

Revisiting Jahn-Teller transitions in correlated oxides with Monte Carlo modeling

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 (Received 2 February 2026; revised 18 June 2026; accepted 18 August 2026; published 22 September 2026)

Jahn-Teller (JT) distortions are a key driver of physical properties in many correlated oxide materials. Cooperative JT distortions, in which long-range orbital order reduces the symmetry of the average structure, are common in JT-distorted materials at low temperatures. This long-range order will often melt on heating via a transition to a high-temperature state without long-range orbital order. The nature of this transition has been observed to vary with different materials depending on crystal structure; in LaMnO_3 , the transition has generally been interpreted as order-disorder, whereas in layered nickelates ANiO_2 ($A = \text{Li, Na}$), there is a displacive transition. However, authors of recent theoretical work have suggested that previous evidence for order-disorder may in fact be a consequence of phonon anharmonicity rather than persistence of JT distortions. In this work, we run Monte Carlo simulations with a simple Hamiltonian that is modified to include terms dependent on the JT amplitude ρ , which is allowed to vary within the simulation. Our simulations yield distributions of JT amplitudes consistent with displacive rather than order-disorder behavior for both perovskites and layered nickelates. We also find significant differences between the transition observed for perovskites compared with layered nickelates, which we attribute to differing extensivity of configurational entropy on the two lattices, suggesting a crucial role for lattice geometry in determining behavior.

DOI: [10.1103/chbx-wzvl](https://doi.org/10.1103/chbx-wzvl)

I. INTRODUCTION

Transition metal oxide octahedra with electronic configurational degeneracy are susceptible to a Jahn-Teller (JT) distortion [1–7], causing their shape to deviate from that of a regular octahedron. Such distortions most commonly manifest as a linear superposition of the $E_g(Q_2, Q_3)$ van Vleck modes [8,9], where Q_2 and Q_3 are planar rhombic and tetragonal distortions, respectively, although the tetragonal Q_3 component tends to dominate. JT distortions have been observed in both molecules [6] and crystals [7]. The JT distortion is relevant to many phenomena including superconductivity in the cuprates [10–12], spin-orbit ordering [13], and ionic mobility [14,15], and can lead to structural transitions on electrochemical cycling in battery electrode materials [14–16].

Within solids, the axes of octahedral elongation can correlate via orbital ordering over macroscopic length scales as a cooperative JT (cJT) distortion, typically manifesting as a decrease in unit-cell symmetry [5,7]. For instance, the perovskites KMnF_3 ($M = \text{Cr, Cu}$) [17,18], LaMnO_3 [19], and $[(\text{CH}_3)_2\text{NH}_2]\text{Cu}(\text{HCOO})_3$ [20] exhibit a cJT distortion with alternating MO_6 ($M = \text{Cu, Cr, V, Mn}$) octahedra elongated

along two orthogonal directions within the xy plane, as shown in Fig. 1(a). Such planes generally show C-type stacking along the c direction, in which adjacent planes have the same orbital ordering [17,19,21,22]. Interestingly, similar orbital ordering driven by t_{2g} orbitals is seen in the vanadate perovskites AVO_3 ($A = \text{Ho, La, Y}$) [21–24], although on heating to high temperatures, some (such as LaVO_3 and YVO_3) have been shown to exhibit out-of-phase stacking along the c direction [23–25] (Fig. S1 in the Supplemental Material [26]). The flexibility of the perovskite structure means that other kinds of ordering can also be exhibited; for instance, $\text{Ba}_{0.5}\text{La}_{0.5}\text{CoO}_3$ exhibits collinear elongational cJT ordering of the CoO_6 octahedra when the La/Ba is disordered [27] but compressive collinear ordering when the La/Ba is ordered [28] (Fig. S2 in the Supplemental Material [26]).

