

Polaron-Driven Switching of Octupolar Order in Doped $5d^2$ Double Perovskite

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We investigate how doping-induced small polarons impact the low-temperature multipolar orders of the $5d^2$ double perovskite $\text{Ba}_2\text{CaOsO}_6$. By computing intersite exchange interactions between $5d^1$ localized hole polarons and $5d^2$ magnetic ions from first principles, we demonstrate the reversal of the dominant octupolar exchange from ferromagnetic to antiferromagnetic. Solving the corresponding effective Hamiltonian, we find this reversal to account for the progressive suppression of the ferro-octupolar order and the reduction of the ordering temperature upon Na doping. These findings clarify previously ambiguous experimental observations and demonstrate that charge doping in the form of small polarons offers a viable route to tuning intersite exchange interactions in spin-orbit-entangled materials, enabling the emergence of novel quantum orders.

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Transition metal oxides with $4d$ and $5d$ magnetic ions have reshaped our understanding of strong spin-orbit (SO) coupled physics in condensed matter [1]. These systems exhibit a wide range of phenomena, from the SO-assisted Mott insulating phase in Iridates [2] to nontrivial topology [3] and possible Kitaev quantum spin liquids [4]. In particular, cubic double perovskites (DPs) containing $5d^1$ and $5d^2$ ions have attracted interest in the past years due to the ordering of high-rank multipoles that, although being detected experimentally, via, e.g., thermodynamic measurements, defy precise identification due to the “blindness” of local probes [5,6]. High-rank multipoles in DPs arise from a cascade of effects. The strong crystal field (CF) of the octahedral environment splits the $L = 2$ levels of the $5d$ shell, pushing the t_{2g} orbitals to lower energy. These carry an effective orbital angular momentum $l = 1$ which, through strong SO entanglement, gives rise to ground state multiplets (GSM) characterized by an effective total angular momentum $J_{\text{eff}} = S + l$. The multipolar moments associated with J_{eff} can have rank up to $K = 2J_{\text{eff}}$, thereby extending beyond conventional dipoles ($K = 1$) whenever $J_{\text{eff}} > 1/2$ [6,7].

Different occupations of the magnetic ion lead to distinct scenarios. In the case of $5d^1$, one finds $J_{\text{eff}} = 3/2$ GSM

that can be further split in two Kramers doublets by distortions of the cubic lattice. This scenario is exemplified by $\text{Ba}_2\text{NaOsO}_6$, where nuclear magnetic resonance (NMR) measurements revealed two distinct phase transitions as the temperature decreases [8]. The first transition, occurring around $T_q \sim 10$ K and often referred to as the “broken local point symmetry” (BLPS) phase, involves a structural distortion of the Os-O octahedra from cubic to lower symmetry, accompanied by the ordering of electric quadrupoles [8]. The second transition, detected at $T_N \sim 7$ K from both magnetization measurements, muon spin resonance (μSR) and NMR, is attributed to the onset of a canted antiferromagnetic phase with the net ferromagnetic moment aligned along the [110] direction [8,9]. Despite clear evidence from NMR, the exact nature of the BLPS phase remains elusive, as other experimental techniques have struggled to detect or characterize it [10–12], such that recent works proposed a dynamical Jahn-Teller effect as explanation for this apparent contradiction [13,14].

$\text{Ba}_2\text{CaOsO}_6$, as well as isoelectronic $5d^2$ osmates of the same family, present an equally intriguing puzzle. They exhibit a single phase transition into a state that breaks time-reversal symmetry (TRS), while lacking observable dipole magnetic moments and maintaining the cubic $\text{Fm}\bar{3}\text{m}$ symmetry [15–18]. In these systems, the $J_{\text{eff}} = 2$ GSM is split by a “remnant” octahedral CF (rcf) in an E_g non-Kramers doublet well separated in energy (10–20 meV) from the excited T_{2g} triplet (see Fig. 1). The E_g doublet lacks a dipolar moment but can host quadrupolar and octupolar moments. Theoretical and experimental works on

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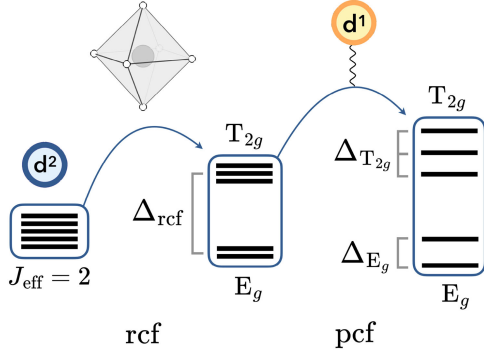


FIG. 1. Evolution of the fivefold degenerate d^2 GSM with $J_{\text{eff}} = 2$ (left) under the “remnant” octahedral crystal field (rcf) with $T_{2g} - E_g$ triplet-doublet splitting (middle) and the polaron crystal field (pcf) acting on the non-Kramers levels causing a further splitting (right).

