Interplay of octahedral rotations and breathing distortions in charge ordering perovskite oxides

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(Dated: February 6, 2014)

We investigate the structure–property relationships in $ABO_3$ perovskites exhibiting octahedral rotations and cooperative octahedral breathing distortions (CBD) using group theoretical methods. Rotations of octahedra are ubiquitous in the perovskite family, while the appearance of breathing distortions – oxygen displacement patterns that lead to approximately uniform dilation and contraction of the $BO_6$ octahedra – are rarer in compositions with a single, chemically unique $B$-site. The presence of a CBD relies on electronic instabilities of the $B$-site cations, either orbital degeneracies or valence fluctuations, and often appear concomitant with charge order metal–insulator transitions or $B$-site cation ordering. We enumerate the structural variants obtained from rotational and breathing lattice modes and formulate a general Landau functional describing their interaction. We use this information and combine it with statistical correlation techniques to evaluate the role of atomic scale distortions on the critical temperatures in representative charge ordering nickelate and bismuthate perovskites. Our results provide microscopic insights into the underlying structure–property interactions across electronic and magnetic phase boundaries, suggesting plausible routes to tailor the behavior of functional oxides by design.

PACS numbers: 61.50.Ks, 31.15.xh, 71.30.+h

I. INTRODUCTION

Perovskite oxides with chemical formula $ABO_3$ and $B$-site transition metal (TM) cations exhibit a range of functional electronic transitions that are intimately tied to the structure of the fundamental building blocks: (i) the number of unique $B$–$O$ bonds within an octahedron, and (ii) the tilting of corner-connected octahedra. Adjacent $BO_6$ units typically fill space in perovskites through nearly rigid rotations, which produce deviations of the $B$–$O$ bond angles away from the ideal 180$^\circ$ found in the cubic aristotype ($Pm\bar{3}m$ symmetry); the rotations are described by two three-dimensional irreducible representations (irreps), $M^e_{3t}$ and $R^e_{1u}$, of the high-symmetry structure. Combinations of these lattice instabilities – cooperative bond length distortions and octahedral rotations – interact across structural phase transitions through elastic stresses and symmetry allowed coupling invariants as described within Landau theory.

Beside changes to crystal symmetry, the transition from high temperature (high symmetry) to low temperature (low-symmetry) can also produce electronic metal–insulator (MI) transitions. Perovskite oxides with $B$-site cations in $t^3_g e^1_g$ ($d^4$), $t^0_g e^1_g$ ($d^5$) and $t^0_g e^3_g$ ($d^8$) electronic configurations are particularly susceptible, because the low-energy electronic structure is dictated by the octahedral crystal-field split antibonding $e_g$ orbitals—the atomic-like $d$-states that are spatially directed at the coordinating oxygen ligands. MI-transitions which occur simultaneously with lattice distortions are common in low-dimensional materials, e.g. Peierls systems. In three-dimensional perovskite oxides, however, the most familiar electronic transitions with concomitant changes in the $B$–$O$ bond lengths and octahedral rotations result from cooperative first-order Jahn-Teller effects: Tetragonal elongations of the $BO_6$ octahedra occur to remedy the orbital degeneracies that localized electrons encounter for particular $B$-site cation configurations. And through these distortions, the crystal maintains a uniform TM valence among all $B$-sites across the transition. The Jahn-Teller distortions are described by irreps $\Gamma^e_4$, $M^e_{5t}$ and $R^e_{3u}$, and their interaction with octahedral rotations are well-established.

Unusually high-valence states or $e^1_g$ electrons in delocalized band states will also produce structural distortions, but in most cases will preserve the uniformity of the $B$–$O$ bonds and the octahedral crystal field of the $BO_6$ units in the process. The $B$ cations will readily adopt mixed valence configurations, e.g. doped perovskites manganites ($\text{Mn}^{3+} + \text{Mn}^{4+}$) and also stoichiometric nickelates ($\text{Ni}^{3+}$) and ferrates ($\text{Fe}^{4+}$). The TM cation will not maintain an integer valence state ($n$) uniformly on all $B$-sites, but rather charge disproportionation (CDP); the simplest case being into two sites as

$$2B^{n+} = B^{(n-\delta)+} + B^{(n+\delta)+},$$

where $\delta$ is a fraction of an electron transferred between $B$-sites. Electronic correlation and on-site Coulomb repulsion effects will prefer to order the valence deviations $\delta$ so that the inequivalent lattice sites, 1 and 2, form a periodic arrangement, changing the translational symmetry. This so-called charge ordering (CO) lowers the potential energy of the crystal and gaps the Fermi surface.

The electronic charge ordering is distinguishable by an associated structural change in the local $BO_6$ building blocks (Figure 1). It appears as a $B$–$O$ bond disproportionation or “breathing distortion,” which causes the octahedra to either dilate (site 1) or contract (site 2) according to the charge $\delta$ transferred between sites, largely
We provide a list of symmetries that perovskite oxides with statistical analysis makes it possible to understand with charge order tendencies and octahedral rotations oxides. The complex interplay pervasive in mixed-metal perovskite a synergistic combination of group-theoretical analysis metal–insulator transitions. Finally, we show that electronic plays in directing the macroscopic atomic structure and bismuthate perovskites. This rigorous mapping of contributions of octahedral breathing distortions and ro-tations across phase boundaries in prototypical nickelate the unit-cell level structural distortions into a symmetry- adaptations of the two cooperative structural breathing distortions that coexists with charge ordering in $ABO_3$ perovskites. In (a) the breathing distortion is two-dimensional, irrep $M_1^{\perp}$, and produces a columnar ordering of the two $B$ cations reducing the symmetry to $P4/mmm$. In (b) a three-dimensional ordering produces a checkerboard arrangement of the $B$ cations and is described by the $R_1^{\perp}$ irrep ($Fm\overline{3}m$ symmetry).

II. COOPERATIVE BREATHING DISTORTIONS

The octahedral breathing distortions, which create two unique crystallographic $B$-sites, must tile in three-dimensions to maintain the corner-connectivity of the $BO_6$ framework—the defining feature of the perovskite crystal structure. Here we consider $B$–O distortions with wavevectors commensurate with the $Pm\overline{3}m$ lattice periodicity, i.e., those modes which occur on the edges and corner of the simple cubic Brillouin zone. The two main cooperative breathing distortions (CBD) are illustrated in Figure 2. Note that the irreps, which we describe next, are defined using the $Pm\overline{3}m$ setting of the $ABO_3$ perovskite with the $B$ cation located at the origin.

The first type of CBD consists of two $BO_6$ building blocks which are tiled to form a columnar arrangement of dilated and contracted octahedra [Fig. 2(a)], that splits the $B$–O bond lengths into a doublet and quartet. This distortion is associated with the active three-dimensional irrep $M_1^{\perp}$ with order parameter $(a, 0, 0)$ and manifests as a zone edge $k = (\frac{1}{4}, \frac{1}{4}, 0)$ lattice instability of the cubic phase. The order parameter (OP) describes a vector in the irrep space and corresponds to specific directions along which the physical distortion may be induced. For the $M_1^{\perp}$ irrep, the OP can have three general components $(a, b, c)$, where the values $a$, $b$ and $c$ correspond to amplitudes of the two-dimensional breathing distortion along each Cartesian direction $x$, $y$ and $z$, respectively. Here we consider only the case where $b = c = 0$, i.e. a restricted one-dimensional space. The possible directions for the OP correspond to $(a, 0, 0)$, $(0, a, 0)$ and $(0, 0, a)$ or columnar arrangements of the CBD along the $x$-, $y$- and $z$-directions, respectively, so that the octahedra distort in the same sense along the given direction. As a result, the symmetry is reduced to tetragonal, $P4/mmm$ (space group no. 123), and the $B$-site Wyckoff position of the cubic aristotype is split as $1a \rightarrow 1a + 1c$, doubling the number of perovskite.

![FIG. 1.](image1.png)  
**FIG. 1.** (Color online.) Illustration of the effect of charge disproportionation (CDP) on the local $BO_6$ octahedral site equivalence. Before the CDP transition all octahedra are equivalent (left); afterwards the $BO_6$ octahedron dispropor-tionate into non-equivalent sites with the simplest two-site case shown here: charge transfer between $B$-sites causes one octahedron to dilate (site 1) and the other octahedron to contract (site 2), resembling a “breathing” mode of the $BO_6$ perovskite building blocks.