The cJT distortions also occur in the layered triangular-lattice nickelate NaNiO_2 [29–35], where diffraction shows a collinear ordering in which NiO_6 octahedra within each layer elongate along a common axis that is preserved from layer to layer [Fig. 1(b)]. By contrast, the electronic structure of LiNiO_2 has long remained under debate, with the as-synthesized material typically not showing a comparable cJT distortion [29,36–38]. This has been attributed to suppression of long-range orbital order by Ni/Li site mixing and related defects [38–41]. Experimental evidence from neutron total scattering [37] and x-ray absorption spectroscopy [42] has shown that JT distortion likely occurs locally in conventional LiNiO_2 , without long-range order. An alternative explanation is charge disproportionation, for which there is evidence from both computational studies [43–45] and x-ray

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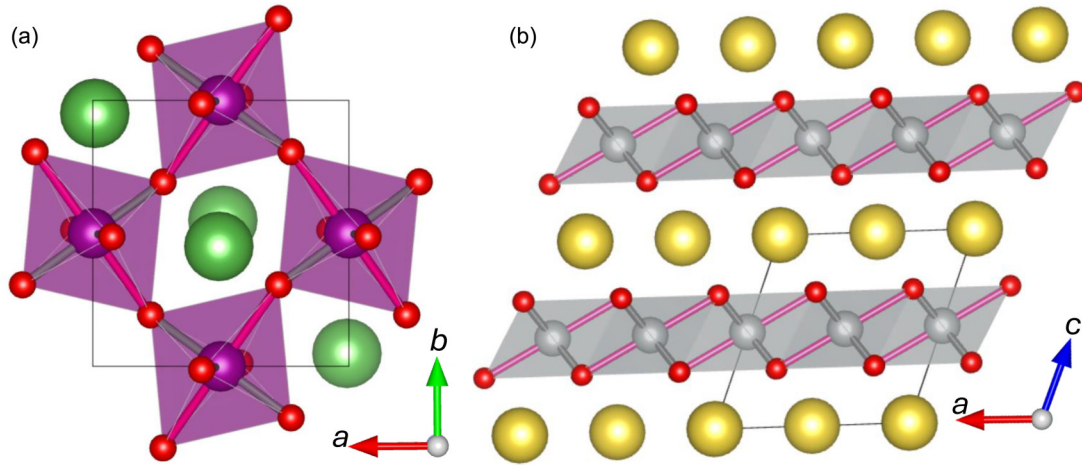


FIG. 1. The room-temperature crystal structures and JT ordering of (a) many JT-ordered perovskites such as KCuF_3 and LaMnO_3 [13], corresponding to phase 5 of the phase diagram of Ahmed and Gehring [81], and (b) layered nickelates such as NaNiO_2 and stoichiometric LiNiO_2 [29,39]. The stacking in (a) is commonly termed C-type orbital order. Pink metal-oxygen bond lengths indicate JT-elongated bonds. Only octahedra associated with JT-active sites are displayed. In the perovskites, purple sites are the JT-distorted sites (i.e., Mn, Cu, Cr), and green sites are the A sites (i.e., La, K). In the nickelates, gray sites are Ni^{3+} , and yellow sites are alkali metal.

absorption spectroscopy measurements [45–47] by analogy to layered silver nickelate [48,49] and nickelate perovskites [50–52]. Authors of more recent studies of carefully prepared stoichiometric LiNiO_2 have reported evidence for a collinear cJT distortion similar to that of NaNiO_2 [39].

Beyond perovskites and layered nickelates, JT-driven orbital order occurs in a range of other materials. The K_2PtCl_6 -type material $(\text{NO})_2\text{VCl}_6$, which has a compressive—not elongational—distortion, exhibits a collinear cJT distortion within the ab plane, but the axis of octahedral compression alternates with layer stacking [53]. The spinels Mn_3O_4 [54], LiMn_2O_4 [55], MgMn_2O_4 [56], and ZnMn_2O_4 [57] (Fig. S4 in the Supplemental Material [26]); wolframite CuWO_4 [58]; Prussian Blue analogs such as $\text{CuPt}(\text{CN})_6$ [59] and $\text{K}_2\text{Cu}[\text{Fe}(\text{CN})_6]$ [60]; and Ruddlesden-Poppers such as A_2CuF_4 ($A = \text{Na}, \text{K}$) [61,62] all exhibit simple collinear cJT distortions, although a pressure-induced change in cJT ordering has been observed in Na_2CuF_4 [62]. The distorted trirutile CuSb_2O_6 [63] also exhibits intraplanar collinear ordering, but alternating ab planes exhibit different axes of elongation. There is clearly a wide range of possible orbital orderings which may be energetically favorable, depending on the geometry of the octahedral interactions and the JT-active cation.