$5d^2$ cubic osmates propose conflicting order parameters: either an antiferro ordering of electric quadrupoles (AFQ) [19,20], which would break cubic symmetry while preserving TRS, or a ferro-ordering of magnetic octupoles (FO) [15,18,21–24]. The latter provides a more consistent description of the experimental findings [15].

In this context, Cong *et al.* [25] obtained valuable data on the doping-driven transition from $5d^1$ to $5d^2$ in $\text{Ba}_2\text{Ca}_{1-\delta}\text{Na}_\delta\text{OsO}_6$ using magnetization measurements, μSR and NMR. They found the BLPS phase across all NMR-accessible Na concentrations followed, upon lowering the temperature, by a region of broken TRS, with the corresponding transition temperature T_o increasing as $\delta \rightarrow 0$. The persistence of the BLPS phase is ascribed to AFQ ordering, suggested to coexist with the AFM order up to $\delta = 0.1$. However, this interpretation conflicts with the full Ca limit ($\delta = 0$), where the E_g doublet forbids dipole moments and where the mutual exclusivity of the AFQ and FO phases leaves the origin of the broken TRS region unresolved.

From a theoretical perspective, Voleti *et al.* [26] applied a density functional theory (DFT) framework to $\text{Ba}_2\text{Ca}_{1-\delta}\text{Na}_\delta\text{OsO}_6$, finding that strain fields generated by dopant Na ions in the small $\delta \rightarrow 0$ limit suppress the FO transition temperature. Clusters of neighboring impurities are predicted to induce “parasitic” dipole moments on adjacent sites through T_{2g} strain fields. While these results offer valuable insight into the effects of local strain on the FO phase [23,26], they do not account for the reported formation of small polarons, which underlies the coexistence of different J_{eff} states [27].

Small polarons are quasiparticles arising from the lattice-assisted trapping of dopant charges [28]. In $\text{Ba}_2\text{Ca}_{1-\delta}\text{Na}_\delta\text{OsO}_6$ they promote the localization of states with distinct $5d^1$ and $5d^2$ electronic configurations, while keeping the system insulating at all δ [27]. Though mobile at high temperatures, they become static at the temperatures

relevant to multipolar orders. Hence, a set of static $5d^1$ polarons coupled by intersite exchanges to a matrix of $5d^2$ ions can give rise to novel ordered phases.

In this Letter we investigate the interplay of polarons and multipolar orders in $\text{Ba}_2\text{Ca}_{1-\delta}\text{Na}_\delta\text{OsO}_6$ close to the $5d^2$ limit ($\delta \leq 0.25$). Using a fully *ab initio* approach, we derive the microscopic Hamiltonian, incorporating mixed intersite exchange interactions (IEI) between $J_{\text{eff}} = 3/2$ and $J_{\text{eff}} = 2$ GSMs while accounting for CF and (hole) doping effects. Our key finding is that the dominant IEI between $5d^1$ polarons and the $5d^2$ matrix is actually antiferro-octupolar (AFO), resulting in the occurrence of AFO polaronic moments within the broader FO order. This octupolar reversal at the polaronic site is accompanied by small dipole moments appearing on its neighboring sites. The sign reversal stems from the distinct physical representations in the one-electron and two-electron manifolds of the relevant local operators in the t_{2g} space having opposite signs. The consequence is a sign change of $d^2 - d^1$ IEI with respect to the same coupling between ions of the same occupancy. Our predicted ordering temperatures show very good agreement with experimental measurements, particularly when the effects of polaron-induced structural distortions are included.

Effective Hamiltonian—The effective Hamiltonian of $\text{Ba}_2\text{Ca}_{1-\delta}\text{Na}_\delta\text{OsO}_6$ is specified by

$$H^J_{\text{eff}} = \sum_{\langle ij \rangle} \sum_{K_i K'_j} V_{K_i K'_j}^{QQ'}(ij) O_{K_i}^Q(i) O_{K'_j}^{Q'}(j) + \sum_i H_{\text{rcf}}^i + \sum_{i \in \text{pol}_{\text{NN}}} H_{\text{pcf}}^i. \quad (1)$$

Here the first summation (ij) runs over the Os-Os bond, and the second runs over the multipolar momenta of the ranks $K_i, K'_j = 1, 2, 3$ for $J_{\text{eff}} = 3/2$ (and 4 for $J_{\text{eff}} = 2$) with projections Q, Q' . The labels K_i and K_j represent the total angular momentum and site-dependent ranks $K(J_i)$ and $K(J_j)$, respectively, consequence of the site-specific GSM. For simplicity, we omit the i and j subscripts from now on. Finally, $H_{\text{rcf}}^i = V_{\text{rcf}}[O_4^0(i) + 5O_4^4(i)]$ is the rcf Hamiltonian, while $H_{\text{pcf}}^i = B_2^0 O_2^0(i) + B_2^2 O_2^2(i)$ is the polaron crystal field Hamiltonian induced by the localized d^1 charge on neighboring polaronic sites (see Fig. 1).