![FIG. 2.](image2.png)  
**FIG. 2.** (Color online.) Schematic octahedral representations of the two cooperative structural breathing distortions that coexists with charge ordering in $ABO_3$ perovskites. In (a) the breathing distortion is two-dimensional, irrep $M_1^{\perp}$, and produces a columnar ordering of the two $B$ cations reducing the symmetry to $P4/mmm$. In (b) a three-dimensional ordering produces a checkerboard arrangement of the $B$ cations and is described by the $R_1^{\perp}$ irrep ($Fm\overline{3}m$ symmetry).
TABLE I. Crystallographic data including the occupied Wyckoff positions (Wyck. Site) for the cooperative breathing distortions (CBD) available to $ABO_3$ perovskites (Figure 2) in the absence of $BO_6$ rotations. Atom positions are given relative to the ideal cubic symmetry such that the relevant CBD imposed on the oxygen positions is indicated by $\Delta$. The value of $\Delta$ controls the amplitude of the $B$–$O$ contraction (elongation) and typically scales with the amount of inter-site charge transfer ($\delta$). The change in cell size is given relative to the pseudo-cubic (pc) lattice constant $a_{pc}$.

| Atom | Wyck. Site | $x$ | $y$ | $z$ |
|------|------------|-----|-----|-----|
| $A$  | 2$c$       | 0   | $\frac{1}{2}$ | $\frac{1}{2}$ |
| $B(1)$ | 1$a$      | 0   | 0   | 0   |
| $B(2)$ | 1$c$      | $\frac{1}{2}$ | $\frac{1}{2}$ | 0   |
| $O(1)$ | 4$j$      | $\frac{1}{4} + \Delta$ | $\frac{1}{4} + \Delta$ | 0   |
| $O(2)$ | 1$b$      | 0   | 0   | $\frac{1}{2}$ |
| $O(3)$ | 1$d$      | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ |

$R_1^+(a, 0, 0)$  \quad $a = b \sim \sqrt{2}a_{pc}, c \sim a_{pc}$

| Atom | Wyck. Site | $x$ | $y$ | $z$ |
|------|------------|-----|-----|-----|
| $A$  | 8$c$       | $\frac{1}{3}$ | $\frac{1}{3}$ | $\frac{1}{3}$ |
| $B(1)$ | 4$a$      | 0   | 0   | 0   |
| $B(1)$ | 4$b$      | $\frac{1}{3}$ | $\frac{1}{3}$ | $\frac{1}{3}$ |
| $O$  | 24$c$     | $\frac{1}{4} + \Delta$ | 0   | 0   |

III. OCTAHEDRAL ROTATION AND CBD SPACE GROUPS

A. Methodology

To enumerate the allowed combinations of CBD and octahedral rotations in perovskite oxides we use the group theoretical program ISOTROPY. We follow the approach of Stokes et al. and consider the changes in lattice symmetry due to the superposition of each CBD pattern (Figure 2) with the 15 octahedral rotation systems derived from the $M_1^+$ and $R_1^+$ three-dimensional irreps describing rotations. The advantage of this approach is that group-subgroup relationships can be established between structural variants, enabling the understanding of the structural and electronic CO transitions within a first- or second-order theory. It should be noted that the analysis of charge order at a particular site in the crystal is effectively the same as analyzing the effects of cation order due to a order–disorder transition, because both valence and chemical species split a Wyckoff position identically. In the latter case, the irrep describes a “composition” mode and reflects the site occupancy.

In this work, we enumerate those mode combinations with well-defined cooperative breathing distortions that are most likely to be observed experimentally. Although the rock salt $B$ cation order has been studied previously in $ABO_3$ perovskites, the layered ordering of $B$ cations, i.e. irrep $M_1^+$, was examined only for the compositionally complex quadruple perovskite $A_4BB'O_6$ oxides. Here, we report the results of the $M_1^+$ irrep on simple $ABO_3$ perovskites in the context of the CBD behavior, where cell-doubling occurs. Specifically for the $M_1^+$ irrep, we retain only those structures with an OP ($a, 0, 0$) such that the second and third vector components are zero, unless an octahedral rotation permits it to be non-zero by symmetry. Furthermore, we follow the convention introduced in Ref. 2 and 21 and only keep structures with coherent rotations—those with a fixed “sense” about each axis. We remove structure variants from our analysis which would allow for a modulation in the amplitude and sense of the rotations about a single axis.

B. Space Groups

We enumerate the space groups (Table II) and associated octahedral tilt pattern, irreps, lattice vectors, and origin allowed by group theory. We follow Glazer’s established notation to denote the magnitude and phase of octahedral tilt patterns in perovskites: The description of octahedral rotations are encoded using the syntax $a^#b^#c^#$, where letters $a$, $b$, and $c$ indicate rotations of $BO_6$ units of equal or unequal magnitude about Cartesian $x$-, $y$-, and $z$-axes. Note that in the case of equal magnitude rotations about different axes, the equivalent letter is duplicated, e.g., $a^#a^#a^#$. The superscript # can take three values: 0, +, or −, for no rotations, in-phase rotations (neighboring octahedra along a Cartesian axis rotate in the same direction), or out-of-phase rotations (adjacent octahedra rotate in the opposite direction), respectively.

Table II provides the possible space group symmetries compatible with CBD and octahedral rotations. The structural data is divided into three main blocks: The first section contains the space group symmetries in the absence of CBD; the second section enumerates the sym-
TABLE II. Possible crystallographic space groups, octahedral rotation patterns and unit cell relationships for \(ABO_3\) perovskites exhibiting rotations of octahedra given by irreps \(M^+_{ij}\) and \(R^+_{ij}\) with order parameter directions given in parentheses \((\eta_1, \eta_2, \eta_3)\) with the CBD \(M^+_{ij}\) or \(R^+_{ij}\). The lattice vectors and origin shifts are given with respect to the high symmetry 5-atom \(Pm3m\) structure (B cation at the origin).

| space group | tilt pattern | \(M^+_{ij}\) | \(R^+_{ij}\) | lattice vectors | origin |
|-------------|--------------|--------------|--------------|----------------|--------|
| 221 \(Pm3m\) | \(a^0a^0a^0\) | \((0,0,0)\) | \((0,0,0)\) | \((1,0,0), (0,1,0), (0,0,1)\) | \((0,0,0)\) |
| 127 \(P4/mmb\) | \(a^0a^0c^+\) | \((a,0,0)\) | \((0,0,0)\) | \((1,1,0), (1,1,0), (0,0,1)\) | \((0,0,0)\) |
| 139 \(I4/mmm\) | \(a^0b^+b^+\) | \((0,0,0)\) | \((0,0,0)\) | \((0,0,2), (0,0,2), (2,0,0)\) | \((\frac{1}{2}\frac{1}{2}\frac{1}{2})\) |
| 204 \(Im3\) | \(a^+a^+a^+\) | \((a,a,a)\) | \((0,0,0)\) | \((2,0,0), (2,0,0), (0,0,2)\) | \((\frac{1}{2}\frac{1}{2}\frac{1}{2})\) |
| 71 \(Imm\) | \(a^0c^+c^-\) | \((0,a,c)\) | \((0,0,0)\) | \((2,0,0), (0,2,0), (0,0,2)\) | \((\frac{1}{2}\frac{1}{2}\frac{1}{2})\) |
| 140 \(I4/mcm\) | \(a^0c^+c^-\) | \((0,0,a)\) | \((0,0,0)\) | \((1,1,0), (1,1,0), (0,0,2)\) | \((0,0,0)\) |
| 74 \(Imma\) | \(a^0b^-b^-\) | \((0,a,c)\) | \((0,0,0)\) | \((0,1,1), (2,0,0), (0,1,1)\) | \((0,0,0)\) |
| 167 \(R\) | \(a^-a^-a^-\) | \((0,0,a)\) | \((0,0,0)\) | \((1,1,0), (0,1,1), (2,2,2)\) | \((0,0,0)\) |
| 12 \(C2/c\) | \(a^+b^-b^-\) | \((0,0,0)\) | \((0,0,0)\) | \((2,0,0), (0,2,0), (0,1,1)\) | \((\frac{1}{2}\frac{1}{2}\frac{1}{2})\) |
| 2 \(I\) | \(a^-b^-c^-\) | \((0,0,0)\) | \((0,0,0)\) | \((2,1,1), (0,1,1), (0,1,1)\) | \((\frac{1}{2}\frac{1}{2}\frac{1}{2})\) |
| 63 \(Cmcm\) | \(a^0b^0c^-\) | \((0,0,a)\) | \((0,0,0)\) | \((2,0,0), (0,2,0), (0,2,0)\) | \((\frac{1}{2}\frac{1}{2}\frac{1}{2})\) |
| 62 \(Pmcm\) | \(a^0b^-b^-\) | \((0,a,0)\) | \((0,0,0)\) | \((0,1,1), (2,0,0), (0,1,1)\) | \((0,0,0)\) |
| 11 \(P2_1/c\) | \(a^0b^-b^-\) | \((0,a,0)\) | \((0,0,0)\) | \((0,1,1), (2,0,0), (0,1,1)\) | \((0,0,0)\) |
| 137 \(P4_2/mnc\) | \(a^0a^0c^-\) | \((0,a,a)\) | \((0,0,0)\) | \((2,0,0), (0,2,0), (0,0,2)\) | \((0,0,0)\) |
| 127 \(P4/mmb\) | \(a^0b^+b^+\) | \((a,0,0)\) | \((0,0,0)\) | \((1,1,0), (1,1,0), (0,0,1)\) | \((0,0,0)\) |
| 83 \(P4/m\) | \(a^0b^0c^-\) | \((a,0,0)\) | \((0,0,0)\) | \((1,1,0), (1,1,0), (0,0,1)\) | \((0,0,0)\) |
| 74 \(Imma\) | \(a^+a^+a^+\) | \((0,0,0)\) | \((0,0,0)\) | \((0,0,2), (0,0,2), (2,0,0)\) | \((0,0,0)\) |
| 69 \(Fmmm\) | \(a^+c^+c^+\) | \((0,0,0)\) | \((0,0,0)\) | \((2,0,0), (2,0,0), (1,1,1)\) | \((\frac{1}{2}\frac{1}{2}\frac{1}{2})\) |
| 12 \(C2/m\) | \(a^+b^0c^+\) | \((0,0,0)\) | \((0,0,0)\) | \((2,0,0), (0,2,0), (0,2,0)\) | \((\frac{1}{2}\frac{1}{2}\frac{1}{2})\) |
| 51 \(Pmna\) | \(a^-a^-a^-\) | \((0,0,0)\) | \((0,0,0)\) | \((0,0,2), (0,0,2), (2,0,0)\) | \((0,0,0)\) |
| 13 \(P2_1/c\) | \(a^-a^-c^-\) | \((0,0,0)\) | \((0,0,0)\) | \((0,0,2), (0,0,2), (2,0,0)\) | \((0,0,0)\) |
| 15 \(C2/c\) | \(a^0b^-c^-\) | \((0,0,0)\) | \((0,0,0)\) | \((2,0,0), (0,2,0), (0,2,0)\) | \((0,0,0)\) |
| 11 \(P2_1/m\) | \(a^-b^-c^-\) | \((0,0,0)\) | \((0,0,0)\) | \((2,0,0), (0,2,0), (0,2,0)\) | \((0,0,0)\) |
| 2 \(I\) | \(a^-b^-c^-\) | \((0,0,0)\) | \((0,0,0)\) | \((1,1,0), (0,2,0), (1,1,0)\) | \((0,0,0)\) |
| 52 \(Pmna\) | \(a^0b^-c^-\) | \((0,0,0)\) | \((0,0,0)\) | \((1,1,0), (0,2,0), (1,1,0)\) | \((0,0,0)\) |
| 62 \(Pmna\) | \(a^0b^-c^-\) | \((0,0,0)\) | \((0,0,0)\) | \((1,1,0), (0,2,0), (1,1,0)\) | \((0,0,0)\) |
| 11 \(P2_1/m\) | \(a^-b^-c^-\) | \((0,0,0)\) | \((0,0,0)\) | \((2,2,0), (2,2,0), (0,0,2)\) | \((0,0,0)\) |