Heating materials with a cJT distortion will often result in a symmetry-raising transition. In many perovskites, an order-disorder transition has been reported, in which JT distortions persist locally in octahedra even when cJT distortions are suppressed. For example, the canonical orbital-ordered material LaMnO_3 shows the melting of long-range orbital order around $T_{\text{JT}} \approx 750 \text{ K}$ [64–76]. Local structure probes such as neutron total scattering [67,73] and extended x-ray absorption fine structure (EXAFS) [70] have typically been interpreted as showing that distortions persist locally within octahedra and correlate over short length scales. KCrF_3 shows a similar transition in crystal symmetry above $\sim 973 \text{ K}$ [77], which is likewise proposed to be order-disorder [77] by analogy to LaMnO_3 . Surprisingly, the isostructural KCuF_3 shows no sign

of the melting of orbital order below its decomposition temperature [78].

In addition to perovskites, there are reports of order-disorder transitions in other systems. The spinel LiMn_2O_4 , although a complex case due to mixed-valence Mn, exhibits a subtle tetragonal $\rightarrow$ cubic JT transition which appears to be order-disorder based on Mn K -edge x-ray absorption spectroscopy [55]. Electron spin-resonance measurements on CuSb_2O_6 have indicated persistence of local JT distortions through the JT transition [79], suggesting an order-disorder transition.

In orbital disordered phases, the cJT distortions are generally suppressed due to the additional thermal energy in the system [5]. Expansion of the crystal lattice weakens the effective interaction between local JT centers mediating cooperativity, reducing the enthalpy gain associated with orbital ordering. Increasing thermal energy also enables octahedra to dynamically cycle through axes of elongation corresponding to different local energy minima, which would suppress a time-averaged cJT distortion *via* a dynamic JT fluctuation [80]. Additionally, free energy becomes dominated by entropic contributions over enthalpic contributions on heating, and so enthalpy minimization due to cJT will be less of a factor in determining the crystal structure [81]; this is important, as there may be significant configurational entropy associated with orbital disorder depending on the geometry of the lattice in question [34]. The common interpretation of JT transitions as order-disorder can therefore be explained in terms of maximizing configurational entropy at high temperature.

The nature of the JT transition in the previously discussed layered nickelate materials has attracted much interest [33–35,39,41,82]. Computational work based on Monte Carlo simulations integrated with density functional theory (DFT) [82] identified that, although the parameter phase space for layered nickelates can accommodate both an order-disorder and a displacive transition, an order-disorder transition is more likely, as in previously studied JT transitions [82]. However, more recently, in x-ray

absorption spectroscopy [34,83], neutron total scattering [34], and *ab initio* molecular dynamics simulations [34,41], layered nickelates exceptionally exhibited displacive JT transitions, in which there is no minimum in the free-energy landscape associated with JT distortions above the transition temperature. This was attributed [34] to the subextensive configurational entropy associated with orbital disorder on a two-dimensional (2D) triangular lattice in which the axes of elongation are geometrically constrained by the chemical instability associated with having multiple axes of elongation pointing at a common O anion. In contrast, we note that evidence for an order-disorder transition in nonstoichiometric LiNiO_2 with site mixing has also been reported from x-ray absorption spectroscopy measurements [83].

