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 PbMg1/3Nb2/3O3-PbTiO3 (PMN-PT) and PbZn1/3Nb2/3O3-PbTiO3 (PZN-PT), exhibit very large piezoelectric coefficients[2].

Properties and performance of the RFE systems Pb(Sc1/2Ta1/2)O3 (PSN) and Pb(Sc1/2Nb1/2)O3 (PST) demonstrate that 2 % to 3 % Vp,Vb causes: 1) a significant reduction in the maximum, \( e_{\text{max}}(\nu) \), of the real part of the dielectric permittivity, \( e(T,\nu) \), which occurs at \( T = T_{\text{max}}(\nu) \) [i.e. at \( T = T_{\text{max}}(\nu) \), \( e(T,\nu) \) is maximized]; and 2) an enlarged T-range for RFE behavior at \( T < T_{\text{max}}(\nu) \) [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 \( V_{p,b} \) [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 \( V_{p,b} \) are introduced, strongly suggests that local “random fields” (RF) from polar defects such as a nearest neighbor (nn) \( V_{p,b} - V_O \) divacancy, \( (V_{p,b}-V_O)_{nn} \), 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 \( V_{p,b} - V_O \) 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 \((V_{p,b}-V_O)_{nn}\), divacancy would be \( \mu(V_{p,b}-V_O)_{nn} = 2e\vec{r}_{nn} \), where \( \vec{r}_{nn} \) is the separation vector between \( V_{p,b} \) and \( V_O \) sites. Electronic structure models indicate that O ions in perovskite titanates are not completely ionized[11], which suggests that \( |\mu(V_{p,b}-V_O)_{nn}| \) might be less than \( 2e\vec{r}_{nn} \). 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 \( |\mu(V_{p,b}-V_O)_{nn}| \) might be larger than \( 2e\vec{r}_{nn} \). In this Letter, we use first-principles calculations and the modern theory of polarization to properly calculate the dipole moment of a \((V_{p,b}-V_O)_{nn}\) 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 Pb_{0.7}Ti_{0.3}O_{23} 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-
The dipole moment, \( \vec{\mu} \), is 3.968 Å.

The value of \( \vec{\mu}(V_{Pb} - V_O)_{nn} \) was calculated using the modern theory of polarization[22], which states that only changes in total polarization \( \vec{\mu} \) 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 \( \vec{\mu}_{cell} = V_{cell}\vec{\mu}[21] \): (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 \( (V_{Pb} - V_O)_{nn} \) divacancy appears problematic, owing to the absence of a known, accessible, insulating, centrosymmetric structure.

The dipole moment, \( \vec{\mu}(V_{Pb} - V_O)_{nn} \), 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 \( \langle \vec{\mu}_0 \rangle_{cell} \) into \( -\langle \vec{\mu}_0 \rangle_{cell} \), so the change in polarization for the path shown in Fig. 2 is \( \Delta\vec{\mu}_{cell} = -2\vec{\mu}(V_{Pb} - V_O)_{nn} \). 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 O₁ and O₂ in the path that remains insulating.

First, we prove that the path shown in Fig. 2 remains insulating. Details of the insulating path are as follows: the coordinates of O₁ and O₂ were changed together such that \((O₁)_x = 0.25 + 0.5t\) and \((O₂)_y = 0.25 + 0.5t\), with \(0 \leq t \leq 1\). At a given value of \(t\): (1) the \(y\) coordinate of O₁ and the \(x\) coordinate of O₂ 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 O₁ and O₂ 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 \(t = (0, 1, 2 \ldots N_s)/N_s\). 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 \(2\pi\). Therefore, \(N_s\) must be large enough that the Berry’s phase changes by significantly less that \(2\pi\) at each step; \(N_s = 10\) is sufficient to keep the Berry’s phase change below about \(\pi/2\) at each step.