The J_{eff} -IEI constants $V_{K_i K'_j}^{QQ'}(ij)$ are calculated with the Force-Theorem in Hubbard-I (FT-HI) approach [29]. The FT-HI derives J_{eff} -IEI from the converged paramagnetic electronic structure obtained by DFT [30] + dynamical mean-field theory [31–34] in the Hubbard-I (HI) approximation [35]. We employ the latest version of the publicly available MagInt code, which implements the FT-HI IEI calculations for different electronic configurations and correlated environments [36]. The method, computational setup, and robustness of solutions with respect to input

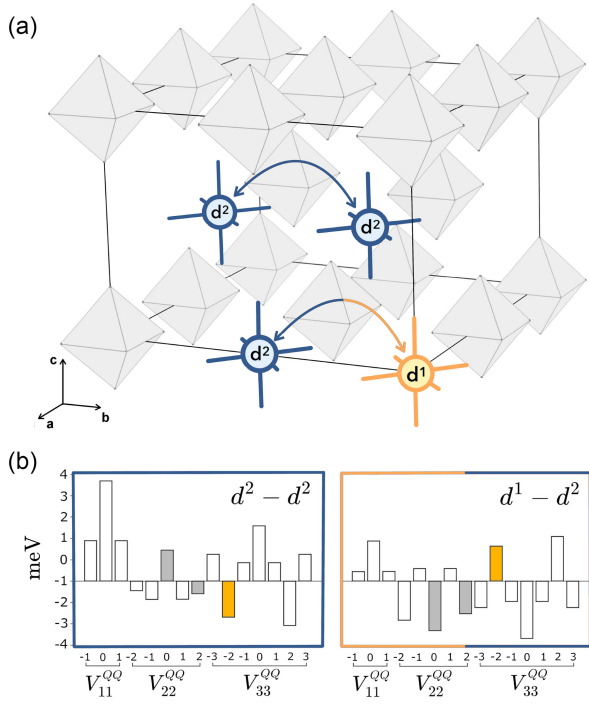


FIG. 2. (a) Used polaronic supercell. The IE paths connecting d^2-d^2 and d^1-d^2 are marked by the blue arrow and the combined blue and orange arrow, respectively. (b) Corresponding diagonal IIEI V_{KK}^{QQ} . The active components within the E_g GSM are indicated by filled colored bins, and the octupole-octupole IE V^{xyz} is highlighted in yellow. The full IIEI matrices are given in SM [37].

parameters are detailed in Supplemental Material (SM) [37] S1 and S2.

Polaron modeling in DFT + HI and crystal fields—Doping at low d^1 concentrations is modeled by employing the tetragonal supercell depicted in Fig. 2(a), containing 8 f.u. To disentangle structural effects from charge ones, we adopt the cubic structure of the pristine d^2 compound of Ref. [16] and account for hole-doping via the virtual crystal approximation with charge localization enforced at the DFT + HI level (see SM [37] S1). Calculations including explicit chemical substitutions for the same structure yield consistent results (see SM [37] S4).

We find that the overall level structure arising from the CF and SO effect is reproduced for both the d^1 and d^2 sites. On the d^1 site the calculated CF and SO splittings are found to be ≈ 4.65 eV and ≈ 0.46 eV, respectively, in good agreement with x-ray absorption near edge structure results and previous *ab initio* works [12,44]. On the d^2 sites the calculated rcf splitting of the $J_{\text{eff}} = 2$ GSM is found to be $\Delta_{\text{ref}} \approx 19$ meV, in very good agreement with specific heat measurements and previously reported DFT + HI calculations [15,21,24]. Both the E_g and T_{2g} manifolds undergo additional splittings induced by the polaron, which lowers the local O_h symmetry. These pcf splittings depend on their

orientation relative to the d^1 site: out-of-plane splittings reach $\Delta_{E_g} \sim 5$ meV and $\Delta_{T_{2g}} \sim 2$ meV, compared to in-plane values $\Delta_{E_g} \approx \Delta_{T_{2g}} \sim 1$ meV. Additional details, wave functions, and CF parameters are provided in SM [37].

