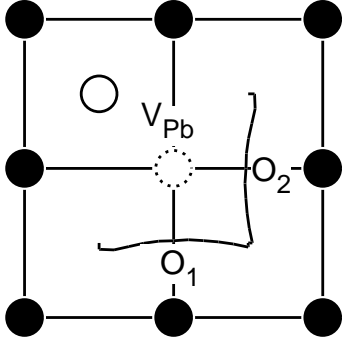


FIG. 3: Nonlinear motion of O_1 and O_2 in the path that remains insulating.

independent of the origin.)

First, we prove that the path shown in Fig. 2 remains insulating. Details of the insulating path are as follows: the coordinates of O_1 and O_2 were changed together such that $(O_1)_x = 0.25 + 0.5t$ and $(O_2)_y = 0.25 + 0.5t$, with $0 \leq t \leq 1$. At a given value of t : (1) the y coordinate of O_1 and the x coordinate of O_2 are fully relaxed; (2) the z coordinates of all ions in the $z \approx 0.25$ and $z \approx 0.75$ layers are fully relaxed. These calculations are supplemented by calculations for $t = 0$ and $t = 1$ with all ions in their ideal perovskite positions. Figure 3 shows the movements of O_1 and O_2 in the insulating path, and Figure 4 proves that the path remains insulating. If coordinated relaxations of other ionic coordinates are not allowed, the system becomes metallic around $t = 0.5$.

Having identified an insulating path, the polarization change along it can be calculated. This was done by subdividing the path into N_s steps and setting $t = (0, 1, 2 \dots N_s)/N_s$. The value of N_s should be small, to reduce the number of calculations, but the electronic contribution to the polarization depends on the Berry's phase, whose value is only determined modulo 2π . Therefore, N_s must be large enough that the Berry's phase changes by significantly less than 2π at each step; $N_s = 10$ is sufficient to keep the Berry's phase change below about $\pi/2$ at each step.

By symmetry, $(\vec{\mu}_{(V_{Pb}-V_O)_{nn}})_x = (\vec{\mu}_{(V_{Pb}-V_O)_{nn}})_y$, therefore, only the change in $(\vec{\mu}_x)_{cell}$ was calculated for the insulating path. Fig. 5 shows the value of $(\vec{\mu}_x)_{cell}$ obtained at each step, relative to the $(\vec{\mu}_x)_{cell}$ of the origi-

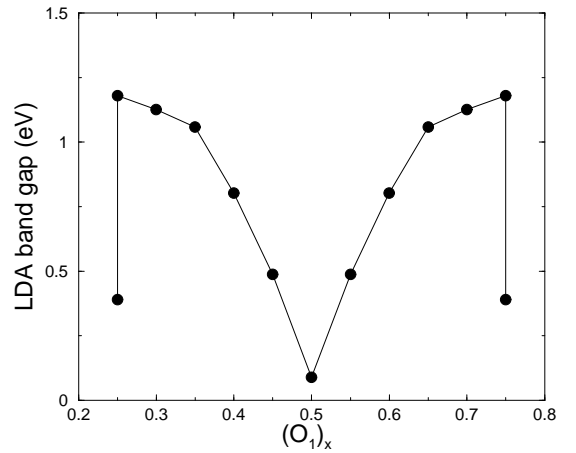


FIG. 4: LDA band gap vs. coordinates in the insulating path.

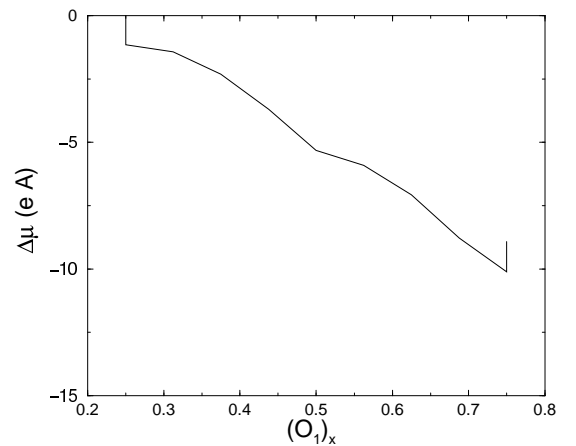


FIG. 5: Change in dipole moment relative to the original state, as a function of O coordinate along the insulating path.

nal configuration. The net change in $(\vec{\mu}_x)_{cell}$ is -8.840 e Å. Therefore, the dipole moment per Pb-O nn vacancy pair is 4.420 e $(\hat{x} + \hat{y}) = 2.228$ e $a_0(\hat{x}/2 + \hat{y}/2) = 2.228$ e \vec{r}_{nn} . This value is larger than expected from the nominal charges of Pb and O in an ionic model for $PbTiO_3$, (+2, -2 respectively). Our results, therefore indicate some additional induced polarization in the rest of the $PbTiO_3$ structure. This anomaly might arise from interactions with image dipolar defects. To test this, we repeated the polarization calculation for a $(V_{Pb}-V_O)_{nn}$ in a $3 \times 3 \times 3$ supercell. Computations for this supercell are extremely expensive, so only a “raw” polarization $(\vec{\mu}_{raw})_x$ was calculated for the reference structure. By properly choosing the origin of the cell (and assuming an insulating double oxygen shift still exists), $(\vec{\mu}_{(V_{Pb}-V_O)_{nn}})_x = (\mu_{raw})_x - 3ea_0 + 3nea_0/2$ (where the second term is the ionic contribution, and

