Origin of the orbital polarization of Co$^{2+}$: a DFT+$U$ study of La$_2$CoTiO$_6$ and (LaCoO$_3$)$_1$+(LaTiO$_3$)$_1$

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The unequal electronic occupation of localized orbitals (orbital polarization), and associated lowering of symmetry and degeneracy, play an important role in the properties of transition metal oxides. Here, we examine systematically the underlying origin of orbital polarization, taking as exemplar the 3d manifold of Co$^{2+}$ in a variety of spin, orbital and structural phases in the double perovskite La$_2$CoTiO$_6$ and the (001) superlattice (LaCoO$_3$)$_1$+(LaTiO$_3$)$_1$ systems. Superlattices are of specific interest due to the large experimentally observed orbital polarization of their Co cations. Based on first principles calculations, we find that robust and observable orbital polarization requires symmetry reduction through the lattice structure; the role of local electronic interactions is to greatly enhance the orbital polarization.

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I. Introduction

The intriguing electronic and magnetic properties of transition metal oxides (TMOs) are governed by the electronic states derived from their $d$ orbitals. The associated energy bands lie near the Fermi level, and the electronic and magnetic properties of TMOs are strongly dependent on the symmetry and degeneracy of the active $d$ orbitals. High-temperature superconductivity in cuprates [1, 2], phase transitions in manganites [3, 4], metal-insulator transitions in titanates, vanadates, and double perovskites [5, 6], and spin-state transitions in cobaltates [6] provide classic examples. The degree of broken orbital degeneracy and resulting differences in orbital populations, termed “orbital polarization”, is an important ingredient and the focus of this work.

Understanding the properties of TMOs is complicated because the spin, lattice, and orbital degrees of freedom are strongly coupled [3, 5]. Due to this coupling, physical properties of and phase transitions in TMOs derive from a combination of electron-electron ($e-e$), electron-lattice ($e-l$), electron-spin ($e-s$), and spin-spin ($s-s$) interactions. Orbital polarization can be induced by $e$-$e$ or $e$-$l$ coupling separately or by mixture of the two. Disentangling the $e$-$e$ and $e$-$l$ effects on the orbital properties in real materials is challenging, since both mechanisms result in orbital polarization/ordering and concomitant lattice distortions. In addition, there are many modes for $e$-$l$ coupling in TMOs such as local Jahn-Teller (JT) distortions or various oxygen octahedral tilts and rotations. Because of these complexities, the fundamental origin and systematic understanding of the conditions leading to strong orbital polarization in TMOs has not been elucidated to date.

Here, we focus on Co cations in TMOs as exemplar systems where strong orbital polarization can be engineered and observed. Co cations can have multiple spin states, and separately can have active (open-shell) $t_{2g}$ or $e_g$ orbitals depending on the spin and valence of the cations. Bulk LaCoO$_3$ (LCO) containing Co$^{3+}$ is well known for having multiple spin states: it is a low-spin (LS) state ($t^6_{2g}$, $S=0$) nonmagnetic insulator at low temperatures [5, 11], a paramagnetic insulator for temperatures between 100 and 500 K with either a high-spin (HS) state ($t^4_{2g}e^2_g$, $S=2$) [11, 12] or an intermediate spin (IS) state ($t^2_{2g}e^4_g$) [13, 14, 16], and is metallic above 500 K. However, the orbital polarization of both the HS and LS states of Co$^{3+}$ is zero in LaCoO$_3$ due to its high symmetry. Recently, we have found remarkably strong orbital polarization of Co$^{2+}$ in LaCoO$_3$+LaTiO$_3$ (LCO+LTO) superlattices [17]. Similar to Co$^{3+}$, Co$^{2+}$ has both HS ($t^2_{2g}e^4_g$) and LS ($t^4_{2g}e^2_g$) states. While the orbital polarization is mainly due to the minority spin $t_{2g}$ orbitals for the HS state, the polarization for the LS state is due to the majority spin $e_g$ bands: this provides a single system where multiple types of orbital polarization can be studied. We note that strong orbital polarization can also be engineered in nickelate superlattices in a similar fashion [18, 14].