Octupolar switching and its microscopic origin—Our calculated diagonal exchange constants V_{KK}^{QQ} are presented in Fig. 2(b) for d^2-d^2 and d^1-d^2 interacting bonds, as illustrated in Fig. 2(a), with the full J_{eff} -IEI matrices reported in SM [37]. As expected, mapping the d^2-d^2 J_{eff} -IEI onto the low-lying E_g subspace yields a dominant octupole-octupole interaction, $V_{33}^{\bar{2}\bar{2}} \equiv V^{xyz}$, in full agreement with the pristine d^2 compound [24]. However, a striking difference arises in the presence of polarons: while this coupling remains ferromagnetic for all d^2-d^2 bonds, it reverses sign and turns antiferromagnetic for d^1-d^2 bonds. This switching of the dominant multipolar channel demonstrates how the introduction of d^1 polarons reshapes the exchange landscape at a fundamental level, providing a microscopic origin for the destabilization of F $\bar{O}$ order and paving the way for competing multipolar phases.

To clarify the origin of this sign reversal, we perform a DFT + HI calculation without SO coupling in the spin + orbital t_{2g} basis. The corresponding effective multipolar t_{2g} -Hamiltonian is written as

$$H^{t_{2g}} = \sum_{\langle ij \rangle} \sum_{\substack{ss', ll' \\ \alpha\alpha', \beta\beta'}} I_{ss', ll'}^{\alpha\alpha', \beta\beta'}(ij) \tau_{s,l}^{\alpha,\beta}(i) \tau_{s',l'}^{\alpha',\beta'}(j), \quad (2)$$

where the second summation runs over the spin (s, s') and orbital (l, l') ranks with components (α, α') and (β, β'), respectively, and $\tau_{s,l}^{\alpha,\beta} = S_s^\alpha \otimes L_l^\beta$ are normalized spin + orbital multipolar operators [6]. The t_{2g} -shell-mediated IIEI couplings (t_{2g} -IEI) $I_{ss', ll'}^{\alpha\alpha', \beta\beta'}(ij)$ were computed within the FT-HI approach.

Although the t_{2g} -IEI are not straightforward to interpret, they can be linked to the $V_{KK}^{QQ'}$ by SO-projection onto the J_{eff} many-electron bases. Specifically, we find that the relevant t_{2g} -IEI contributing to V^{xyz} are the diagonal $I_{11,22}^{zz,(xy)(xy)}$ terms, coupling dipole spin (z) and orbital quadrupole (xy), and corresponding permutations ($\alpha = x, \beta = yz$), ($\alpha = y, \beta = xz$).

Our SO-projection reproduces the correct sign of all J_{eff} -IEI for both d^2-d^2 and d^1-d^2 bonds, but with reduced magnitude beyond dipole-dipole terms, likely due to neglecting of SOC in excited d^1 and d^3 states. Crucially, the sign reversal between the d^1-d^2 and d^2-d^2 bonds already appears in the $I_{11,22}^{\alpha\alpha', \beta\beta}$ couplings, showing that this effect is not induced by SO coupling. Specifically, it originates from the different representations of the one-electron t_{2g} -shell operators in the many-electron d^1 and d^2 bases: the one-electron t_{2g} -shell operators with ($s = 1, l = 2$) acquire a minus sign when expressed in the d^2