By symmetry, \((\vec{\mu}_{(V_{\text{Pb}}-V_{\text{O}})}_{\text{nn}})_x = (\vec{\mu}_{(V_{\text{Pb}}-V_{\text{O}})}_{\text{nn}})_y\), therefore, only the change in \((\vec{\mu}_{x})_{\text{cell}}\) was calculated for the insulating path. Fig. 5 shows the value of \((\vec{\mu}_{x})_{\text{cell}}\) obtained at each step, relative to the \((\vec{\mu}_{x})_{\text{cell}}\) of the original configuration. The net change in \((\vec{\mu}_{x})_{\text{cell}}\) is \(-8.840\) e \(\AA\). 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 \(\hat{r}_{\text{nn}}\). This value is larger than expected from the nominal charges of Pb and O in an ionic model for PbTiO₃, (+2, −2 respectively). Our results, therefore indicate some additional induced polarization in the rest of the PbTiO₃ structure. This anomaly might arise from interactions with image dipolar defects. To test this, we repeated the polarization calculation for a \((V_{\text{Pb}}-V_{\text{O}})_{\text{nn}}\) in a \(3 \times 3 \times 3\) supercell. Computations for this supercell are extremely expensive, so only a “raw” polarization \((\vec{\mu}_{\text{raw}})_x\) was calculated for the reference structure. By properly choosing the origin of the cell (and assuming an insulating double oxygen shift path still exists), \((\vec{\mu}_{(V_{\text{Pb}}-V_{\text{O}})}_{\text{nn}})_x = (\vec{\mu}_{\text{raw}})_x - 3e a_0 + 3e a_0/2\) (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 \textit{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 \(\tilde{\mu}_{(V_{Pb} - V_{O})_{nn}} = 2.263 \, e \, \tilde{r}_{nn}\).\[25\] Assuming the scaling relation \(\tilde{\mu}_{(V_{Pb} - V_{O})_{nn}}(\text{supercell}) = \tilde{\mu}_{(V_{Pb} - V_{O})_{nn}}(\text{isolated}) + A/V_{\text{supercell}}, \quad \tilde{\mu}_{(V_{Pb} - V_{O})_{nn}}(\text{isolated})\) is approximately 2.277 \(e \, \tilde{r}_{nn}\).

The anomaly in \(\tilde{\mu}_{(V_{Pb} - V_{O})_{nn}}(\text{isolated})\) 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 \(Z^*_O \approx 2.50\), where \(Z^*_O\) is the magnitude of \(Z^*_O\) in the Pb-O planes. In Pb\(_7\)Ti\(_8\)O\(_{23}\), we estimate \((Z^*_O)_{xx}\) by considering the change in \((\tilde{\mu}_x)_{\text{cell}}\) vs. change in \(O_1\) and \(O_2\) \(x\) coordinates as they are moved: \((Z^*_O)_{xx} \approx (\Delta(\tilde{\mu}_x)_{\text{cell}})/(a_0(\Delta(O_1)_x + \Delta(O_2)_x)\). This expression is not exact because \((Z^*_O)_{xx} \neq (Z^*_O^*_{xx}),\) and because off-diagonal effective charge elements of the moving ions also contribute slightly to \((\Delta(\tilde{\mu}_x)_{\text{cell}})\). The approximation is nonetheless justified because \(a_0 \Delta(O_1)_x (Z^*_O)_{xx}\) dominates \((\Delta(\tilde{\mu}_x)_{\text{cell}})\). The estimated \((Z^*_O)_{xx}\), is shown in Fig. 6. It varies from \(-0.58\) to \(-3.61\) as \(O_1\) is moved, but is close to the \(Z^*_O\) 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 be physical. In PbTiO\(_3\), experimental values of polarization in the tetragonal phase at room temperature range from 2.2 to 2.9 \(e \, \text{Å}\) per primitive cell.\[27\] The polarization per cell at zero temperature has been estimated to be 3.40 \(e \, \text{Å}\) from FP calculations.\[28\] A first-principles-based model for the RFE PSN yields a similar rhombohedral ground state polarization magnitude of 3.08 \(e \, \text{Å}\) per primitive cell.\[29\] The value \(|\tilde{\mu}_{(V_{Pb} - V_{O})_{nn}}(\text{isolated})| = 6.39 \, e \, \text{Å}\), 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 \(\tilde{\mu}_{(V_{Pb} - V_{O})_{nn}}(\text{nn})\) 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 \(e \, \tilde{r}_{nn}\), where \(\tilde{r}_{nn}\) 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 \(\tilde{\mu}_{(V_{Pb} - V_{O})_{nn}}(\text{isolated})\) is about twice as large as typical values for the 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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REFERENCES

[17] In the supercell geometry in this work, there are actually two \((V_{\text{Pb}}-V_{\text{O}})_{\text{nnn}}\) per supercell, considering image defects.
[25] It may seem counterintuitive that a denser lattice of dipoles has a lower dipole moment per dipole. It makes sense, however, from the simple viewpoint that \(\text{PbTiO}_3\) with more vacancies per volume has fewer polarizable ions per volume.