In this work, we use first principles electronic structure calculations based on DFT+$U$ theory [20] to study these TMO systems. We elucidate the origin of orbital polarization in both $e_g$ and $t_{2g}$ manifolds and disentangle the role of $e$-$e$ and $e$-$l$ couplings.

II. Computational Details

We use density functional theory (DFT) with the projector augmented wave (PAW) method [21] and the revised version of the generalized gradient approximation (GGA) proposed by Perdew et al. (PBEsol) [22] as implemented in the VASP software [23]. In all cases, the spin-dependent version of the exchange correlation functional is employed. A plane wave basis with a kinetic energy cutoff of 500 eV is used. We study the (001) (LaCoO$_3$)$_1$+(LaTiO$_3$)$_1$ superlattice, denoted as LCO+LTO below. For the high symmetry structure with $a^0b^0c^0$ octahedral tilts (i.e., no oxygen octahedron tilts or rotations), corresponding to the $Fm\overline{3}m$ and $P4_1/mmm$. 

space groups, we used 10 atom unit cells (i.e., a (1×1) interfacial unit cell). We used 20 atom unit cells (i.e., c(2×2) interfacial unit cells) for the a−a−b+ tilt structure which has the P21/n space group. We used Γ-centered k-point meshes of size 9×9×9 (Fm̅3m) and 13×13×7 (Pn̅m/mnm) for the 10 atom cells, and 9×9×7 for the 20 atom cells. For more precise calculations of the energy differences listed in Table I, we used a kinetic energy cutoff of 700 eV and 17×17×17 k-point meshes. Atomic positions within the unit cells were relaxed until the residual forces were less than 0.01 eV/Å. For cases with reduced symmetry, the stress was relaxed only along the z axis to be below 0.02 k bare, while the in-plane lattice parameters a and b were set equal and took the values 3.811, 3.851, or 3.891 Å in order to simulate the realistic experimental situation where the superlattice is grown as an epitaxial thin film on a substrate. For the double perovskite La2CoTiO6, we used a face-centered cubic unit cell containing 10 atoms, and the lattice parameters correspond to 3.891 Å. We note that 3.891 Å is obtained from by minimizing all stresses with UCo = UCo = 3 eV.

The GGA+U scheme within the rotationally invariant formalism together with the fully localized limit double-counting formula 20 is used to study the effect of electron interactions. The electronic and structural properties critically depend on the UCo value used for the Co 3d manifold, and we explore a range of values. We also explore how the results depend on U/Ti, which plays a secondary but still important role in the physics of these materials. We do not employ an on-site exchange interaction J for any species, as the exchange interaction is already accounted for within the spin-dependent DFT exchange-correlation potential 24,25.

III. Orbital polarization of Co2+

A. LS and HS states: basics

We begin with a discussion of the basic electronic and magnetic properties of LCO+LTO superlattices which is summarized in our previous studies 17,26. In LCO+LTO superlattices as well as the double perovskite La2CoTiO6, there is a charge transfer from Ti3+(d6) to Co3+(d5), resulting in Ti4+(d5) and Co2+(d5). The role of electron transfer between Ti and Co has been discussed in prior work 17.

We now highlight some basic facts about the Co2+ spin states in the systems studied here. Since the electronic structure of Co2+ is strongly dependent on the crystal structure, in this subsection we will focus only on the P21/n phase of the superlattice, which is the most stable phase we have found 17,26.

The LS state (t2g6eg0) has S = 1/2 and is illustrated by Fig. 1(a): the t2g states are fully occupied, while the one remaining electron is in the eg channel. In the superlattice, the degeneracy of the eg manifold is already broken at UCo = 0 due to interface formation and epitaxial strain, with a lower energy dxz band and higher energy dxz−y2 band. When UCo ≥ 1.5 eV, the eg bands completely split in energy, resulting in an insulating phase: only the spin-up dxz is filled in the LS state while the spin-up dxz−y2 and spin-down eg bands are empty (see the supplementary materials for associated densities of states). As a result, the LS state has strong eg orbital polarization: we find that the polarization is nonzero at UCo = 0, and UCo > 0 simply enhances it.