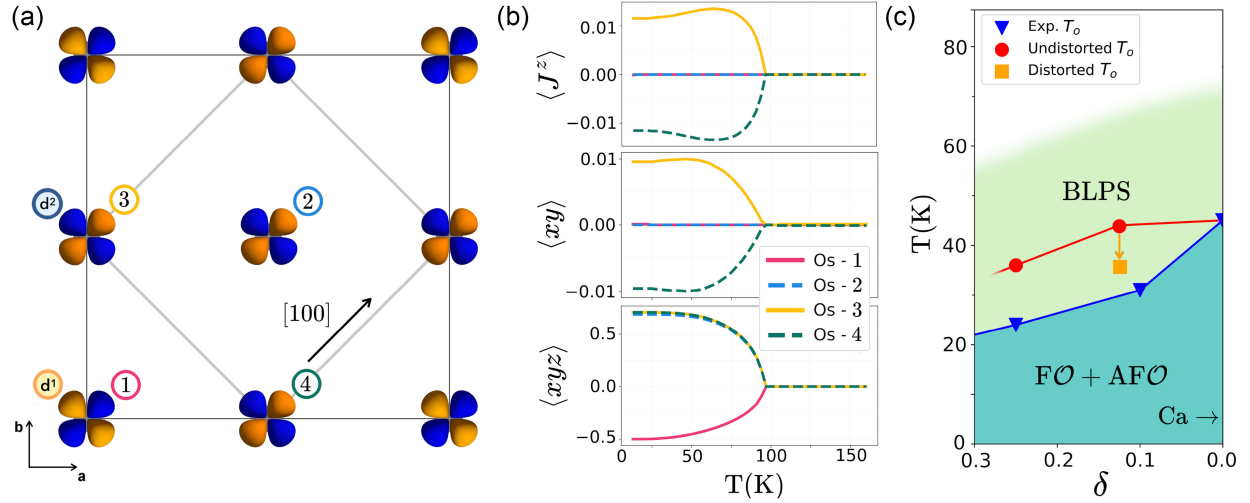


FIG. 3. (a) $F\mathcal{O}$ and $AF\mathcal{O}$ order in $Ba_2Ca_{1-\delta}Na_\delta OsO_6$ in the supercell used (top view). The labels 1-4 are related to the subfigure (b), where the MF values of dipole J^z , quadrupole xy , and octupole xyz are shown as function of temperature. (c) Evolution of the ordering temperature T_o with doping for the experimental data (blue triangles) and the undistorted cubic structure (red circles). The temperature shift at $x = 0.125$ arising from polaronic structural distortions is indicated by the orange square.

many-electron Hilbert space. This sign switch is compensated on $d^2 - d^2$ bonds but remains explicit on $d^1 - d^2$ ones (see End Matter for the detailed derivation).

Finally, to clarify the physical meaning of the spin + orbital $\tau_{s,l}^{\alpha,\beta}$ operator, we express $\tau_{0,2}^{0,\beta}$ in terms of one-electron occupancy operators $n_{\gamma,\delta}$ of the t_{2g} shell, as is standard in model Hamiltonian methods [45–48]. We find $\tau_{0,2}^{0,xy} \propto n_{xz,yz} + n_{yz,xz}$ with $n_{yz,xz} = i(c_{yz}^\dagger c_{xz} - c_{xz}^\dagger c_{yz})$, highlighting the role of intraorbital mixing in the emergence of high-rank multipolar phases.

Ordered phase—We solve the full effective Hamiltonian of Eq. (1), incorporating both d^1 and d^2 sites, within the single site mean field (MF) approximation using the “McPhase” package [49] together with an in-house module. To simplify the treatment of mixed-valence interactions, we exclude the couplings to hexadecapole operators ($K = 4$) present in both $d^1 - d^2$ and $d^2 - d^2$ J_{eff} -IEI, as these contributions are expected to be negligible.

We find two second-order phase transitions occurring at $T_o \sim 93$ K and $T \sim 4$ K. While we do not discuss the latter in detail here, as its very low temperature in MF makes it less significant, additional details are provided in SM [37] S3. The first transition is noteworthy and leads to a complex order that combines a $F\mathcal{O}$ order of xyz octupoles on all sites except on the polaronic one, where the xyz octupole is $AF\mathcal{O}$ ordered [see Fig. 3(a)]. Additionally, the polaronic nearest neighbors in the a - b plane develop small AF magnetically ordered dipole moments of $\approx 0.01\mu_B$. These are oriented along the z axis and accompanied by the ordering of t_{2g} electric quadrupoles with xy character [see Fig. 3(b) for the MF values].

Thus, both T_{2g} distortions induced by dopants [23] and polaronic charges alter the $J_{\text{eff}} = 2$ CF to an extent that

parasitic dipole moments emerge. Interestingly, despite the stronger out-of-plane $\Delta_{T_{2g}}$ splitting compared to the in-plane one, no dipoles form on the out-of-plane sites. This is attributed to the ground state wave functions, which do not couple to the first T_{2g} excited state via the z -dipole operator (see SM [37] S3).

It is worth noting that within the $5d^1 J_{\text{eff}} = 3/2$ manifold all multipolar degrees of freedom are, in principle, active and can order. Our results demonstrate that the ref on the d^2 sites quenches all multipolar IE channels except those allowed within the E_g doublet, thereby imposing an “effective” CF on the polaronic site.

Ordering temperature evolution—We investigate how hole doping affects the transition temperature in $Ba_2Ca_{1-\delta}Na_\delta OsO_6$. The outcome is not obvious *a priori*: although the $d^1 - d^2$ J_{eff} -IEI interactions can be up to $\sim 80\%$ weaker than in the pristine d^2 case [24], the V^{xyz} coupling remains comparable (see SM [37] S3).

To track the evolution of the ordering temperature, we compute the J_{eff} -IEI at higher Na concentration $\delta = 0.25$. Two distinct polaron geometries are considered, with the extra d^1 charge residing either in-plane (next-nearest neighbor) or out-of-plane (nearest neighbor). The corresponding MF solutions confirm the robustness of octupolar order against charge doping at these low Na concentrations, with two $AF\mathcal{O}$ ordered polarons stabilized in each configuration. Notably, the undistorted results already reproduce the overall experimental trend [Fig. 3(c), red circles], where the MF transition temperature has been rescaled to match the experimental T_o at $\delta = 0$. The overestimation by approximately 57% is consistent with the approximations employed (DFT + HI, MF) and in line with previous applications of this method [24,50].