While the observation of displacive behavior in nickelates appeared exceptional at the time it was reported, authors of a recent study [84] have shown that experimental total scattering data for the LaMnO_3 case can be reproduced without well-defined and prevalent octahedral elongations. This would indicate that dynamics, rather than configurational entropy, is the key driver of behavior through JT transitions. This raises the possibility that displacive JT transitions are more common than previously assumed and that many historical assignments of order-disorder character may warrant re-examination.

The cJT distortion in perovskites was previously studied using Monte Carlo simulations by Ahmed and Gehring [81], which were applied to the case of LaMnO_3 [85,86]. In their model, an anisotropic Potts variable on each site successfully reproduced the cJT ordering at room temperature in LaMnO_3 [81,85] and the dependence of lattice parameters on temperature through the JT transition [86]. However, their simple model did not include amplitudes of JT distortion or the possibility of JT-undistorted MnO_6 octahedra, and so an order-disorder transition was implicitly built into the model. More recently, Tragheim *et al.* [76] developed a more complex model in which JT amplitude may vary as a consequence of the octahedral tilts and shapes, which are the varying parameters; however, they did not apply this directly to the temperature-induced JT transition.

For the layered nickelates, Radin *et al.* [82] used an anharmonic vibrational Hamiltonian with continuous JT modes and Monte Carlo sampling, parametrized from DFT. Unlike the model of Ahmed and Gehring, this more complex approach [82] contains a regime in the phase space of starting parameters, termed the *stiff-lattice regime*, which can lead to displacive behavior. However, they predicted that layered nickelates would occur in the soft-lattice regime where order-disorder transitions are predicted by the Monte Carlo simulations.

In the present work, we extend the relatively simple model of Ahmed and Gehring with variable amplitude ρ of JT distortion on each site and a single-ion term in the Hamiltonian to simulate the enthalpy saving associated with JT distortion. Using this model, we simulate the JT transitions in perovskites such as LaMnO_3 . We then develop a similar simple model for the layered nickelates.

We find that the mean magnitude of JT distortion decreases through the transition but remains nonzero, with the high-temperature magnitude being larger in the perovskite lattice than the 2D nickelate lattice, consistent with experimental

results which are interpreted in terms of an order-disorder transition. However, the distribution of values of JT magnitude does not resemble that at low temperatures. For an order-disorder transition, we would expect to see a well-defined peak in the distribution at finite, nonzero ρ , with negligible density at $\rho = 0$. Instead, we see little preference for any particular ρ value at high temperatures for perovskites, which appears consistent with dynamic exploration of the $E_g(Q_2, Q_3)$ phase space. Our findings therefore suggest that a Potts-like model with variable JT amplitude is consistent with the interpretation of Batnaran *et al.* [84], in which the high-temperature JT phase departs from the conventional order-disorder picture of persistent local distortions. Our model provides a minimal framework for exploring departures from the fixed-amplitude order-disorder limit.

II. METHODOLOGY

A. Hamiltonian

We define a global classical Hamiltonian, for a system with N JT-active octahedra, as follows:

$$H = E_{\text{single-ion}} + E_{\text{geometric}}. \quad (1)$$

1. Single-ion term

In this Hamiltonian, $E_{\text{single-ion}}$ is the enthalpic impetus to JT distortion. It is defined following a Landau-like second-order expansion of the free energy [5] thus:

$$E_{\text{single-ion}} = \sum_i^N [\alpha \rho_i^2 + \beta \rho_i^4], \quad (2)$$

in which ρ_i is the magnitude of the JT distortion at the i th JT-active site. Here, α and β are empirical parameters which determine the functional dependence of enthalpy on ρ . We require $\alpha < 0$ and $\beta > 0$ for a stable minimum. In the simulations presented here, where variable-magnitude ρ is enabled, $\alpha = -1$ and $\beta = 1/2$, with the ratio $\beta = -\alpha/2$ chosen arbitrarily so that $E_{\text{single-ion}}$ is minimized when $\rho = 1$. The magnitudes of α and β place $E_{\text{single-ion}}$ approximately on the same energy scale as $E_{\text{geometric}}$. In Sec. S5 in the Supplemental Material [26], we show that increasing or decreasing the value of α relative to $E_{\text{geometric}}$ does not impact broader conclusions, but may lead to insensible behavior at low temperatures.