\(a\) In the absence of octahedral rotations, the axes are unique due to the CBD.

\(b\) The CBD makes the z-direction unique.

\(c\) The \(b'\) denotes that this is a secondary distortion that is symmetry allowed. In this case in-phase rotations about the z-direction. The Glazer tilt is defined for the case \(b' = 0\).

\(d\) The \(R^+_{ij}\) mode acts along the body diagonal and does not create a unique axis in the crystal as in the case of the the three-dimensional \(M^+_{ij}\) irrep. Only the octahedral rotations lifts the axes equivalence.

metries that result from the planar CBD with octahedral rotations; and the third section includes those obtained from the three-dimensional CBD combined with rotations. Structures appearing in bold in Table II correspond to CBD without any octahedral rotations and are given first at the top of block two and three. Note that perovskites with rotations and the \(M^+_{ij}\) CBD, there may be more than one structure possible for a given rotation,
because the relative orientation of the tilt pattern with respect to the column arrangement of dilated and contracted octahedra alters the crystal symmetry differently.

Table II directly reveals the effect of the superposition of octahedral rotation patterns and the CBD on the crystal symmetry lowering. Consider the middle block \((M_1^+ \oplus M_2^+ \oplus R_1^+)\). The seemingly similar tilt patterns \(a^0a^0c^+\) and \(a^+a^0c^0\), depending on the crystallographic axes they act upon, yield two different space groups, \(P2/m\) and \(Imma\), respectively.

Furthermore, there are a number of space groups appearing in each of the blocks of Table II: \(C2/m\) appears both in the rotation only block (\(sans\) any CBD) and in the third block with the \(R_1^+\) CBD. Formally the crystallographic symmetries are identical in each case; however, physically the rotation patterns adopted by the crystals are different. For instance, when only rotations associated with irrep \(R_1^+\) and order parameter \((a, 0, b)\) are present in the crystal structure, space group \(C2/m\) allows the out-of-phase rotations about the \(y\)- and \(z\)-axes to be of different magnitude (tilting pattern is \(a^0b^−c^−\)). Now, consider the direct sum \(R_1^+ \oplus R_4^+\) for a vector space corresponding to the order parameter \((a, 0, 0, b, 0)\) that includes CBD. Even though the resulting space group is \(C2/m\), the corresponding octahedral tilt pattern changes to \(a^0b^−c^−\), where the out-of-phase rotations about the \(y\)- and \(z\)-axes are of the same magnitude. On the other hand, the direct sum \(M_1^+ \oplus R_4^+\) for a vector space corresponding to the order parameter \((a, 0, 0, b, c, 0)\) is found to preserve the \(a^0b^−c^−\) tilting pattern, but the overall symmetry reduces to \(C2/c\). Also note that, in the case of rotations without CBD, the tilt pattern \(a^0b^−c^−\) corresponds to the higher symmetry \(Imma\) space group. Such restrictions imposed on the rotation axes equivalence are described next, and for the reason previously described explains why “none” appears as an entry in Table III.

### C. Compatible CBD and Rotation Symmetries

In Table III, we aggregate the results of the change in space group symmetry due to the superposition of tilt patterns of \(M_1^+\) and \(R_1^+\) irreps with each of the 15 simple octahedral tilt systems. This information is schematically shown in Figure 3. Only one symmetry exists, \(P1\), where the breathing distortion is geometrically compatible with the symmetry of the perovskite structure with octahedral rotations alone \((a^−b^−c^−)\), meaning “no change” in unit cell or translational symmetry is required to accommodate the multiple distortions. Table III also reveals that the \(P2_1/m\) symmetry is compatible with two different octahedral rotation patterns and the \(M_1^+\) CBD: \(a^0b^−c^−\) and \(a^+b^−c^−\). While \(P1\) is compatible with both \(M_1^+\) and \(R_1^+\) irreps, \(P2_1/m\) only exists for the \(M_1^+\) irrep.

For entries containing “none,” the direct sums, \(R_1^+ \oplus M_1^+ \oplus M_2^+ \oplus R_1^+\) and \(M_1^+ \oplus M_2^+ \oplus R_1^+\), do not yield an isotropy subgroup. This is made clear by examining the \(a^−a^−a^−\) rotation pattern, which corresponds to an equal amplitude of out-of-phase rotations about each axis, or equivalently a single out-of-phase rotation about the three-fold axis. The trigonal symmetry is incompatible with a distortion that would require a loss of the three-fold axis and therefore need at a minimum a symmetry reduction to a lattice with tetragonal geometry. Thus, ‘none’ appears in the \(M_1^+\) column corresponding to the row with the \(a^−a^−a^−\) rotation pattern. Such incompatibility with the \(M_1^+\) CBD is alleviated if the rotation pattern about any two crystallographic axes are of different magnitudes, e.g., \(a^−b^−c^−\), yielding space group \(P2_1/c\) (Table III).

![Figure 3](image-url) (Color online.) Representation of the rotation patterns that are compatible with each (or both, given by the intersection of the) CBD without requiring a further symmetry reduction.
The superposition of the three-dimensional CBD $R^+_1$ and the rotation pattern gives a seven-dimensional order parameter space, i.e., $(\beta, \eta_+, 0, 0, 0, \eta_-, \eta_-)$, which we contract to an effective four-dimensional space to obtain the $P2_1/c$ space group (cf. Table II). Without assuming which transition occurs first—whether the rotations precede or follow the CBD—we construct a Landau free energy expansion about the cubic phase $(\beta = \eta_+ = \eta_- = 0)$ as

$$F(\beta, \eta_i) = \phi^2 + \phi^4 + C_1 \beta^2 \eta_+^2 + C_2 \beta^2 \eta_-^2 + D_3 \eta_+^2 \eta_-^2,$$

where $\phi^2$ and $\phi^4$ describe the homogeneous quadratic and quartic terms for each order parameter, and $C_i$ are the coefficients coupling the CBD to the in- or out-of-phase rotations, and $D_3$ describes the biquadratic coupling of the different $B0_i$ rotation “senses” in the $a^+b^-b^-$ tilt pattern. The group-subgroup relationships are depicted in Figure 4.