The reduction of T_o upon doping arises from a subtle interplay of several factors: polaron-induced changes in the $E_g - T_{2g}$ ref splittings; modifications of the pcf at higher δ , slightly weakened xyz IE; and the different multiplicity of the magnetic ion's GSMs within the supercell (see End Matter).

Structural distortions are also expected to play an essential role since polaron localization necessarily involves local lattice relaxation. To examine this effect, we performed a full relaxation of the structure for $\delta = 0.125$ using the Vienna *Ab Initio* Simulation Package [51] within the constrained DFT + U method. The on-site density matrices were initialized with the combined $F\bar{O} + AF\bar{O}$ configuration, as obtained at the DFT + HI level. The approach, detailed in Ref. [52] and summarized in SM [37] S1, accurately captured high-rank multipolar phases in DFT. From the optimized distorted structure we computed J_{eff} -IEI and the ground-state properties within FT-HI. At the MF level, we recover the previously identified $AF\bar{O}$ polaron embedded in the $F\bar{O}$ matrix, albeit with stronger parasitic dipole moments, now distributed across all osmium sites (see SM [37] S5).

Including polaron-induced structural distortions improves the agreement with experiment by a large extent [Fig. 3(c), orange square]. Such distortions are expected to become increasingly important at higher doping levels, a regime whose proper treatment would require a larger supercell both to avoid spurious interactions with periodic images and to address polaron-polaron interactions. These refinements, together with explicit accounting of chemical substitution and averaging over several distributions of Na dopants, along the lines of Ref. [26], could bring the computed T_o to an even closer quantitative agreement with experiment.

Conclusions—To bridge the distinct physical regimes of $5d^1$ and $5d^2$ double perovskites and connect their different J-effective multipolar phases, we derived and solved from first principles the effective Hamiltonian of $\text{Ba}_2\text{Ca}_{1-\delta}\text{Na}_\delta\text{OsO}_6$, explicitly accounting for polaronic charges at low Na-doping levels through material-specific DFT calculations. Our analysis demonstrates a polaron-induced reversal of the dominant octupolar exchange, originating from different representation of t_{2g} -shell spin + orbital operators in one-electron and two-electron bases. This reversal of the octupolar IEI provides direct evidence for a coupling between polaronic degrees of freedom and magnetic interactions, an effect not previously reported. It is expected that polarons can reshape the magnetic landscape also in the opposite regime of low Ca doping. In fact, while the dominant dipole-dipole interactions do not switch sign, specific quadrupole-quadrupole interaction do, notably the z^2 component, explicitly observed to order in other $5d^1$ double perovskites [53]. Moreover, vibronic couplings between the Jahn-Teller active E_g doublet and the $J_{\text{eff}} = 3/2$ GSM may promote novel hidden quadrupolar

phases. Taken together, these findings go beyond explaining the experimentally observed suppression of the ordering temperature with doping and open a pathway to designing and controlling novel quantum orders in spin-orbit systems through charge doping.

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Data availability—The data that support the findings of this Letter are openly available. Additional data can be provided upon request.

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End Matter

From t_{2g} - to J_{eff} -Hamiltonian—The t_{2g} -Hamiltonian of Eq. (2) is defined in the spin + orbital many-electron basis states $|\tilde{\Gamma}(i)\rangle$, which, for the two-electron case, belong to the Hund’s rule GSM with the degeneracy $(2l + 1)(2S + 1) = 9$ for $S = 1$ and $l = 1$. The corresponding intersite exchange interactions (t_{2g} -IEI) can be downfolded onto the J_{eff} many-electron basis $|\Gamma(i)\rangle$. Here i is the magnetic site index (1 for d^1 and 2 for d^2 for simplicity). To this end, we introduce the projector operator $P_{LS}(i) = |\Gamma(i)\rangle\langle\tilde{\Gamma}(i)|$, such that any many-electron t_{2g} -shell operator $\tau_{s,l}^{\alpha,\beta}$ can be J_{eff} -projected as

$$\tilde{O}_{s,l}^{\alpha,\beta}(i) = P_{LS}(i)\tau_{s,l}^{\alpha,\beta}(i)P_{LS}^\dagger(i). \quad (\text{A1})$$

The multipole many-electron operators O_K^Q are expanded in terms of the projected operators through coefficients

$c_{sa,l\beta}^{KQ}(i) = \text{Tr}[\tilde{O}_{s,l}^{\alpha,\beta}(i)O_K^Q]$. Specifically, for the $(K, Q) = (3, -2)$ component, corresponding to the xyz octupole in Cartesian coordinates, this expansion yields the values listed in Table I for both d^1 and d^2 configurations.

TABLE I. Expansion coefficients for the octupolar operator O_3^{-2} in the spin + orbital basis.