The HS state (t2g6eg2) with S = 1 is depicted in Fig. 1(b): the spin-up d bands are fully occupied, while spin-down d bands have two electrons in the t2g channel. Unlike LS state, the HS state is not even metastable if UCo < 1 eV. When UCo = 1 eV, the t2g bands split into two nearly-degenerate bands (dxz and dyz) and a single dxy band (see the supplement for the relevant densities of states). We note that dxz and dyz are degenerate for the tetragonal phase (Pn̅m/mnm), but this degeneracy is broken in the monoclinic phase (P21/n). For 1.5 ≤ UCo < 2.5 eV, the dxy band is completely split in energy from the dxz/dyz bands. However, the spin-down dxy band is partially occupied and the spin-up dxz−y2 bands is partially empty, thus the system remains metallic. When UCo ≥ 2.5 eV, the spin-down dxy becomes empty, and the spin-up dxz−y2 band is fully occupied, resulting in an insulating phase (see the supplementary material for relevant densities of states).

B. Structural phases

The eg polarization of the LS state and the t2g polarization of the HS state can be due to e−e and/or e−l coupling. To disentangle the effect of these two interactions on the orbital polarization, we consider and compare several reference lattice structures as presented in Fig. 2 (a) We start with the ideal double perovskite La2CoTiO6, which has the Fm̅3m space group and no octahedral distortions (Fig. 2(a)) and where a = b = c and the atomic positions are frozen at ideal cubic perovskite coordinates. (b) Next, we have a (LaCoO3)1+(LaTiO3)1 superlattice ob-
tained by swapping half the Ti and Co in the ideal double perovskite to create a layered superlattice while keeping idealized atomic coordinates and lattice parameters (this has the $P4/nmm$ space group; see Fig. 2(b)). (c) Another $P4/nmm$ phase superlattice where only the atomic positions and the stress along the $c$ axis are relaxed (see Fig. 2(c)). (d) Finally, a $P2_1/n$ phase of the LCO+LTO superlattice which has the $a^-a^-b^+$ type of octahedral tilt and is the ground state of the superlattice. The $P2_1/n$ phase is monoclinic, but since we have assumed the epitaxial strain condition where $a = b \neq c$, this differs from a generic monoclinic structure where $a \neq b \neq c$.

**C. LS state: $e_g$ orbital polarization**

In this subsection, we focus on the low-spin (LS) state, which has $e_g$ orbital polarization. We define the orbital polarization of the LS state as

$$P(e_g) = \frac{(n_{z^2}^+ + n_{x^2}^-) - (n_{z^2}^- + n_{x^2}^+)}{(n_{z^2}^+ + n_{x^2}^-) + (n_{z^2}^- + n_{x^2}^+)}$$  \hspace{1cm} (1)$$

where the occupancy $n_i^\sigma$ is the electron population of orbital $i$ with spin $\sigma$ which is found on the diagonal elements of the single particle density matrix in the Co $3d$ manifold. Figs. 3(a)-(d) present the orbital polarization $P(e_g)$ for the four different structural phases in the LS state as a function of $U_{Co}$ and $U_{Ti}$.

We begin our analysis with the $Fm\bar{3}m$ space group La$_2$CoTiO$_6$ double perovskite structure (Figs. 2(a) and 3(a)). While $P$ for the $Fm\bar{3}m$ is zero for $U_{Co} \lesssim 1$ eV, it becomes significant for $U_{Co} \geq 2$ eV. This happens because of spontaneous electronic symmetry breaking: for large enough $U_{Co}$, the DFT+$U$ total energy is lowered by having the $e_g$ electron occupy one of the two $e_g$ orbitals more than the other. However, $P \neq 0$ for $Fm\bar{3}m$ does not necessarily indicate an actual nonzero orbital polarization in the true interacting system because a single-determinant DFT+$U$ description cannot capture the fluctuations between the $d_{z^2}^{-1}d_{x^2-y^2}^{1}$ and $d_{z^2}^{1}d_{x^2+y^2}^{1}$ configurations. But, the total energies of the two separate configurations should be well captured by DFT+$U$. Table

**FIG. 2:** Schematics of the atomic-scale structures of structures studied in this work. Each structure is labeled by its space group and octahedral rotation pattern. (a) ideal La$_2$CoTiO$_6$ double perovskite, (b) (c) and (d) shown one repeat of LCO+LTO (001) superlattices where the (001) direction is vertical. La atoms are not shown for clarity.