The rotations and the CBD couple biquadratically, which indicates that the interactions across the transitions could be either cooperative or antagonistic. It is possible that the particular rotations could suppress CO by eliminating the structural octahedral breathing distortion altogether through the interaction terms containing the $C_i$ coefficients. However, in most cases, the rotation amplitudes are weakly modified across the electronic CO transition, suggesting that the strength of the coupling $C_i$ is in general small. We explore this in the Section V through a statistical approach.

We also note that while the order of the coupling is important, the difference in temperature scales at which the rotation and charge ordering occurs is also important in determining how the structural order parameters influence each other. The strongest interaction occurs when the temperatures are similar, while if they are far apart, the two structural transitions will weakly couple.

### V. STRUCTURE–FUNCTIONALITY RELATIONSHIPS

In this section, we apply our group theory results to quantitatively explore the relationship between structure and physical properties of experimentally known rare-earth nickelate and bismuthate perovskites. There is significant interest in developing strategies – both experimentally and theoretically – to rationally control octahedral distortions through the interplay of chemical pressure, epitaxial strain engineering, and ultrathin superlattice heterostructure formation\cite{25–28} for property control. Although several octahedral distortion metrics, e.g., the crystallographic tolerance factor or bending of the $B–O–B$ bond angle,\cite{29,30} have played an important role in the understanding of the electronic and magnetic properties of perovskite oxides,\cite{31} they have had limited success in materials design of non-thermodynamic phases in thin film geometries. Knowledge of quantitative structure–property octahedral distortion relationships are required to accelerate materials discoveries.

Distortion-mode decomposition analysis is an alternative approach\cite{5,18,32} (widely practiced and followed in the crystallography literature) to study displacive\cite{33} phase transitions in perovskites. It involves describing a distorted (low-symmetry) structure as arising from a (high-symmetry) parent structure with one or more static symmetry-breaking structural distortions.\cite{32} In the undistorted parent structure, each symmetry breaking distortion-mode has zero amplitude. The low-symmetry phase, however, will have finite amplitudes for each irrep compatible with the symmetry breaking. Said another way, the low-symmetry phase is rigorously described through a series expansion of static symmetry breaking structural modes that “freeze” into the parent structure. Critically, the weights or amplitudes assigned to each irrep are obtained according to the contribution that each irrep is present and the requirement that linearity
is maintained.

What is of particular utility in formulating quantitative relationships connecting octahedral distortions, which are now described mathematically, to macroscopic properties for materials design is that each irrep carries a physical representation of the displacive distortions—the unique atomic coordinates describing various symmetry-adapted structural modes. The relative importance of these modes on properties may then be mapped by means of \textit{ab initio} computational methods.\textsuperscript{34} Accessibility to computational methods make the distortion-mode analysis powerful, because it is possible to independently study various distortions and directly assess their role in structural and electronic phase transition mechanisms. Furthermore, the distortion-mode analysis relies solely on crystal structural data, which enables both bulk and thin film stabilized structures with identical compositions to be evaluated on equal-footing. Such direct comparison is not possible through aggregate parameters such as the tolerance factor, \textit{i.e.} when the composition is fixed, or other metrics widely followed in the literature.

In the remainder of this section, we use the distortion-modes to form the basis for the quantitative description of octahedral distortions and CBD on material properties. Using bulk RNiO\textsubscript{3}, where \(R\) is a rare-earth element, and Ba\textsubscript{1-x}K\textsubscript{x}BiO\textsubscript{3} perovskite compounds as prototypical charge-ordering materials, we decompose available low-symmetry structural data into symmetry-adapted structural distortion modes. We then evaluate and correlate the amplitudes of the distortion-modes to macroscopic materials behavior to uncover trends linking octahedral distortions to the structural and physical properties. We use the group-theory program ISODISTORT\textsuperscript{18} for distortion-mode decomposition analysis and R\textsuperscript{35,36} for the statistical analysis. For readers interested in reproducing our work, we have deposited the raw data and the R-script in the supplementary materials section available at http://link.aps.org/supplemental/XYZ.

**A. RNiO\textsubscript{3} Nickelates**

Rare-earth perovskite nickelates, RNiO\textsubscript{3}, where \(R = \text{Y}, \text{Ho, Er, Dy, Lu, Pr, or Nd},\) exhibit non-trivial changes in structure and physical properties, including sharp first-order temperature-driven MI-transitions, unusual antiferromagnetic order in the ground state, and site- or bond-centered charge disproportionation.\textsuperscript{29,37,38} At the MIT temperature (\(T_{MI}\)), the crystal symmetry lowers from orthorhombic \(P\text{nma}\) to monoclinic \(P2_1/c\) symmetry\textsuperscript{19} (Figure 4), where the Ni cation no longer maintains a unique uniform valence on all sites, and disproportionates as

\[
\text{2Ni}^{3+} = \text{Ni}_{\text{site 1}}^{(3-\delta)+} + \text{Ni}_{\text{site 2}}^{(3+\delta)+}.
\]

Moreover, the insulating ground-state displays a complex antiferromagnetic order (Type-\(T'\)) below a Néel temperature (\(T_N\)). Several previous studies\textsuperscript{29,30,40–43} have suggested the likely existence of a complex interplay between octahedral rotations, transport, and magnetic properties. To extract deeper insight into these interrelationships, we (i) identify all active distortion modes in each composition, (ii) determine the individual amplitudes for each modes, and (iii) explore the statistical correlation between individual distortion-modes and the physical properties, specifically \(T_{MI}\) and \(T_N\).

1. **Structure Decomposition**

We follow the procedure outlined by Campbell \textit{et al.}\textsuperscript{18} to decompose the \(P2_1/c\) monoclinic crystal structure data, obtained from previously published diffraction studies,\textsuperscript{14–47} into the orthonormal symmetry-modes. Diffraction data for YNiO\textsubscript{3}, ErNiO\textsubscript{3}, LuNiO\textsubscript{3}, and HoNiO\textsubscript{3} were measured at 295 K; DyNiO\textsubscript{3} at 200 K; NdNiO\textsubscript{3} at 50 K; and finally, PrNiO\textsubscript{3} at 10 K. \(T_{MI}\) and \(T_N\) were obtained from the review article by Catalan.\textsuperscript{30}

The \(P2_1/c\) structure decomposes into eight algebraically independent symmetry-modes corresponding to the following irreps: \(R^+_1, R^+_2, R^+_3, R^+_5, X^+_5, M^+_2, M^+_3,\) and \(M^+_5\). The relative amplitudes for each of the distortions are given in Table IV, with the physical representation of each irrep and its consequence on the octahedral framework schematically illustrated in Figure 5.

The sequence of structures involved in the phase transition could be written as follows: \(P3m1\rightarrow P\text{nma}\rightarrow P2_1/c\). Five distortions participate in the \(P3m1\rightarrow P\text{nma}\) transition, namely \(R^+_1, R^+_2, X^+_5, M^+_2,\) and \(M^+_3\). Within Landau theory, the \(P\text{nma}\) structure results from the condensation of two zone-boundary phonons of different wavevectors: one at the \(R\)-point of the cubic Brillouin zone that transforms as the irrep \(R^+_1\), and the other at the \(M\)-point, which transforms as the irrep \(M^+_3\). Not surprising, the two most common octahedral distortion-modes that describe the \(a^+b^-b^-\) rotation pattern, \(R^+_1\) and \(M^+_3\), emerge

| TABLE IV. Summary of the amplitudes of each irrep (notation given with respect to the \(Pm\text{nma}\) parent space-group) in the \(P2_1/c\) structure (units in \(\text{Å}\)). Std. Err. = \(\sigma/N\), where \(\sigma\) is the standard deviation and \(N (=7)\) is the sample size, gives an estimate of the sampling error. The total distortion amplitude is given in the column indicated by \(\Sigma\). |
|---|---|---|---|---|---|---|---|
| RNiO\textsubscript{3} | \(R^+_1\) | \(R^+_2\) | \(R^+_3\) | \(X^+_5\) | \(M^+_2\) | \(M^+_3\) | \(M^+_5\) | \(\Sigma\) |
| HoNiO\textsubscript{3} | 1.499 | 0.195 | 0.826 | 0.048 | 1.153 | 0.172 | 0.024 | 0.025 | 2.081 |
| ErNiO\textsubscript{3} | 1.535 | 0.203 | 0.842 | 0.048 | 1.179 | 0.145 | 0.022 | 0.020 | 2.127 |
| LuNiO\textsubscript{3} | 1.648 | 0.248 | 0.907 | 0.063 | 1.229 | 0.153 | 0.004 | 0.016 | 2.268 |
| YNiO\textsubscript{3} | 1.502 | 0.196 | 0.835 | 0.055 | 1.161 | 0.128 | 0.011 | 0.072 | 2.089 |
| NdNiO\textsubscript{3} | 1.179 | 0.117 | 0.445 | 0.030 | 0.751 | 0.126 | 0.050 | 0.283 | 1.505 |
| PrNiO\textsubscript{3} | 1.093 | 0.063 | 0.362 | 0.004 | 0.690 | 0.091 | 0.012 | 0.000 | 1.347 |
| DyNiO\textsubscript{3} | 1.442 | 0.207 | 0.780 | 0.073 | 1.144 | 0.241 | 0.025 | 0.168 | 2.041 |

