Valence skipping, internal doping and site-selective Mott transition in PbCoO₃ under pressure

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We present a computational study of PbCoO₃ at ambient and elevated pressure. We employ the static and dynamic treatment of local correlation in form of density functional theory + U (DFT+U) and + dynamical mean-field theory (DMFT). Our results capture the experimentally observed crystal structures and identify the unsaturated Pb 6s–O 2p bonds as the driving force beyond the complex physics of PbCoO₃. We provide a geometrical analysis of the structural distortions and we discuss their implications, in particular, the internal doping, which triggers a transition between phases with and without local moments and a site selective Mott transition in the low-pressure phase.

I. INTRODUCTION

Transition metal oxides with perovskite structure host a plethora of interesting electronic phenomena including high-Τc superconductivity, colossal magnetoresistance, metal-insulator transitions, ferro- as well as antiferromagnetism, and charge or orbital ordering. One of the key parameters affecting their physical properties is filling of the 3d orbitals. It can be altered by doping, in the ABO₃ perovskite structure usually achieved by a combination of divalent alkali-earth metals and trivalent rare-earth ions on the A sublattice. The A-site ions do not participate in formation of the low-energy valence and conduction states, playing a passive role of electron donor, with rare exceptions such as the Pr ion in the (Pr₁₋ₓYₓ)₂Ca₁₋ₓCoO₃ [5]. Thanks to quasi-degeneracy of Pr³⁺ and Pr⁴⁺ valence states their abundance varies with temperature or pressure [6 7], leading to internal doping with a substantial impact on the physical properties [8].

Another path to internal doping is by growing materials with valence skipping ions Bi or Pb on the A site. A famous example of BiNiO₃ exhibits a colossal negative thermal expansion as well as temperature and pressure induced metal-insulator transition [9][12]. Unlike the Pr⁵⁺ ↔ Pr⁴⁺ crossover, which is an intra-atomic effect, the valence skipping between formal 6s⁰ (Pb⁴⁺, Bi⁵⁺) and 6s² states (Pb⁵⁺, Bi³⁺) is a metaphor since its origin lies in strongly covalent character of A–O bond. In the PbMO₃ (M is a 3d metal) series the formal Pb valence changes from Pb²⁺Ti⁴⁺O₃ to Pb⁴⁺Ni²⁺O₃ with a peculiar behavior for M = Co and Fe in the middle [13–19].

In this article, we present a theoretical study of the electronic and crystal structure of PbCoO₃ (PCO) and its evolution under pressure. Using the density functional theory (DFT) combined with a static and dynamical mean-field treatment of the electron-electron interaction within the Co 3d shell we show that the physics of PCO arises from the coexistence of several phenomena: (i) valence skipping and internal doping similar to BiNiO₃, (ii) site disproportionation (SD) of the Co sublattice and breathing mode (BM) distortion of CoO₆ octahedra as in rare-earth nickelates RNiO₃ [20, 21] (iii) spin-state crossover as in La₁₋ₓSrₓCoO₃ and iv) lattice distortion as in CaCuₓFe₄O₁₂ [22, 23] associated with tilting of rigid CoO₆ octahedra common to many transition metal perovskites. A combination of these phenomena leads to complex changes of electronic and structural properties with applied pressure, the root cause of which can be traced back to the general tendency of materials to reduce or eliminate their Fermi surface.

At ambient pressure PCO forms a quadruple perovskite structure, with two distinct Pb sites. Based on x-ray absorption, photoemission and magnetic susceptibility measurements with a DFT+U calculation, the authors in Ref. [13] suggested SD of the Pb²⁺Pb⁴⁺Co²⁺Co⁵⁺O₁₂ type, which, in addition to the charge gap, survives well above the magnetic transitions temperature of 7.8 K. Curie-Weiss susceptibility observed at high temperatures was attributed to a high-spin configuration of the Co²⁺ ion. Recently, Liu et al. [14] reported a pressure-induced insulator-insulator transitions from cubic to tetragonal structure with an intermediate regime between 15 and 30 GPa, in which a bad metal behavior was observed at elevated temperatures.

We employ two approaches. The computationally cheap DFT+U (static mean-field approximation) allows us to find equilibrium atomic positions and lattice parameters, while we have to admit an unrealistic (ferromagnetic) magnetic order to capture the high-spin state of Co. We use computationally expensive DFT+ dynamical mean-field theory (DMFT) to capture the fluctuating local moment and dynamical correlation effects to verify

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the DFT+U results in the low- and high-pressure structures.