**FIG. 3:** (a)-(d) show the orbital polarization $P(e_g)$ of the LS state structures with different space groups versus $U_{Co}$ and as a function of $U_{Ti}$). Empty and filled points indicate metallic and insulating phases, respectively. Insets show schematic side views of the octahedral tilts and distortions of the CoO$_6$ and TiO$_6$ oxygen octahedra. (e) and (f) present Co–O bond lengths along the $c$ axis of the $P4/nmm$ and $P2_1/n$ phases, respectively. Dashed lines represent in-plane Co–O bond lengths which depend weakly on $U$. 

\[ \text{La}_2\text{CoTiO}_6 \]
TABLE I: Energy difference (in meV/Co) between different Co configurations in the same structure with \( U_{\text{T1}} = 3 \text{ eV} \) and \( U_{\text{Co}} = 5 \text{ eV} \). The configurations are written assuming majority up spin electrons, and only the occupancy of the orbitals of interest are shown. E.g., for the LS \( e_g \) case, the full configuration corresponding to the nomenclature \( d_{x^2-y^2} \) is \( d_{x^2-y^2}^1 d_{z^2}^1 \). For \( Fm\overline{3}m \), \( d_{2y_z}^1(d_{x^2-1y^2}/d_{y_\perp})^1 \) means that either the \( d_{x^2-1} \) or \( d_{y_\perp} \) is filled for all Co cations. For \( P4/mmm \), \( d_{1y_z}(d_{x^2-1}/d_{y_\perp})^1 \) means checkerboard orbital ordering and alternating \( d_{x^2-1} \) and \( d_{y_\perp} \) Co occupations.

| Structure | \( e_g \) | HS \( t_{2g} \) |
|-----------|-------|------|
| \( Fm\overline{3}m \) | \( d_{x^2-1} \) | \( d_{1y_z} \) |
| \( a = b = c \) | \(-30\) | \(0\) |
| \( P4/mmm \) | \( d_{1y_z} \) | \(0\) |
| \( a = b \neq c \) | \(21\) | \(150\) |

\( e_g \) shows that these two configurations are essentially degenerate in energy for \( Fm\overline{3}m \) (a fully converged DFT+U calculation should find them exactly degenerate): the degeneracy means that we should expect fluctuations and zero mean orbital polarization in a beyond band theory description of this system.

Next, we consider the \( P4/mmm \) superlattice with \( a = b = c \) (Figs. 2(b) and 3(b)). In this phase, the nearest neighbor environment of each Co is still perfectly cubic just as for the \( Fm\overline{3}m \) phase, but the global cubic symmetry is broken by the formation of the superlattice along \( (001) \). Therefore, the two \( e_g \) bands are no longer degenerate even at \( U_{\text{Co}} = 0 \) (see the supplementary material for relevant densities of states). Clearly, \( U_{\text{Co}} \neq 0 \) is not a necessary condition to split the \( e_g \) degeneracy: as expected, symmetry reduction by forming a superlattice is enough, but \( U_{\text{Co}} > 0 \) enhances the magnitude of \( P \) greatly. The orbital polarization is small but negative for \( U_{\text{Co}} \leq 1 \text{ eV} \) but becomes substantially negative once \( U_{\text{Co}} \geq 2 \text{ eV} \) (i.e., \( d_{x^2-1y^2} \) is more occupied than \( d_{z^2} \)). Table 1 shows that the \( d_{1y_z} \) configuration is lower in energy than \( d_{z^2} \) by 30 meV/Co when \( U_{\text{Co}} = 5 \text{ eV} \): the orbital polarization should survive fluctuations and exist in the interacting realization. We note that for this system, \( P(e_g) < 0 \) for all \( U_{\text{Co}} \) considered.