Std. Err. = 0.029 | 0.009 | 0.031 | 0.003 | 0.032 | 0.007 | 0.002 | 0.015
as the primary modes. A secondary mode with $X_5^+$ symmetry also appears with relatively high amplitude, and it contains A cation displacements. Such anti-parallel displacements of the A cations are established to be correlated with the amplitudes of the octahedral rotations in perovskites.\cite{note48}

In the symmetry lowering $Pnma\rightarrow P2_1/c$ structural phase transition, irrep $R_1^+$ with order parameter $(a)$ is the primary order parameter capturing the CDP behavior. The $R_1^+$ and $M_5^+$ are secondary distortions in the phase transition that accompany $R_1^+$. This is seen in Table IV, where the largest amplitude for modes not already present from the transition to $Pnma$ is almost always given by $R_1^+$. NdNiO$_3$ is found to be the exception to this rule and the origin of $Pnma\rightarrow P2_1/c$ phase transition in NdNiO$_3$ could be different compared to other bulk RNiO$_3$ compounds.

In the nickelate literature, generally NdNiO$_3$ is discussed in conjunction with PrNiO$_3$, because together they represent a unique case where $T_{MI}$ and $T_N$ coincide. In NdNiO$_3$, we find that the distortion amplitude for $M_5^+$ is twice that of $R_1^+$, indicating that irrep $M_5^+$ acts as the primary distortion mode instead of $R_1^+$. Indeed our group theoretical analysis shows that for the direct sum, $M_5^+ \oplus R_1^+ \oplus M_5^+$, whose tilt system correspond to the order parameter containing only three free parameters: $(a, 0, 0, b, c, 0, 0, c, 0, c, -c)$, the required space group is $P2_1/c$ monoclinic structure, an isotropy subgroup of $Pnma$, indicating that $M_5^+$ could be the pri-
mary distortion mode in the phase transition if it also provides the greatest energetic stability to the structure. The latter constraint requires evaluation of the lattice dynamics using a technique beyond group theory. Interestingly for the experimental bulk PrNiO$_3$ structure, irrep $M^+_2$ is found to have zero amplitude.

To summarize this discussion, we have introduced an alternative symmetry-mode description of the structural distortions in nickelates that identifies bulk NdNiO$_3$ compound as anomalous in the series. Combining temperature-dependent diffraction studies with mode decomposition analysis could provide key insights necessary to fully understand the evolution of the primary and secondary distortions with the thermodynamic origin of phase transition.

We now shift our attention to the weak secondary distortion modes, particularly to the observation of two types of Jahn-Teller distortions to the NiO$_6$ units, $M^+_2$ and $R^+_3$ (Figure 5). Although $M^+_2$ and $R^+_3$ are practically negligible and are the secondary distortion modes in the $Pm3m\rightarrow Pnma\rightarrow P2_1/c$ transition, their presence could still have significant implications on the physical properties. The motivation for critically analyzing secondary distortion modes in nickelates comes from the study of improper phase transitions,$^{19-51}$ e.g., where spontaneous electric polarization arises as a secondary effect accompanying complex non-polar distortions through anharmonic interactions$^{52-55}$ in improper ferroelectrics. Similarly, we are interested in exploring the role of secondary order parameters on the electronic properties of nickelates.

Experimental observations based on giant oxygen O$^{16}$, O$^{18}$ isotope effect$^{40}$ indicate the presence of dynamic Jahn-Teller polarons; however, the interpretation of orbital-ordering has lacked conclusive support from diffraction experiments.$^{30}$ More recently, ultra-thin films of nickelates are being increasingly investigated for rational control of orbital polarization.$^{56-58}$ The identification of a Jahn-Teller bond elongations and contractions from our symmetry analysis in the bulk compounds suggests the nickelates should have tendencies to orbital (ordering) polarizations. Misfit strain, superlattice formation, or symmetry mismatch at the thin film–substrate interface may be used to selectively enhance the contributions of Jahn-Teller modes, described by irreps $M^+_2$ and $R^+_3$, as recently proposed in Ref. 59. Alternatively, orbital-ordering could emerge in nickelates, e.g., LaNiO$_3$ where the Jahn-Teller modes are prohibited by symmetry in the bulk ground-state structure, through quantum confinement effects in the limits of ultra-thin films,$^{56,57}$ although in this case, strain-induced Jahn-Teller distortions would likely result in larger energetic penalties.

2. Statistical Analysis

We now evaluate the statistical correlation between the amplitude of the symmetry-adapted modes and the macroscopic $T_{MI}$, and $T_N$ transition temperatures. The physical motivation behind the statistical analysis is to uncover hidden associations between the cooperative atomic displacements and electronic/magnetic phase transitions. The goal is to quantitatively identify structure–functionality relationships that could be rigorously evaluated at the ab initio level.

We begin by constructing a dataset containing seven RNiO$_3$ nickelates, where each rare-earth nickelate in our set is described using eight distortion-modes, $T_{MI}$, and $T_N$, resulting in a $7 \times 10$ matrix. We scaled the data by subtracting the mean of each column from its corresponding columns (this process is also known as centering), and then divided the centered columns by their standard deviations. To evaluate the degree of linear relationship between the structural distortions, $T_{MI}$, and $T_N$, we calculate the sample covariance of the centered and scaled dataset as

$$\text{Cov}[X] = \frac{1}{n-1} \sum_{i=1}^{n} (\bar{x}_i)(\bar{x}_j),$$

where $n = 7$ is the total number of RNiO$_3$ compounds in our dataset; $\bar{x}_i$ and $\bar{x}_j$ are the centered and scaled column vectors of our data matrix $X$, respectively. Results from the covariance analysis are summarized as a correlation heat map in Figure 6.

A strong positive correlation is found between irreps that describe distortions to the NiO$_6$ octahedra: $M^+_2$ (a planar Jahn-Teller mode), $M^+_4$, $X^+_2$, $R^+_4$, and $R^+_5$ modes. Even though the distortion-modes are orthonormal by construction, when they are collectively evaluated for a series of RNiO$_3$ compounds, our analysis reveals that they (the modes describing the distortions) are statistically dependent and coupled. These modes largely describe bond angle distortions and are positively correlated with the electronic transition $T_{MI}$. The conventional route to describe variations in $T_{MI}$ primarily focus on tolerance factor and average $\langle \text{Ni–O–Ni} \rangle$ bond angle, whereby bending of the $\langle \text{Ni–O–Ni} \rangle$ angle further from the ideal case of $180^\circ$ decreases the bandwidth, promoting the insulating state over the metallic state.$^{23,30,60}$ While we recover this behavior, we also identify the unique displacement patterns that geometrically sum to give the aggregate bond angle: irreps $M^+_2$, $M^+_4$, $X^+_2$, $R^+_4$, and $R^+_5$ cooperatively act to bend the Ni–O–Ni angle. These five irreps fully describe the $Pnma$ crystal structure relative to the cubic phase found in the metallic nickelates at high-temperature, reinforcing the concept that the orthorhombic distortions are largely responsible for the bandwidth-controlled transport behavior in nickelates, and hence prepare the electronic system for the MIT.

Intriguingly, the $R^+_1$ CBD distortion, which is the usual signature for CO has only a moderate effect on $T_{MI}$, indicating that the dominant structural route to engineer the electronic transition may not be solely through isotropic bond length distortions. Moreover, anisotropic bond distortions obtained with the $a$-type $R^+_3$ Jahn-Teller mode or the $M^+_5$ tilting mode do not contribute significantly to $T_{MI}$. In fact, we find they are anti-correlated with the
electronic transition temperature (Figure 6). Our conclusion to this point is that the geometry (tilt pattern) of the oxygen framework structure is the important atomic scale feature governing the MI-transition.

We now shift our attention to the Type-E′ antiferromagnetic ordering. Unlike the transport behavior, where the (Ni–O–Ni) bond angle concept appears to be sufficient to explain its variability, the origin of antiferromagnetic ordering is much more complex. Previous high-resolution photoemission measurement and pressure dependent studies of $T_N$ have established the existence of two distinct regimes for RNiO$_3$ with $T_{MI} = T_N$ and $T_{MI} > T_N$, indicating that simple tolerance factor and (Ni–O–Ni) superexchange interaction arguments are insufficient. Lee et al. used two-band model and Hartree-Fock theory to classify nickelates with $T_{MI} = T_N$ as itinerant, whereas those with $T_{MI} > T_N$ show stronger electron correlation. Nonetheless, we are unaware of a unique descriptor available in the literature that captures all the variance in the $T_N$ ordering temperature.