II. COMPUTATIONAL METHOD

The internal parameters as well as the $c/a$ ratio were optimized for each structure with the DFT$+U$ method using the Vienna ab initio simulation package (VASP) [24–25]. We have employed the local density approximation [26, 27] to the exchange correlation potential and the so-called fully localized limit [28] form of the double-counting correction in the DFT$+U$ calculations with $U_{\text{eff}} = 5.9$ eV. The atomic positions for all structures can be found in the supplemental material (SM) [29]. The total energies were then calculated for the optimized structures with the all-electron linearized augmented plane wave method as implemented in WIEN2K code [30]; see Fig. 1.

DFT+DMFT calculations [31] proceed in two steps: (i) construction of a tight-binding model from DFT bands for a structure and (ii) solution of the DMFT self-consistent equation [32–33]. In step (i) we use the optimized crystal structures described above, calculate the electronic band structure [30] with the local density approximation, and construct a lattice model on the basis of Wannier orbitals using WANNIER90 code [34, 35]. The Wannier projection provides a freedom in choosing the covered orbital space. We use two settings. The spd model spanned by the Co 3d, O 2p, and Pb 6s basis, which represents exactly the bands in the range -10 – 2 eV, is used in the DMFT calculations presented in the text. The sd model spanned by the Co 3d and Pb 6s basis, represents the Co 3d-like and Pb 6s – O 2p anti-bonding bands. It was obtained using the band disentanglement technique [36], which is used to isolate the Pb 6s – O 2p anti-bonding band. The DMFT results obtained with the sd model (consistent with those obtained with the spd model) are presented in the SM [29].

In step (ii) the tight-binding lattice model is augmented with an on-site interaction term within the Co 3d parametrized in terms of the Coulomb $U$ and Hund’s $J$ parameters [37, 38]. Following previous studies on LaCoO$_3$ [39, 40], we use $(U, J) = (6.0$ eV, 0.8 eV) for the spd model and $(U, J) = (3.0$ eV, 0.6 eV) for the sd model [29]. The fully localized form of the double-counting correction is employed [28, 41–42]. The strong-coupling continuous-time quantum Monte-Carlo method [43–46] is used to solve the auxiliary Anderson impurity model (AIM) in the DMFT calculation. The spectral functions are calculated from the self-energy analytically continued by the maximum entropy method [47]. Weights of the atomic states given as the partial traces of the reduced density matrix and the imaginary time local spin-spin correlation function $(S_z(\tau)S_z(0))$ are measured directly in the quantum Monte-Carlo simulation.

III. RESULTS AND DISCUSSION

In Fig. 1 we compare the energy vs volume dependencies for several structures: simple perovskite (Pm3m), cubic quadruple perovskite with BM distortion ($c$-structure; Pn3), cubic quadruple perovskite without BM distortion ($c^*$-structure; I43m) and tetragonal (t-structure; I4/mmm) obtained with DFT$+U$ approach. The calculations capture the experimental observation of the $c$-structure having the lowest energy at ambient pressure and the t-structure having the lowest energy at elevated pressure. The transition pressure of 30 GPa as well as the discontinuous volume change of 3.4% agrees fairly well with the experimental observations [14]. We did not identify the intermediate pressure phase of Ref. [14] however, a near degeneracy of several phases in the vicinity of the transition indicates a flat energy landscape with the possibility of additional stable structures possibly with larger unit cell.

A. Parent perovskite structure

While the simple perovskite structure is unstable for all studied volumes shown in Fig. 1 it provides a useful reference and sets the energy scales in PCO. The DFT$+U$ spectra in Fig. 2 reveal that the main effect of electron-electron interaction within the Co 3d shell is to enhance the octahedral crystal field and open a gap between Co t$_{2g}$ and e$_g$ states. A strong Pb 6s – O 2p hybridization positions the half-filled anti-bonding band at the Fermi level. Moderate Pb 6p – O 2p hybridization distinguishes PCO from the ferroelectric perovskite BiCoO$_3$, where strongly hybridized Bi 6p – O 2p bonding states appear in the vicinity of the Fermi level while the Bi 6s – O 2p hybridization is substantially weaker than in PCO. This difference results from deeper Bi 6s and 6p levels; see the SM [29]. The combination of 6s – O 2p anti-bonding and 6p – O 2p bonding bands is decisive
for the occurrence and type of structural distortions in Pb and Bi oxides [48]. We conjecture the dominance of Pb 6s − O 2p hybridization to be the reason for approximately centrosymmetric coordination of Pb sites in all PCO structures [44].