We now move to the \( P4/mmm \) phase with \( a = b \neq c \) (Figs. 2(c) and 3(c)). In this structure, the Co ions experience a tetragonal environment due to the relaxation. Similar to the previous \( P4/mmm \) \( a = b = c \) case, the \( e_g \) degeneracy is broken even at \( U_{\text{Co}} = 0 \), and the polarization magnitude is enhanced by \( U_{\text{Co}} > 0 \). Most notably, the \( P \) for the \( P4/mmm \) \( a = b \neq c \) phase can be negative or positive depending on the choices of \( U_{\text{Co}} \) and \( U_{\text{T1}} \) values (see Fig. 3(c)). While it is clear that \( U_{\text{Co}} \) changes the splitting of Co 3d bands and also the magnitude of \( P \), it is particularly interesting that \( P \) also depends strongly on \( U_{\text{T1}} \) (compare the three \( U_{\text{Co}} = 5 \) eV results in Fig. 3(c)). Since LCO+LTO is a charge-transfer heterostructure, \( U_{\text{T1}} \) determines the amount of electron transfer from Ti to Co by adjusting the energy of the Ti 3d orbitals. Specifically, larger \( U_{\text{T1}} \) results in the higher energy 3d states and thus a larger amount of electron transfer to Co. Larger transfer induces stronger local electric fields from the TiO\(_2\) to CoO\(_2\) layers, and the field pushes the oxygen anions and increases out-of-plane Co–O bond lengths. The relation between the apical Co–O bond length and \( P \) is explained by simple crystal field theory. Long-out-of-plane Co–O bonds result the lowering of the energy of the out-of-plane orbital \( (d_{z^2}) \) since \( O \) is farther from Co along the \( c \) axis, and thus \( d_{z^2} \) becomes more occupied and \( P > 0 \). Conversely, shorter out-of-plane Co–O bonds increase the energy of the \( d_{z^2} \) band, so \( d_{x^2-1y^2} \) becomes more occupied and \( P < 0 \). We find that when \( P < 0 \), the Co \( d \) bands are always metallic. On the other hand, when \( P > 0 \) and large enough, the two \( e_g \) bands are completely split in energy, and the system is in the insulating regime.

Finally, we consider the \( P2_1/n \) phase which is our most stable structural phase. Similar to the \( P4/mmm \) \( a = b = c \) and \( P4/mmm \) \( a = b \neq c \) phases, \( P \neq 0 \) at \( U_{\text{Co}} = 0 \) and increases as a function of \( U_{\text{Co}} \). As shown in Fig. 3(d), the \( P \) of the \( P2_1/n \) phase is always positive, as per our previous work [26]. The \( d_{z^2} \) band is significantly lower in energy when \( U_{\text{Co}} = 0 \) and the material is insulating due to the energy splitting in the \( e_g \) manifold (see the supplementary material for plots of the densities of states).

The sign of the orbital polarization \( P \) is one of the interesting features of our results. Since \( P \) can be both positive and negative for the \( P4/mmm \) \( a = b \neq c \) phase, it is clear that the sign of \( P \) is not due to the space group symmetry reduction alone. Indeed, it is strongly determined by the local octahedral distortions, i.e., the relative in-plane and out-of-plane Co–O bond lengths. In the superlattice, the out-of-plane Co–O bond is well elongated by the local electric field between Co and Ti ions [26]. Since the Co has interfaces at both sides and thus both of its out-of-plane Co–O bonds are elongated, the octahedral distortion of CoO\(_6\) in \((\text{LCO})_1+(\text{LTO})_1\) has standardized symmetry label \( A_1g + E_g \) [27]. If the in-plane Co–O bond is longer than out-of-plane Co–O bond, \( P \) becomes positive (Figs. 3(c) and (f)). If the out-of-plane Co–O bond is longer than in-of-plane Co–O bond, \( P \) becomes negative (Fig. 3(c)).

D. \( e_g \) orbital polarization: strain dependence

Now we discuss the effect of the strain on the \( e_g \) orbital polarization for the LS phase. Since the sign and the magnitude of \( P(e_g) \) depend on the relative sizes of the in-plane and out-of-plane Co–O bonds, strain can enhance, reduce, or change the sign of \( P \), since the Co–O bond lengths can be strongly altered by the epitaxial strain. We consider the \( P4/mmm \) \( a = b \neq c \) phase with in-
pressive strain, apical Co–O bonds are always longer than the in-plane lattice parameters. Empty and filled points indicate metallic and insulating phases, respectively. (b), (d) out-of-plane Co–O bond lengths with different in-plane lattice parameters. Dashed lines represent the in-plane Co–O bond lengths, which weak functions of $U$.

plane lattice parameters of $a = 3.811$ and 3.851 Å and the results are summarized in Fig. 4 (the data for $a = 3.891$ Å is in Figs. (c) and (e)).