Our analysis reveals the existence of a strong linear relationship between $T_N$ and two irreps, $R_3^+$ and $M_5^+$: the three dimensional Jahn-Teller mode, where in each NiO$_6$ octahedron four bonds contract and two elongate, and the in-phase tilting mode, respectively. The linear relationship is valid for both $T_{MI} = T_N$ and $T_{MI} > T_N$ nickelates (Figure 7), indicating that $R_3^+$ and $M_5^+$ irreps contain additional information that is not captured by either the conventional (Ni–O–Ni) angle or tolerance factor descriptors.

The $R_3^+$ distortion is more strongly correlated with $T_N$ than the $M_5^+$, indicating an underlying structural relationship between the long-range antiferromagnetic order and the local and subtle Jahn-Teller bond distortions. We also note that $R_3^+$ and $M_5^+$ irreps appear in the monoclinic $P2_1/c$ crystal structure and are not allowed by symmetry in the $Pnma$ orthorhombic space group. New insights gained thus far support the potential feasibility of tailoring an isosymmetric $P2_1/c \rightarrow P2_1/c$ phase transition driven by misfit strain, interfaces and surfaces, thermodynamic state variables, and/or any combinations thereof, which would result in the preferential enhancement of atomic displacements transforming as $R_3^+$ and $M_5^+$ distortions relative to $R_1^+$.

We conjecture that with deterministic control over the atomic structure, e.g., enhancing $R_3^+$ relative to other distortion modes, it could be possible to fully decouple $T_{MI}$ from $T_N$, shifting the equilibrium phase boundaries dividing the metallic/insulating states from the paramagnetic/ordered regions to create non-equilibrium phases. Although it is compelling to extend our interpretation beyond correlation to full causation, we emphasize that first-principles calculations and detailed structural characterization are essential to establish the physical origin underlying the statistical associations we have identified.

**B. Ba$_{1−x}$K$_x$BiO$_3$ Bismuthates**

BaBiO$_3$ is a CO insulator which undergoes a series of phase transitions with temperature. At room temperature it has a monoclinic crystal structure with space group $I2/m$. In the monoclinic $I2/m$ structure, the octahedrally coordinated tetravalent Bi cation charge disproportionates into Bi$(4+\delta)^+$ and Bi$(4-\delta)^+$. Previous optical conductivity

**FIG. 6.** (Color online.) Correlation heat map capturing the degree of linear relationship between unit cell level structural distortion modes and macroscopic transition temperatures, $T_{MI}$, and $T_N$ in RNiO$_3$ perovskites. Dark blue (red) indicates a strong positive (negative) correlation and white indicates no statistical correlation between between the two variables. Units for the irreps and temperatures are given in Å and Kelvin (K), respectively.
measurements\textsuperscript{63} attribute the appearance of an electronic gap in the stoichiometric \textit{I2/m} phase to structural CBD and octahedral rotations.

Chemical doping of BaBiO\textsubscript{3} with potassium by random substitution on the Ba sites, Ba\textsubscript{1-\textit{x}}K\textsubscript{\textit{x}}BiO\textsubscript{3}, produces a sequence of structural and electronic phase transitions. Increasing the potassium concentration leads to crystal structures of higher symmetry: An orthorhombic \textit{Immm} phase is stable over the range 0.12 \textless \textit{x} \textless 0.37. At \textit{x} \approx 0.37, a tetragonal \textit{I4/mcm} phase is stable and for 0.37 < \textit{x} < 0.53 BaBiO\textsubscript{3} transforms to \textit{Pm\textbar 3m} cubic.\textsuperscript{64,65} The electronic transport properties also evolve concomitantly with these structural changes: The system transforms from a robust insulating state in the monoclinic phase to semiconducting in the orthorhombic phase, and finally to a superconducting state in the tetragonal and undistorted cubic phases. Although there are strong evidences supporting an apparent association between structure, doping, and onset of superconductivity, a quantitative assessment of the relationship linking structure to superconductivity is still lacking. Our objective here is to decompose the crystal structure of Ba\textsubscript{1-\textit{x}}K\textsubscript{\textit{x}}BiO\textsubscript{3} as a function of K-doping for 0 \textless \textit{x} \textless 0.4 with emphasis placed on the role of the symmetry-adapted modes and CBD rotation symmetries.

We decompose the low-symmetry crystal structures of Ba\textsubscript{1-\textit{x}}K\textsubscript{\textit{x}}BiO\textsubscript{3} across the phase boundaries using five chemical compositions: BaBiO\textsubscript{3}, Ba\textsubscript{0.9}K\textsubscript{0.1}BiO\textsubscript{3}, Ba\textsubscript{0.8}K\textsubscript{0.2}BiO\textsubscript{3}, Ba\textsubscript{0.63}K\textsubscript{0.37}BiO\textsubscript{3}, and Ba\textsubscript{0.60}K\textsubscript{0.40}BiO\textsubscript{3}, for which high-resolution diffraction data exists.\textsuperscript{64,66} When we constructed the hypothetical parent reference structure, we assigned to both K and Ba atoms the same \{(x, y, z)\} coordinates and we employed fractional site occupancies to treat the random K-substitution on the Ba-site. This treatment ensures that the parent structure is \textit{Pm\textbar 3m} as opposed to any other space group, in which case the \{(x, y, z)\} coordinates for the two cations would be different in the unit cell, \textit{i.e.}, the A-site Wyckoff orbit would split into two, and the space group of the resulting structure would not be the cubic \textit{Pm\textbar 3m} aristotype.

In practice, the occupancy mode amplitudes are calculated by taking into account the site multiplicity and the fractional occupancy. In this work, for consistency, the fractional site occupancies for the Ba and K atoms in both the hypothetical parent and the experimentally observed distorted structures were kept the same. As a result, \textit{Pm\textbar 3m} (or for that matter \textit{I2/m}, \textit{Ibamn}, and \textit{I4/mcm}) are treated as random solid solutions, rather than with periodic ordering. Although the static symmetry modes are unable to accurately capture all the nuances of the configurational entropy governing random occupations of Ba/K-atoms, the amplitudes of the primary and secondary distortion modes do provide insight into the origin of the doping-dependent structural distortions reported in average structure x-ray diffraction measurements. This approach is particularly useful to build an understanding of the interplay of doping and structure in the bismuthates, because computational modeling of Ba\textsubscript{1-\textit{x}}K\textsubscript{\textit{x}}BiO\textsubscript{3} phases present non-trivial challenges due to the random nature of the solid solution. Such configurations necessitate the construction of large supercells and may require computationally-demanding hybrid functionals to accurately reproduce the electronic structure.\textsuperscript{65}

The results from our analysis are summarized in Figure 8. The \textit{I2/m} structure is described by four irreps \textit{R}\textsubscript{1}\textsuperscript{\text{+}}, \textit{R}\textsubscript{4}\textsuperscript{\text{+}}, \textit{R}\textsubscript{1}\textsuperscript{\text{\textbar}}, and \textit{R}\textsubscript{4}\textsuperscript{\text{\textbar}}, which capture the CBD, a Jahn-Teller distortion, out-of-phase octahedral rotations, and out-of-phase bond stretching, respectively. Although the \textit{I2/m} monoclinic symmetry is maintained at small doping, as with Ba\textsubscript{0.9}K\textsubscript{0.1}BiO\textsubscript{3}, our mode decomposition analysis reveals that the amplitude of the \textit{R}\textsubscript{3}\textsuperscript{\text{+}} distortion vanishes completely. The relative amplitudes of the \textit{R}\textsubscript{1}\textsuperscript{\text{+}} CBD and out-of-phase octahedral rotation modes also decrease, whereas the amplitude of the out-of-phase bending distortion increases [Figure 8 (inset)].

With further increase in K concentration, for example in Ba\textsubscript{0.8}K\textsubscript{0.2}BiO\textsubscript{3}, the crystal structure becomes orthorhombic \textit{Immm}. Interestingly, even in the absence of the CBD distortion (\textit{R}\textsubscript{1}\textsuperscript{\text{+}}), which we find has zero amplitude at \textit{x} = 0.2, the electronic structure remains insulating.\textsuperscript{65} At the same time, the amplitude of the \textit{R}\textsubscript{1}\textsuperscript{\text{\textbar}} distortion continues to increase in the presence of out-of-phase octahedral rotations, described by \textit{R}\textsubscript{4}\textsuperscript{\text{+}}. Upon further increase in K, the amplitude of \textit{R}\textsubscript{1}\textsuperscript{\text{\textbar}} distortion disappears completely, yielding tetragonal \textit{I4/mcm} Ba\textsubscript{0.63}K\textsubscript{0.37}BiO\textsubscript{3} with only the \textit{R}\textsubscript{4}\textsuperscript{\text{+}} irrep, which correspond to modes with out-of-phase octahedral tilting at reduced amplitude. Across this structural transition, the compound becomes metallic and superconducting\textsuperscript{64} with a critical transition temperature of 27 K. Finally, for \textit{x} \sim 0.4, the superconducting phase is also stable in the cubic \textit{Pm\textbar 3m} structure without any octahedral rotations or distortions.