2. Geometry term

The $E_{\text{geometric}}$ term is defined uniquely based on the structure in question. For the case of perovskites, this $E_{\text{geometric}}$ term is equivalent to the anisotropic Potts model Hamiltonian defined by Ahmed and Gehring [81,85,86], reproduced as follows over a deduplicated list of all nearest-neighbor JT-active pairs i, j :

$$E_{\text{geometric}}^{\text{perovskite}} = \frac{1}{2} \sum_{\langle i, j \rangle} w(\rho_i, \rho_j) J_{S_i}(\hat{\mathbf{e}}_{ij}) \delta_{S_i, S_j}. \quad (3)$$

In this equation, S_i is the direction of octahedral elongation at JT-active B -site cation i , representing the orbital state of the JT-active B -site cation; it can take one of three possible values: δ_{S_i, S_j} is the Kronecker delta which enforces that only

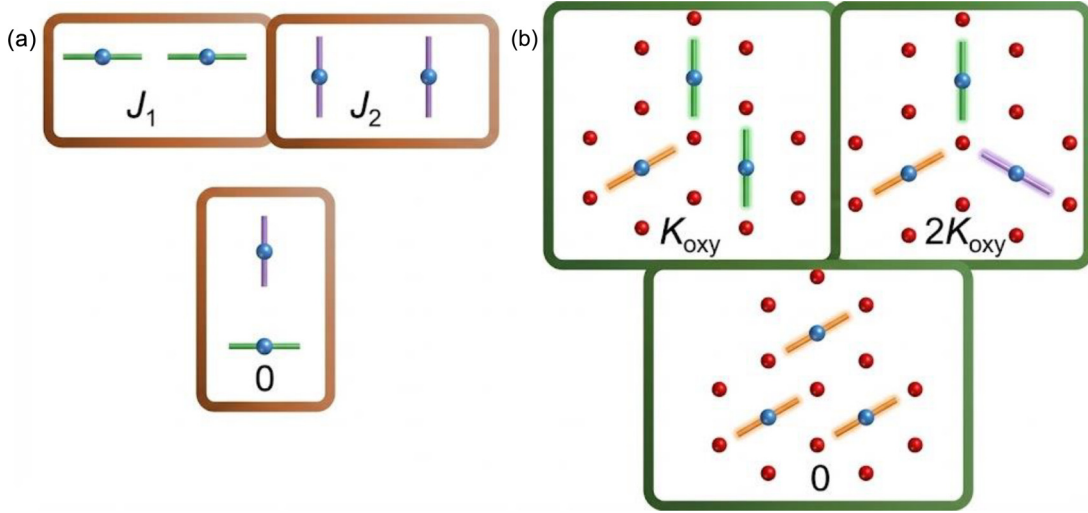


FIG. 2. Diagram showing the JT configurations associated with zero and nonzero geometric energies as used in Eqs. (3) and (5). (a) The case for perovskites, which is a reproduction of the Potts model of Ahmed and Gehring [81,85,86]. (b) The case for intralayer nearest-neighbor NiO_6 octahedra within layered nickelates assuming all sites have $\rho = 1$. Blue solid circles indicate JT-active sites, red solid circles (for the layered nickelate case) indicate O atoms, and solid lines indicate JT elongations.

like-orbital pairs contribute to the interaction energy; $\hat{\mathbf{e}}_{ij}$ is the unit vector pointing from site i toward site j ; and $J_{S_i}(\hat{\mathbf{e}}_{ij})$ is the anisotropic interaction constant, which takes a value J_1 if the direction of $S_i = S_j$ matches $\hat{\mathbf{e}}_{ij}$, a value of J_2 if $S_i = S_j$ is perpendicular to $\hat{\mathbf{e}}_{ij}$, or a value of zero otherwise, as shown in Fig. 2(a).