Spin+orbital operator		$c_{sa,l\beta}^{KQ}$	
s, α	l, β	d^1	d^2
1, x	2, yz	−0.5757	−0.3826
1, y	2, xz	−0.5757	−0.3826
1, z	2, xy	0.5757	0.3826

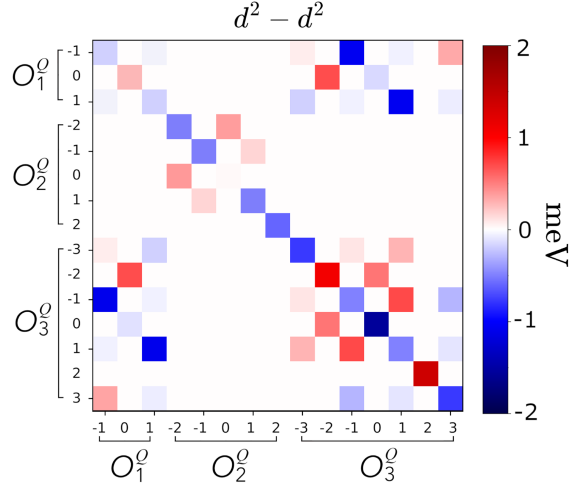


FIG. 4. Difference between the SO-projected t_{2g} -IEI and the IEI with DFT + SO for the $d^2 - d^2$ interaction bond $\mathbf{R}_{ij} = [0, 0.5, 0]$ in the supercell reference frame.

The J_{eff} -IEI are then obtained by contracting these coefficients with the original interaction matrix elements:

$$V_{KK'}^{QQ'}(ij) = \sum_{s,l} \sum_{\alpha,\beta} I_{ss',ll'}^{\alpha\alpha',\beta\beta'}(ij) c_{sa,l\beta}^{KQ}(i) c_{sa,l\beta}^{K'Q'}(j). \quad (\text{A2})$$

The difference between the resulting SO-projected t_{2g} -IEI matrix and the initial J_{eff} -IEI is shown in Fig. 4. The SO-projected IEI reproduce the overall structure (see SM [37]), with excellent agreement in the dipole-dipole channels, while higher-order multipolar terms are systematically underestimated. For instance, the octupole-octupole coupling V^{xyz} is ~ -0.6 meV for the $d^2 - d^2$ bond, compared to the expected -1.6 meV. This discrepancy likely originates from neglecting SO coupling in the excited d^1 and d^3 configurations in the superexchange processes, though further investigation is required.

Origin of sign switch—As mentioned in the main text, we observe a reversal of the IEI already without SO coupling and within the t_{2g} -shell treatment. This is shown in Table II, where the t_{2g} -IEI are written, for the t_{2g} -shell operators leading to the V^{xyz} coupling.

To understand the origin of the sign switch, we compute the matrix elements of the d^1 one-electron t_{2g} -shell operator $\tau_{s,l}^{\alpha,\beta}(1)$ in the many-electron d^2 spin + orbital basis via

$$[\tau_{s,l}^{\alpha,\beta}(2)]_{MM'} = \langle \tilde{\Gamma}(2)M | \tau_{s,l}^{\alpha,\beta}(1) | \tilde{\Gamma}(2)M' \rangle. \quad (\text{B1})$$

We then express the resulting operator in terms of d^2 many-electron operators $\tau_{s',l'}^{\alpha',\beta'}(2)$ by fitting its components through $t_{ss',ll'}^{\alpha\alpha',\beta\beta'} = \text{Tr}[\tau_{s',l'}^{\alpha',\beta'}(2) T_{s,l}^{\alpha,\beta}(2)]$. In the expansion, we find the correct matrices of 2-electrons operators ($s = s', l = l', \alpha = \alpha', \beta = \beta'$), but with different signs for different components: (i) $t_{ss,ll}^{\alpha\alpha,\beta\beta} = -1$ for $(s, l) = (0, 2)$,

TABLE II. t_{2g} -IEI couplings for $\tau_{s,l}$ with $(s, l) = (1, 2)$, i.e., spin-dipole and orbital-quadrupole operators. The corresponding (α, β) components are listed. These couplings project onto the spin-orbit V^{xyz} octupole-octupole intersite exchange. Values are reported for $\mathbf{R}_{ij} = [0, 0.5, 0]$ in the supercell reference frame of Fig. 2(a).

	$d^2 - d^2$			$d^1 - d^2$		
	$x; yz$	$y; xz$	$z; xy$	$x; yz$	$y; xz$	$z; xy$
$x; yz$	-2.62			2.97		
$y; xz$		-2.62			2.97	
$z; xy$			1.23			-1.39

i.e., for pure orbital-quadrupole terms, and (ii) $t_{ss',ll'}^{\alpha\alpha,\beta\beta} = 1$ for both $(s, l) = (0, 1)$ dipole-orbital terms and $(s, l) = (1, 0)$ spin-dipole terms. The sign reversal thus arises in cases where multiplicative contributions remain uncompensated, for instance, when a spin-dipole coupled to an orbital-quadrupole on a d^2 site interacts with the corresponding spin-dipole orbital-quadrupole term on a d^1 site.