Unlike in rare-earth cobaltites, where the tilting of CoO₆ is driven by electrostatic instability of the small rare-earth ion in the Co−O matrix, the structural distortions in PCO and other active A-site perovskites [41][49] originate from covalent Pb−O bonding. Formulated in the language of electronic bands, a structural distortion leads to energy lowering if it opens a (partial) gap at the Fermi level while keeping the elastic energy cost low. A textbook example is the Peierls instability of one-dimensional (1D) systems driven by perfect Fermi surface nesting. In general 3D systems the Fermi surface nesting can only be approximate and a finite distortion may be necessary to achieve energy lowering. In fact, the numerical results below classify the distortion-induced band splitting rather as a strong coupling effect (splitting is larger or comparable to the bandwidth) and thus Fermi surface nesting does not play an important role.

While the calculations presented in Fig. 1 take the whole system into account, understanding them requires breaking the system into functional components and identification of leading interactions within and between them. Such simplifications can usually be justified only a posteriori. We start our discussion by analyzing the geometry of the distorted structures.

B. Geometry considerations

Distortions of simple perovskite structure into the low-pressure cubic (c) and high-pressure tetragonal (t) structure can be viewed as tilts of (approximately) rigid CoO₆ octahedra, shown in Fig. 3(a). Small tilting of a CoO₆ octahedron corresponds to shifting of the O atoms within the PbO planes subject to constraints $Z_x = -X_z$, $Z_y = -Y_z$, and $X_y = -Y_x$, which reduce the number of independent parameters to 3 as expected for a 3D rotation of a rigid body. Sharing corners by neighboring octahedra implies further constraints on possible O-displacements in the PbO and CoO₂ planes. Let us consider layers parallel to the (0, 0, 1) plane. Allowed O-displacements in the PbO layer fulfill $Z_x(R + e_x) = -Z_x(R)$ and $Z_y(R + e_y) = -Z_y(R)$ [50], which reduces the the number of independent parameters on the $N \times N$ lattice from $2N^2$ for the case of independent octahedra to $2N$. To extend this reasoning to the 3D structure we observe the following: (i) The displacement pattern in one PbO layer uniquely determines the displacements in all remaining PbO layers. (ii) After fixing $Z_x(R)$ and $Z_y(R)$, it remains to determine the $X_y(R)$ in the adjacent CoO₂ layer. Fixing this parameter for an arbitrary O site, e.g., $X_y(0, 0, R_z)$, uniquely determines the displacements for all remaining O sites in the layers and thus is a sole free parameter. (iii) $X_y(0, 0, R_z)$ in distinct CoO₂ layers are independent. As a result the allowed tilts on the $N \times N \times N$ lattice are described by $3N$ independent parameters (no periodicity assumed). The allowed tilts are severely limited if the inversion symmetry of the Pb sites is to be preserved. In the $(0, 0, 1)$ plane it adds the conditions $Z_x(R + e_y) = Z_x(R)$ and $Z_y(R + e_y) = Z_y(R)$ to those above, which implies that the displacement of a single O atom determines uniquely the whole layer. Extending the argument to 3D shows that a tilt of a single
CoO$_6$ octahedron (three parameters) determines the pattern throughout the entire crystal.

Symmetry suggests to search for local energy minima for displacements along high symmetry directions, i.e., along the cubic edges or face diagonals as shown in Figs. 3(b) and 3(c). Both the $c$ and $t$ structures can be obtained from these two patterns. The $c$-structure, shown in Fig. 3(b), arises from diagonal displacements in all three PbO planes (cubic faces). As a result, 3/4 of the Pb atoms belong to PbO$_4$ plaquettes with short Pb–O bonds and 1/4 of Pb atoms remain “lone”. The $t$-structure, shown in Fig. 3(c), originates from diagonal displacement in the $(0,0,1)$ plane and $z$-parallel displacement in the $(1,0,0)$ and $(0,1,0)$ planes. This gives rise to three inequivalent Pb sites: 1/4 of Pb atoms forms PbO$_4$ plaquettes as in the $c$-structure, 1/4 of Pb atoms form short-bond cuboids and 1/2 of Pb atoms remain lone.