The multiplier $w(\rho_i, \rho_j)$ is used in this case to reduce the contribution to the geometry term of undistorted octahedra without incentivizing infinite distortion, with $w(\rho_i, \rho_j) \rightarrow 2$ as $\rho_i \rho_j \rightarrow \infty$. It is defined thus:

$$w(\rho_i, \rho_j) = 2\rho_i\rho_j/(1 + \rho_i\rho_j). \quad (4)$$

The function $J_{S_i}(\hat{\mathbf{e}}_{ij})$ takes the values J_1, J_2 , or zero; J_1 and J_2 are empirical constants, the values of which will determine the ground-state cJT ordering. Ahmed and Gehring found that [85] the cJT in room-temperature LaMnO_3 is reproduced by $J_1 > 0$, $J_2 < 0$, and $|J_2/J_1| < 1/2$. The collinear JT ordering found, for instance, in $\text{Ba}_{0.5}\text{La}_{0.5}\text{CoO}_3$ [27] could be reproduced for $J_2 < 0$ and $J_1 < -J_2$.

For the layered nickelates, the geometric energy term is based on the chemical instability associated with underbonding of O anions. For instance, authors of an earlier work [37] proposed a trimerlike cJT ordering in LiNiO_2 in which three elongated Ni–O bonds point at the same oxygen anion, but authors of subsequent computational studies using DFT [87] showed this to be highly unstable relative to collinear or zigzag models in which a single elongated bond points at each oxygen anion. We calculate this by summing over all O anions in the simulation as follows:

$$E_{\text{geometric}}^{\text{nickelate}} = \frac{K_{\text{oxy}}}{2} \sum_{\text{O}} [\max(0, s_{\text{O}} - 1)]^2, \quad (5)$$

where $K_{\text{oxy}} > 0$ is an empirical parameter that determines the strength of this O underbonding penalty, with the implication of this equation shown in Fig. 2(b) assuming all $\rho = 1$. The underbonding density term s_{O} is given by summing over all

three nearest-neighbor Ni cations to a given O anion:

$$s_{\text{O}} = \sum_{i \in N(\text{O})} \delta_{\vec{\rho}_i, \vec{r}_{i\text{O}}} \rho_i, \quad (6)$$

where $\delta_{\vec{\rho}_i, \vec{r}_{i\text{O}}}$ is 0 or 1 depending on whether the elongated Ni–O bond ($\vec{\rho}_i$) matches the vector between Ni and the O anion ($\vec{r}_{i\text{O}}$).

We note that the nature of the Hamiltonian we use here renders us insensitive to the possibility of disproportionation as proposed in some prior works for both layered nickelates [43–45] and perovskites [50–52,88].

The perovskite and nickelate $E_{\text{geometric}}$ terms share the same degrees of freedom (a three-state elongation axis and a continuous amplitude ρ) but differ qualitatively in their interaction terms: pairwise orbital alignment in the perovskite case versus oxygen-underbonding constraints in the nickelate case. Consequently, the nickelate geometry term is no longer an anisotropic Potts Hamiltonian as the perovskite geometry term is.

B. Model cell

Simulations are run over periodic cells in 2D or 3D for the layered nickelate and perovskite case, respectively. For the perovskite case, a cubic cell is used with an $8 \times 8 \times 8$ grid of 512 B-site cations. For the layered nickelate case, the cell is a 10×30 parallelogram-shaped grid of Ni cations (300 atoms), where the two basis vectors enclose 60° . The use of a 2D lattice for the layered nickelates relies on the assumption that interlayer interactions are not significant for the JT ordering. Unless otherwise indicated, the starting configuration for all runs was one in which JT distortions were randomly distributed within the unit cell, all with identical magnitude $\rho = 1$.