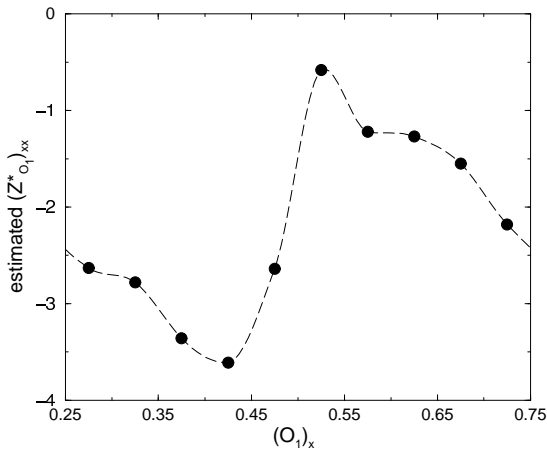


FIG. 6: Estimated Born effective charge component $(Z^*_{O_1})_{xx}$ as a function of the coordinate $(O_1)_x$.

the third term is a partial electronic contribution due to the *a priori* unknown Berry's phase winding number n). We choose n so that the polarization is closest to the value obtained for the $2 \times 2 \times 2$ cell, yielding $\vec{\mu}_{(V_{Pb}-V_O)_{nn}} = 2.263 e \vec{r}_{nn}$. [25] Assuming the scaling relation $\vec{\mu}_{(V_{Pb}-V_O)_{nn}}(\text{supercell}) = \vec{\mu}_{(V_{Pb}-V_O)_{nn}}(\text{isolated}) + A/V_{\text{supercell}}$, $\vec{\mu}_{(V_{Pb}-V_O)_{nn}}(\text{isolated})$ is approximately $2.277 e \vec{r}_{nn}$.

The anomaly in $\vec{\mu}_{(V_{Pb}-V_O)_{nn}}(\text{isolated})$ arises from the dipolar defect electronically polarizing the surrounding lattice, and manifests the same factors that lead to anomalously large ionic Born effective charge tensors Z^* in perovskites such as PbTiO_3 . In pure PT, we find $Z^*_{O\perp} = 2.50$, where $Z^*_{O\perp}$ is the magnitude of Z^* in the Pb-O planes. In $\text{Pb}_7\text{Ti}_8\text{O}_{23}$, we estimate $(Z^*_{O_1})_{xx}$ by considering the change in $(\vec{\mu}_x)_{\text{cell}}$ vs. change in O_1 and O_2 x coordinates as they are moved: $(Z^*_{O_1})_{xx} \approx (\Delta(\vec{\mu}_x)_{\text{cell}})/(a_0(\Delta(O_1)_x + \Delta(O_2)_x))$. This expression is not exact because $(Z^*_{O_1})_{xx} \neq (Z^*_{O_2})_{xx}$, and because off-diagonal effective charge elements of the moving ions also contribute slightly to $(\Delta(\vec{\mu}_x)_{\text{cell}})$. The approximation is nonetheless justified because $a_0\Delta(O_1)_x(Z^*_{O_1})_{xx}$ dominates $(\Delta(\vec{\mu}_x)_{\text{cell}})$. The estimated $(Z^*_{O_1})_{xx}$, is shown in Fig. 6. It varies from -0.58 to -3.61 as O_1 is moved, but is close to the $Z^*_{O\perp}$ for pure PbTiO_3 at the beginning and end of the path.

The path for O motion (Figure 2) is not meant to be physical. In perovskites, O diffusion is believed to traverse octahedral edges [26]. This more physical path might remain insulating without coordinated displacements of other ions, but it also breaks mirror symmetry in the $z = 0.5$ plane, increasing the computational burden.

Compare $\vec{\mu}_{(V_{Pb}-V_O)_{nn}}$, $|\vec{\mu}_{(V_{Pb}-V_O)_{nn}}|$, with the typical dipole moment per cell of the polarized state of a Pb-based FE. In PbTiO_3 , experimental values of polarization in the tetragonal phase at room temperature range from 2.2 to 2.9 e Å per primitive cell. [27], The polariza-

tion per cell at zero temperature has been estimated to be 3.40 e Å from FP calculations [28]. A first-principles-based model for the RFE PSN yields a similar rhombohedral ground state polarization magnitude of 3.08 e Å per primitive cell. [29]. The value $|\vec{\mu}_{(V_{Pb}-V_O)_{nn}}|(\text{isolated}) = 6.39 e \text{Å}$, is about twice as large as typical spontaneous polarization dipole moments per unit cell in Pb-based ferroelectrics. It is therefore not surprising that the local RF produced by a relatively small number of Pb-O vacancy pairs can significantly affect physical properties.

In summary, the dipole moment $\vec{\mu}_{(V_{Pb}-V_O)_{nn}}$ of a nn Pb-O vacancy pair $((V_{Pb} - V_O)_{nn})$ in PbTiO_3 has been calculated from first principles, using the modern theory of polarization. Its value is about $2.28 e \vec{r}_{nn}$, where \vec{r}_{nn} is the vector from the V_{Pb} site to the V_O site. This anomalously large dipole moment reflects dynamical charge anomalies. The calculated value of $\vec{\mu}_{(V_{Pb}-V_O)_{nn}}$ is about twice as large as typical values for the average spontaneous polarization per cell in Pb-based ferroelectrics, indicating that Pb vacancies compensated by O vacancies can be an important source of local polarization and electric fields in Pb-containing perovskites.

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