Mean field analysis of T_o —A detailed analysis of the evolution of T_o with Na concentration is necessary. As discussed in the main text, the V^{xyz} octupolar interaction changes only weakly between $x = 0$ and $x = 0.125$. Yet the ordering temperature decreases noticeably, especially at higher doping levels ($x = 0.25$) in the undistorted cubic structure. Interestingly, at these Na concentrations,

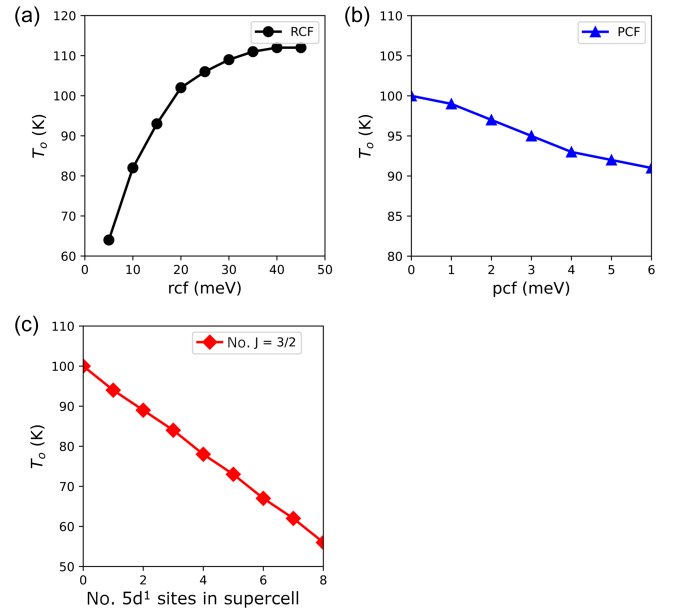


FIG. 5. Mean-field ordering temperature T_o as a function of (a) remnant crystal field (rcf) within the $J_{\text{eff}} = 2$ ground state multiplet (GSM), and (b) polaron crystal field (pcf) for the IEI computed in the full d^2 BCOO compound. (c) T_o as a function of the number of hole-polarons ($J_{\text{eff}} = 3/2$ GSMs) in the supercell with only the V^{xyz} octupole-octupole IEI active.

despite the sign change in the IEI, the system remains nonfrustrated: reversing both the interactions and the order parameters leaves the total energy unchanged.

To isolate the microscopic origin of the lowering of T_o upon Na doping, we performed a *gedankenexperiment* in which we fixed IEI for the FO ordered pristine case ($\delta = 0$), while varying the rcf and pcf splittings incrementally [see Figs. 5(a) and 5(b)]. The results show a strong dependence of T_o on the rcf, saturating at ~ 45 meV to ≈ 112 K and decreasing to roughly half the value when the rcf is reduced to ~ 6 meV. Any lower rcf makes the T_{2g} levels magnetically active and promotes dipolar order. By contrast, the pcf exerts only a weak, nearly linear influence: increasing it up to 6 meV lowers T_o by only a few percent. Higher values were not explored as stronger pcf terms would induce significant T_{2g} mixing in the E_g doublet and alter the qualitative physics.

While variations in the rcf and pcf account for part of the observed suppression of T_o , they do not capture the full picture. An additional factor is the difference in the total angular momentum GSMs between the d^2 ($J_{\text{eff}} = 2$) and d^1 ($J_{\text{eff}} = 3/2$) configurations. Indeed, as seen in

Fig. 5(a), even for rcf values of ~ 20 meV, the $J_{\text{eff}} = 2$ GSM does not yet fully project onto a pseudospin-1/2 subspace, with clear implications in the ordering behavior.

To assess the effect of GSM mismatch, we performed a second *gedankenexperiment* in which all intersite exchange interactions except the octupole-octupole V^{xyz} were set to zero. The doping concentration was then varied by progressively substituting d^2 sites with d^1 ones, effectively replacing the $J_{\text{eff}} = 2$ GSM (with its ~ 20 meV rcf) by the $J_{\text{eff}} = 3/2$ GSM [Fig. 5(c)]. This procedure preserves the stability of the FO solution across all doping levels and isolates the role of the GSMs. The resulting T_o decreases linearly with increasing d^1 concentration, again in agreement with the trend observed both in our calculations and in experimental observations.

Additional mechanisms, such as static or dynamic Jahn-Teller effects on the d^1 polarons or $d^1 - d^1$ quadrupole-quadrupole dimerization and dopant-induced strains may also affect the ordering temperature, but their investigation is beyond the scope of the present Letter.