An outstanding question concerning the electronic phase diagram of Ba\textsubscript{1-\textit{x}}K\textsubscript{\textit{x}}BiO\textsubscript{3} is the presence of the wide semiconducting or insulating region with doping. Our mode decomposition analysis provides an alternative interpretation of the phase diagram. In Ba\textsubscript{1-\textit{x}}K\textsubscript{\textit{x}}BiO\textsubscript{3}, the octahedral rotations corresponding to irrep \textit{R}\textsubscript{1}\textsuperscript{\text{+}} is found to be the primary distortion and it couples with other secondary distortions, namely \textit{R}\textsubscript{3}\textsuperscript{\text{+}}, \textit{R}\textsubscript{1}\textsuperscript{\text{\textbar}}, and \textit{R}\textsubscript{4}\textsuperscript{\text{\textbar}} depending on the concentration of K. Particularly, we focus on the \textit{R}\textsubscript{3}\textsuperscript{\text{+}} and \textit{R}\textsubscript{4}\textsuperscript{\text{\textbar}} distortions. Even though \textit{R}\textsubscript{3}\textsuperscript{\text{+}} is a secondary distortion, it has a significant non-zero amplitude (0.12 Å) near the insulator–superconductor phase boundary. To the best of our knowledge, no previous study has examined the role of primary and secondary distortions on the insulator–superconductor phase boundary.

In the insulating regime, the amplitude of \textit{R}\textsubscript{1}\textsuperscript{\text{\textbar}} monotonically decreases with increasing K. On the other hand, the amplitude of \textit{R}\textsubscript{3}\textsuperscript{\text{+}} distortion is found to monotonically increase with K. The trend in \textit{R}\textsubscript{1}\textsuperscript{\text{\textbar}} and \textit{R}\textsubscript{3}\textsuperscript{\text{+}} distortion pattern bears a remarkable resemblance with the evolution in the dielectric response reported by Nishio \textit{et al.} on single crystal samples.\textsuperscript{67} Nishio \textit{et al} identified two features in their optical spectra: the first was associated with the excitation from the lower Peierls band to the bipolaron.
defect state, which showed an increase in intensity with K-concentration similar to the increase in amplitude of $R_{5}^{+}$. The second feature was assigned with the magnitude of the Peierls gap, which decreased with increasing K concentration like $R_{5}^{+}$. Our analysis suggests that the stability of the polaronic defects and the magnitude of the gap in the orthorhombic bismuthates may be intimately tied to the amplitude of the $R_{4}^{+}$ (rotations) and $R_{5}^{+}$ (bond stretching) distortions.

Electronic structure calculations would allow us to unravel this association and glean insights into the persistence of wide semiconducting or insulating regions in Ba$_{1-x}$K$_{x}$BiO$_{3}$ compounds. To do so, we propose a computational experiment to test the relationship between octahedral distortions and the optical spectra. One could “freeze-in” the $R_{5}^{+}$ (or alternatively $R_{5}^{+}$) distortion and map the energy landscape as a function of the amplitudes of $R_{5}^{+}$ (or the corresponding $R_{4}^{+}$) distortion. For each structures, the complex frequency-dependent dielectric function would be computed following the computational approach of Franchini et al, who has successfully demonstrated that hybrid functionals are capable of describing both octahedral distortions and the complex electronic states.\textsuperscript{65} This would permit the independent assessment of the relative role of $R_{4}^{+}$ and $R_{5}^{+}$ distortions on the closing of the Peierls gap and the stability of the bipolaron defect states. While our computational proposal may appear seemingly simple, this is by no means a trivial set of computations.

VI. SUMMARY

We applied group theoretical methods to evaluate the interplay between octahedral rotations and electronic charge ordering, which we parameterized structurally as octahedral “breathing” or cooperative bond length distortions through irreducible representations of the aristotype space group. We enumerated the possible space groups available to perovskites from the intersection of these distortions. This crystallographic data should prove useful for experimental structure refinements or serve as a well-defined set of symmetry-unique structures for which the stability of transition metal compounds susceptible to charge ordering may be evaluated with first-principles total energy methods.

With this information, we combined structural mode decomposition techniques with statistical methods to extract unbiased structure–property relationships from available experimental diffraction data on representative charge ordering oxides. The crystal structures of perovskite nickelates and bismuthates were decomposed in terms of symmetry-adapted distortion-modes and the evolution in the amplitude of each mode tracked as a function of an external chemical parameter. We illustrated that this alternative set of descriptors provides a useful construct...
beyond the traditional tolerance factor paradigm found in perovskites to understand the atomic scale origin of physical properties, specifically how unit cell level modifications correlate with macroscopic functionality.

Our statistical analysis uncovered previously unappreciated relationships that may be harnessed for electronic structure by design, some of which are being carried out within our group and will be reported later. We emphasize that the application of statistics to the decompositions does not require solely experimental data; the analysis can be performed with computationally obtained data alone. Importantly, the relationships established with these techniques may be cross-validated by the construction of hybrid data sets, which combine theoretical results with experiment data, making it possible to extract and validate new insight into the material physics of oxides with correlated electrons. We anticipate that this approach will spawn a number of additional studies in diverse crystal classes since it is immediately generalizable: the synergy of applied group theoretical methods with statistical analysis and subsequent first-principles calculations provides a platform to achieve rational structure-driven design of complex materials.

**ACKNOWLEDGMENTS**

P.V.B. was supported by The Defense Advanced Research Projects Agency (DARPA) under grant no. N66001-12-4224. J.M.R. was supported by the U.S. Office of Naval Research (ONR), under grant number N00014-11-1-0664. The views, opinions, and/or findings reported here are solely those of the authors and do not represent official views of DARPA or ONR. We thank our group members, D. Puggioni and A. Cammarata, for useful discussions.

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1. N. A. Benedek, A. T. Mulder, and C. J. Fennie, *J. Solid State Chem.* **195**, 11 (2012).
2. C. J. Howard and H. T. Stokes, *Acta Crystallographica Section B* **54**, 782 (1998).
3. E. Canadell, M.-L. Doublet, and C. Iung, *Orbital Approach to the Electronic Structure of Solids* (Oxford University Press, New York, 2012).
4. A. J. Millis, P. B. Littlewood, and B. I. Shraiman, *Phys. Rev. Lett.* **74**, 5144 (1995).
5. M. A. Carpenter and C. J. Howard, *Acta Crystallographica Section B* **65**, 134 (2009); *Acta Crystallographica Section B* **65**, 147 (2009).
6. J. B. Goodenough and F. Rivadulla, *Modern Physics Letters B* **19**, 1057 (2005).
7. M. B. Salamon and M. Jaime, *Rev. Mod. Phys.* **73**, 583 (2001).
8. J. B. Goodenough, *Reports on Progress in Physics* **67**, 1915 (2004).
9. J. Matsuno, T. Mizokawa, A. Fujimori, Y. Takeda, S. Kawasaki, and M. Takano, *Phys. Rev. B* **66**, 193103 (2002).
10. The MI-transition results from electronic localization, which can be intrinsic and electrostatic in nature (electron-electron repulsion), or extrinsic, due to defects or disorder.
11. Y. Quan, V. Pardo, and W. E. Pickett, *Phys. Rev. Lett.* **109**, 216401 (2012); H. Park, A. J. Millis, and C. A. Mariannetti, *Phys. Rev. Lett.* **109**, 156402 (2012); A. Cammarata and J. M. Rondinelli, *Phys. Rev. B* **86**, 195144 (2012).
12. Not all charge-ordering transitions require an concomitant change in structure, see for example the case of LaSr₂Fe₅O₁₂.
13. T. Saha-Dasgupta, Z. S. Popović, and S. Satpathy, *Phys. Rev. B* **72**, 045143 (2005).
14. T. Mizokawa, D. I. Khomskii, and G. A. Sawatzky, *Phys. Rev. B* **60**, 7309 (1999).
15. The list is for B-site ordered perovskites where breathing distortions is not due to the spontaneous electron instability, but present because of ordered arrangement of B-site element.
16. This distortion is not a Jahn-Teller elongation of the octahedra, because the equatorial oxygen of a single octahedron either all elongate (contract) in the same direction; a Jahn-Teller distortion is rather seen as a two-in-two-out distortion of the equatorial oxygen atoms.
17. G. King and P. M. Woodward, *J. Mater. Chem.* **20**, 5785 (2010).
18. B. J. Campbell, H. T. Stokes, D. E. Tanner, and D. M. Hatch, *Journal of Applied Crystallography* **39**, 607 (2006).
19. C. J. Howard and H. T. Stokes, *Acta Crystallographica Section A* **61**, 93 (2005).
20. C. J. Howard and H. T. Stokes, *Acta Crystallographica Section B* **60**, 674 (2004).
21. H. T. Stokes, E. H. Kisi, D. M. Hatch, and C. J. Howard, *Acta Crystallographica Section B* **58**, 934 (2002).
22. A. M. Glazer, *Acta Crystallographica Section B* **28**, 3384 (1972).
23. J. B. Torrance, P. Lacorre, A. I. Nazzal, E. J. Ansald, and C. Niedermayer, *Phys. Rev. B* **45**, 8209 (1992).
24. S. J. May, J.-W. Kim, J. M. Rondinelli, E. Karapetrova, N. A. Spaldin, A. Bhattacharya, and P. J. Ryan, *Phys. Rev. B* **82**, 014110 (2010).
25. J. M. Rondinelli, S. J. May, and J. W. Freeland, *MRS Bulletin* **37**, 261 (2012).
26. J. Chakhalian, J. M. Rondinelli, J. Liu, B. A. Gray, M. Kareev, E. J. Moon, N. Prasai, J. L. Cohn, M. Varela, I. C. Tung, M. J. Bedzyk, S. G. Altendorf, F. Strigari, B. Dabrowski, L. H. Tjeng, P. J. Ryan, and J. W. Freeland, *Phys. Rev. Lett.* **107**, 046805 (2011).
27. A. Blanca-Romero and R. Pentcheva, *Phys. Rev. B* **84**, 195450 (2011).
28. A. V. Boris, Y. Matiks, E. Benckiser, A. Frano, P. Popovich, V. Hinkov, P. Wochner, M. Castro-Colin, E. Detemple, V. K. Malik, C. Bernhard, T. Prokscha, A. Suter, Z. Salm, E. Morenzoni, G. Cristiani, H.-U. Habermeier, and B. Keimer, *Science* **332**, 937 (2011).
29. J.-S. Zhou, J. B. Goodenough, and B. Dabrowski, *Phys. Rev. Lett.* **95**, 127204 (2005).
30. G. Catalan, *Phase Trans.* **81**, 729 (2008).
31. J. B. Goodenough, in *Structure and Bonding, Localized