For $a = 3.811$ Å, where the CoO$_6$ octahedra feel compressive strain, apical Co–O bonds are always longer than the in-plane Co–O bonds. Thus, the $d_{x^2-y^2}$ band is always lower in energy than the $d_{x^2-y^2}$ band, and $P > 0$ as per simple crystal field theory. In addition, $U_{Co} > 0$ further increases the splitting between the $e_g$ bands; as a result, both apical Co–O bond lengths and $P$ are monotonically increasing functions of $U_{Co}$.

For $a = 3.851$ Å, which represents weaker compressive strain, the apical bonds are elongated but not always longer than the in-plane bonds. Therefore, similar to the $a = 3.891$ Å case, the sign of $P$ depends on both $U_{Co}$ and $U_{Ti}$. The biggest difference between $a = 3.851$ and 3.891 Å is evident for the $(U_{Co} = 5, U_{Ti} = 0)$ case: $P > 0$ for $a = 3.851$ Å but $P < 0$ for $a = 3.891$ Å.

E. HS state: $t_{2g}$ orbital polarization

We consider three structures: (i) $Fm3m$ space group and $a^0a^0a^0$ tilt, (ii) $P4/mmm$ with $a = b = c$, (iii) and $P4/mmm$ with $a = b \neq c$. We do not examine the $P2_1/n$ case: the local $t_{2g}$ states on each Co become mixed due to the octahedral tilts, and the off-diagonal elements of the density matrix in the $t_{2g}$ manifold become large and non-negligible: this makes unambiguous extraction of individual orbital occupancies difficult.

Fig. 5(a) shows that $P$ for the highest symmetry $Fm3m$ structure is generally non-zero for even modest $U_{Co}$ values: this means that the $t_{2g}$ subsystem has a stronger propensity to spontaneously break electronic symmetry at the DFT+$U$ level when compared to the $e_g$ system above. We believe this is due to the narrower $t_{2g}$ energy bands and the more localized electronic states on the Co cations. However, the total energies of the three equivalent configurations $d_{xy}^1d_{xz}^1d_{yz}^0$, $d_{xy}^1d_{xz}^0d_{yz}^1$, and $d_{xy}^0d_{xz}^1d_{yz}^1$ differ by only 0.1 meV/Co (see Table II). Again, this indicates that the actual interacting $Fm3m$ system will probably have significant fluctuations between these configurations and zero mean orbital polarization.

Next, in both $P4/mmm$ phases, we expect the orbital polarization predicted in Figs. 5(b,c) to be observable because, as Table II shows, the $d_{xy}^0d_{xz}^1d_{yz}^1$ configuration has significantly lower energy than the other competing configurations (which are the orbitally ordered $d_{xy}^1d_{xz}^1d_{yz}^0$ and $d_{xy}^1d_{xz}^0d_{yz}^1$ systems).

Permitting the local octahedra to elongate in going from the $P4/mmm$ $a = b = c$ to the $a = b \neq c$ phase...
and in some sense crude: it breaks symmetry in both the $e_g$ and $t_{2g}$ systems. This goes hand in hand with the structure of the system: Fig. 5(d) shows that the HS $t_{2g}$ system has longer out-of-plane Co–O bonds than the $e_g$ LS case, and its out-of-plane bonds are always longer than the in-plane bonds.

### IV. Summary

In this work, we have shown that orbital polarization in the cobaltate systems we have studied has its fundamental origin in the structure and symmetry of the material (the crystalline environment of the Co cations); strong electronic interactions can enhance the polarization but are not necessary to generate it. The crystalline symmetry reduction in our cases is oxygen octahedral elongation which then breaks the electronic symmetry in the Co $e_g$ and $t_{2g}$ manifolds.

We note that this symmetry breaking mode is simple and in some sense crude: it breaks symmetry in both the $e_g$ and $t_{2g}$ and is unable to selectively do so in one or the other manifold. In principle, we can envision symmetry breaking operations that selectively remove degeneracy in only one manifold, but they require control over the electronic potential in a fine-grained microscopic manner that goes beyond simply distorting cation-oxygen bonds. Whether such an advanced level of control is feasible in actual materials is, in our mind, an interesting open question.

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