C. Low-pressure structure

The total energies in Fig. 1 show that all the considered structural distortions lead to energy lowering. The absence of the Co 3$d$ spectral density in the vicinity of the Fermi level, shown in Fig. 2, as well as the fact that different distortion patterns ($t$ and $c^*$) lead to similar energy lowering suggest that the distortion is driven by Pb–O bonding. In the reciprocal space, this can be understood as a tendency to open a gap (at the Fermi level) in the Pb–O anti–bonding band, similar to the Peierls instability. In the direct space, this can be viewed as disproportionation of Pb–O bonds into saturated ones (empty anti–bonding state) and non-bonds associated with lone Pb ions (occupied anti–bonding state).

The $t$-distortion splits the anti–bonding band into a low-energy doublet and two singlets. The $c^*$-distortion splits the anti–bonding band into a low-energy singlet and a triplet, referring to a Pb$_4$Co$_4$O$_{12}$ unit cell in both cases. To demonstrate this behavior we have constructed a $ds$ model spanning the Co 3$d$ and anti-bonding Pb 6$s$–O 2$p$ bands, where the O 2$p$ are only implicitly included in the Co and Pb centered Wannier orbitals. This construction is justified by the strong Pb – O, which well separates the bonding and anti–bonding bands; the exception is near the $R$ point of the Brillouin zone, where Pb – O hybridization vanishes, but the corresponding states play no role in the studied physics as they lie far below the Fermi level. To further reduce complexity of the problem, we switch off the $d$–$s$ hybridization (its effect is shown in the SM [29]) and thus isolate the physics of the Pb – O anti–bonding band. In Fig. 4 we show the corresponding band structures unfolded to the Brillouin zone of the simple perovskite structure.

While the $c^*$-distortion already lowers the energy relative to the simple perovskite, it leaves the Pb–O bonds of the triplet unsaturated – the anti–bonding state is occupied by two electrons. Further energy lowering is possible by transfer of the excess electrons from the triplet Pb–O anti–bonding state to the Co bands. In a non-interacting system, such a transfer cannot lead to energy lowering, because the extra electron must go to the unoccupied Co $e_g$ bands, located above the Pb–O anti–bonding state. In an interacting system, however, doping is not equal to simply filling or emptying of electronic bands as is known for hole- [52–54] as well as electron- [55] doped cobaltites. Sakai et al. [13] showed that the $c^*$-distortion is accompanied by transfer of, on average, 1/2 electron per Co ion. This state is stabilized by site disproportionation of Co into high-spin Co$^{2+}$ and low-spin Co$^{3+}$.

While our total energy calculations assumed ordered magnetic moments on the Co sites, because only such a state can be described by the static DFT+$U$ approach, PCO is a paramagnetic insulator down to 7.8 K [13] before it magnetically orders. To capture the paramagnetism and dynamical correlation effects as well as to allow a “fair” competition between disproportionated insulating and uniform metallic states [56], we have performed DFT+DMFT calculation in the $c$-structure using the structural parameters available for ambient pressure [13] [29]. The results, summarized in Figs. 5 and 6, confirm the formation of a local moment on 1/2 of Co sites. It leads to partial filling of the Co $e_g$–O 2$p$ anti–bonding states and weakens the Co–O bond - a physicist’s way of saying that high-spin state has a larger ionic ra-
FIG. 5. Left: DFT+DMFT orbital-resolved densities of states in the \(c\) structure (low-pressure structure) on (a) Co LB site, (b) Co SB site, and (c) Pb lone and plaquette, and O sites. (The orbitals correspond to the Wannier basis.) The imaginary parts of the DMFT self-energies \(\Sigma(\omega)\) of the Co 3\(d\) orbitals are shown in the insets of panels (a) and (b). Right: DFT+DMFT orbital-resolved projected density of states in the \(t\) structure (high-pressure structure) on (d) Co site, (e) Pb lone, plaquette, and cuboid. The element resolved spectra are shown in panel (f). The inset in panel (e) shows the low-energy region.

D. High-pressure structure

In Figs. 5(d)–(f) we show the orbital resolved spectral densities in the high-pressure \(t\)-structure obtained by the DFT+DMFT method for the theoretical structural parameters [29] corresponding to \(P = 73\ \text{GPa}\) of Fig. 1(b). The Co bands resemble the simple perovskite spectrum with the occupied \(t_{2g}\) band separated by a crystal-field gap from the empty \(e_{g}\) bands. The location of Fermi level inside the crystal-field gap makes the Co \(d\) states play rather passive role.