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to Itinerant Electronic Transitions in Perovskite Oxides, Vol. 98, edited by J. B. Goodenough (Springer, 2001).

32 J. M. Perez-Mato, D. Orozengo, and M. I. Aroyo, Acta Crystallographica Section A 66, 558 (2010).

33 M. T. Dove, American Mineralogist 82, 213 (1997).

34 O. Diéguez, O. E. González-Vázquez, J. C. Wojdel, and J. Íñiguez, Phys. Rev. B 83, 094105 (2011).

35 R Core Team, R: A Language and Environment for Statistical Computing, R Foundation for Statistical Computing, Vienna, Austria (2012), ISBN 3-900051-07-0.

36 D. Sarkar, Lattice: Multivariate Data Visualization with R (Springer, New York, 2008) ISBN 978-0-387-75968-5.

37 J. A. Alonso, J. L. García-Muñoz, M. T. Fernández-Díaz, M. A. G. Aranda, M. J. Martínez-Lope, and M. T. Casais, Phys. Rev. Lett. 82, 3871 (1999).

38 The first origin choice is only used for notation purposes to avoid confusion. Our actual mode-decomposition was performed using $P2_1/n$ space group as reported in the literature.

39 M. Medarde, P. Lacorre, K. Conder, F. Fauth, and A. Furrer, Phys. Rev. Lett. 80, 2397 (1998).

40 V. I. Anisimov, D. Bukhvalov, and T. M. Rice, Phys. Rev. B 59, 7901 (1999).

41 I. I. Mazin, D. I. Khomskii, R. Lengsdorf, J. A. Alonso, W. G. Marshall, R. M. Ilberson, A. Podlesnyak, M. J. Martínez-Lope, and M. M. Abd-Elmeguid, Phys. Rev. B 80, 161106 (2011).

42 J. A. Alonso, J. L. García-Muñoz, M. A. G. Aranda, M. J. Martínez-Lope, and M. T. Casais, Phys. Rev. B 61, 1756 (2000).

43 B. Lau and A. J. Millis, Phys. Rev. Lett. 110, 126404 (2013).

44 J. A. Alonso, M. J. Martínez-Lope, M. T. Casais, J. L. García-Muñoz, and M. T. Fernández-Díaz, Phys. Rev. B 61, 1756 (2000).

45 M. Medarde, M. T. Fernández-Díaz, and P. Lacorre, Phys. Rev. B 78, 212101 (2008).

46 J. L. García-Muñoz, M. A. G. Aranda, J. A. Alonso, and M. J. Martínez-Lope, Phys. Rev. B 79, 134432 (2009).

47 A. Munoz, J. Alonso, M. Martínez-Lope, and M. Fernandez-Díaz, Journal of Solid State Chemistry 182, 1982 (2009).

48 A. T. Mulder, N. A. Benedek, J. M. Rondinelli, and C. J. Fennie, Advanced Functional Materials 10.1002/adfm.201300210.

49 V. Dvorák and J. Petzel, Physics Letters A 35, 209 (1971).

50 A. P. Levanyuk and D. G. Sannikov, Sov. Phys.-Usp. 17, 199 (1974).

51 J. Tolédano and P. Tolédano, The Landau Theory of Phase Transitions (World Scientific, 1987).

52 J. M. Perez-Mato, P. Blaha, K. Schwarz, M. Aroyo, D. Orozengo, I. Etxebarria, and A. García, Phys. Rev. B 77, 184104 (2008).

53 I. Etxebarria, J. M. Perez-Mato, and P. Boullay, Ferroelectrics 401, 17 (2010).

54 N. A. Benedek and C. J. Fennie, Phys. Rev. Lett. 106, 107204 (2011).

55 A. Stroppa, P. Barone, P. Jain, J. M. Perez-Mato, and S. Picozzi, Advanced Materials 25, 2284 (2013).

56 J. Chakhalian, J. M. Rondinelli, J. Liu, B. A. Gray, M. Karcev, E. J. Moon, N. Prasai, J. L. Cohn, M. Varela, I. C. Tung, M. J. Bedzyk, S. G. Altendorf, F. Strigari, B. Dabrowski, L. H. Tjeng, P. J. Ryan, and J. W. Freel, Phys. Rev. Lett. 107, 116805 (2011).

57 J. W. Freel, J. Liu, M. Karcev, B. Gray, J. W. Kim, P. Ryan, R. Pentcheva, and J. Chakhalian, EPL (Europhysics Letters) 96, 57004 (2011).

58 H. Chen, D. P. Kumah, A. S. Disa, F. J. Walker, C. H. Ahn, and S. Ismail-Beigi, Phys. Rev. Lett. 110, 186402 (2013).

59 I. C. Tung, P. V. Balachandran, J. Liu, B. A. Gray, E. A. Karapetrova, J. H. Lee, J. Chakhalian, M. J. Bedzyk, J. M. Rondinelli, and J. W. Freel, Submitted, March (2013).

60 X. Obradors, L. M. Paulius, M. B. Maple, J. B. Torrance, A. I. Nazzal, J. Fontcuberta, and X. Granados, Phys. Rev. B 47, 12353 (1993).

61 I. Vobornik, L. Perfetti, M. Zacchigna, M. Grioni, G. Margaritondo, J. Mesot, M. Medarde, and P. Lacorre, Phys. Rev. B 60, R8426 (1999).

62 S. Lee, R. Chen, and L. Balents, Phys. Rev. B 84, 165119 (2011).

63 M. A. Karlow, S. L. Cooper, A. L. Kotz, M. V. Klein, P. D. Han, and D. A. Payne, Phys. Rev. B 48, 6499 (1993).

64 M. Braden, W. Reichardt, E. Elkaim, J. P. Lauriat, I. Vobornik, L. Perfetti, M. Zacchigna, M. Grioni, G. Margaritondo, J. Mesot, M. Medarde, and P. Lacorre, Phys. Rev. B 60, R8426 (1999).

65 C. Franchini, G. Kresse, and R. Podloucky, Phys. Rev. Lett. 102, 256402 (2009).

66 S. Pei, J. D. Jorgensen, B. Dabrowski, D. G. Hinks, D. R. Richards, A. W. Mitchell, J. M. Newsam, S. K. Sinha, D. Vaknin, and A. J. Jacobson, Phys. Rev. B 41, 4126 (1990).

67 T. Nishio, J. Ahmad, and H. Uwe, Phys. Rev. Lett. 95, 176403 (2005).