The \(t\)-distortion distinguishes three Pb sites: the lone site (Pb1), the plaquette site (Pb2) with a saturated bond to four O neighbors and the cuboid (Pb3) with a saturated bond to eight O neighbors. The Pb-projected spectra [Fig. 5(e)] reveal a pseudogap separating the Pb1 and Pb2+Pb3 anti-bonding bands. The Pb2 and Pb3 peaks above the Fermi level are rather narrow, which reflects the isolated location of both PbO\(_4\) plaquettes and PbO\(_8\) cuboids in the structure (O ions participating in a saturated bonds are not shared by more than one Pb ion). The Pb1 anti-bonding band exhibits a broader two-peak structure from \(-4\) to \(0\) eV. It originates from a broad Pb1 anti-bonding band, see Fig. 4(c), which is split by hybridization with a narrow Co \(t_{2g}\) band; see the SM [29].
The spin-correlation function $\chi$ and (b) Co SB site calculated by the DFT+DMFT method. The main observations of Liu et al. [14] can be summarized as follows: (i) resistivity in the c-phase drops with temperature substantially faster than in t-phase, (ii) resistivity in the c-phase increases with pressure, (iii) resistivity in the t-phase decreases with pressure, but the trend possibly reverses at higher temperatures [60]. The observation (i) is consistent with finding a larger gap in the low-pressure c-phase. The pressure dependence (ii) can be understood assuming that the charge transport is controlled by the crystal-field gap, which increases with pressure. The t-phase exhibits a pseudogap between the Pb–O anti-bonding bands, i.e., the gap is smaller than in the c-phase, and the character of the valence and conduction bands is different, which is consistent with (i). The decrease of resistivity with pressure (iii) may simply reflect increasing quasi-particle mobility (band broadening), but naming a specific mechanism based on the present results would be rather speculative. The upturn of resistivity (iv) at high temperature is consistent with a small gap or pseudogap situation in which a thermal excitation of charge carriers competes with increasing electron-electron or electron-phonon scattering. Such a behavior is known for example from small-gap semiconductor FeSi [61, 62].

IV. CONCLUSIONS

We have presented a computational study of the electronic structure of PbCoO$_3$ (PCO) under pressure using DFT+$U$ and DFT+DMFT approaches. Our results correctly capture the low- and high-pressure structures as well as their insulating character and magnetic properties. As pointed out in the experimental studies [13, 14] PCO hosts several interesting effects observed separately in other materials: valence skipping, site disproportionation, internal doping and spin state transition. These effects are a consequence of the covalent Pb–O bond, which distinguishes PCO from ABO$_3$ perovskites with rare-earth or alkali-earth metals on the A site, and correlation effects on the Co site.

Analyzing the numerical results we have attempted to disentangle these effects and put PCO into context of other transition metal perovskites. Starting from a hypothetical simple perovskite structure, we find that the key mechanism determining the crystal structure is an instability of the unsaturated Pb 6s – O 2p bond. Unlike in other materials such as BiCoO$_3$ or PbVO$_3$, where a 6s – O 2p anti-bonding state is nominally occupied and the A 6p play an important role in non-centrosymmetric displacement of the A ion, Pb 6p states in PCO do not play any important role. The structural distortion thus distinguishes the Pb sites into one with a saturated bond (empty anti-bonding state) and non-bonding ones (occupied anti-bonding state). We have shown that both the distortion into the low-pressure cubic c-structure and the high-pressure tetragonal t-structure can be viewed to the leading order as tilts of rigid CoO$_6$ octahedra, which preserve the inversion symmetry of the Pb site. While the c-structure allows opening of a larger gap in the Pb–O anti-binding band, a transfer 1/2 electron to nominally Co 3d band is necessary to position the gap at the Fermi level. This internal charge transfer is stabilized by disproportionation of Co into a high-spin site with Mott insulator like spectral density and low-spin band insulator like spectral density. The price paid is the expansion

![Graph](image-url)
of the O₆ octahedron around the high-spin site due to reduced Co 3d–O 2p covalency. This results in the so-called breathing distortion and overall expansion of the structure, which makes it less favorable at elevated pressure, and it is eventually replaced by the non-magnetic tetragonal structure.

Internal doping is a clean way to qualitatively modify materials properties. The rich physics of PCO provides an example of its realization.

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See Supplementary Material for computational details of the DFT+U and DFT+DMFT simulation, and the analysis of the ds-only model.

All calculations were performed at the temperature of 300 K.

Static approaches such as DFT+U are known to exaggerate ordering tendencies.

The experiments performed only up to the room temperature found the upturn only at intermediate pressures.