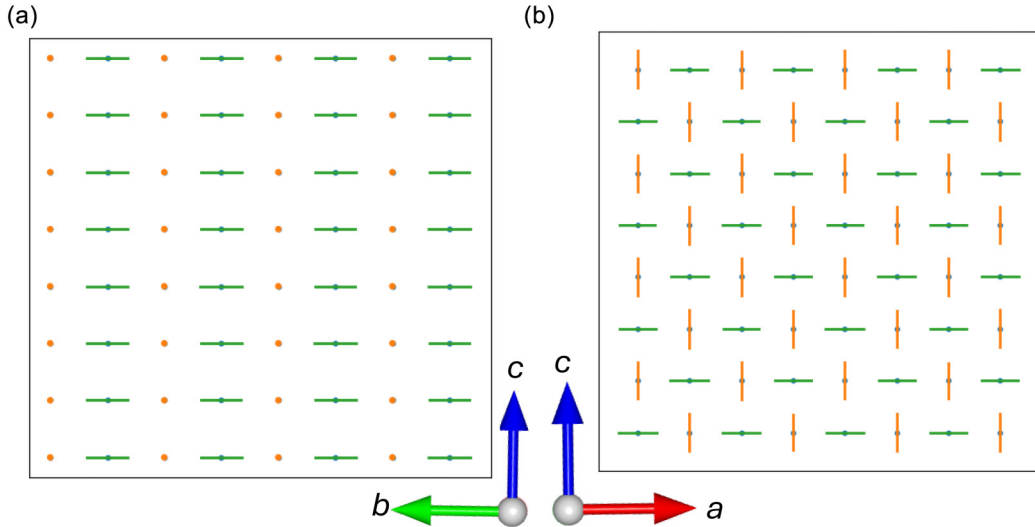


FIG. 3. The results of a Monte Carlo simulation with dynamic ρ ($P_{\text{switch}} = 1/2$), reproducing phase 5 (C-type) of the Ahmed and Gehring [81] phase diagram for the anisotropic Potts model in an $8 \times 8 \times 8$ perovskite supercell. (a) Example configuration in the bc plane in a randomly selected cross-section. (b) Example configuration in the ac plane in a randomly selected cross-section. Energy parameters $\alpha = -1$, $\beta = 1/2$ from Eq. (2). Simulated annealing was used before settling on a final $T = 0.001$. This run lasted for 10^7 iterations. Plots of energy and $\langle \rho \rangle$ with iteration can be seen in Fig. S12 in the Supplemental Material [26].

C. Metropolis algorithm

The Monte Carlo simulation runs over a number of iterations (10^5 – 10^7) using the Metropolis algorithm [89]. At each iteration, a metal site is selected at random. With probability $0 \leq P_{\text{switch}} \leq 1$, a ρ shift occurs in which the magnitude of ρ is varied randomly by some amount, with $-0.1 \leq \Delta\rho \leq 0.1$ (with ρ capped at 0 at the lower limit and 1.5 at the upper limit). Alternatively, with probability $P_{\text{flip}} = 1 - P_{\text{switch}}$, a direction shift occurs, in which the axis of elongation of the metal site is shifted randomly. Either way, energy is then recalculated according to Eq. (1). If $\Delta E \leq 0$, the change is accepted. Otherwise, the change is accepted with probability $\exp[-\Delta E/T]$. For most testing in this work, P_{switch} was set arbitrarily at 0.5.

Where indicated, a simulated annealing procedure is used to avoid being stuck in local minima. This is discussed in the Appendix.

D. Software

Code was written in Python 3 [90], with assistance from generative large-language models ChatGPT [91] version 5. Graphs are prepared using Matplotlib [92]. Crystal structures prepared using VESTA3 [93].

III. RESULTS: JT-DISTORTED PEROVSKITE

Before allowing ρ to vary (i.e., by setting all metal sites to have constant nonzero JT magnitude and setting $P_{\text{switch}} = 0$), we tested our model where the Hamiltonian consisted of the $E_{\text{perovskite}}^{\text{geometric}}$ term only (i.e., $\alpha = \beta = 0$), as shown in Sec. S2 in the Supplemental Material [26]. This reproduced all phases of the (J_1, J_2) anisotropic Potts model phase diagram of Ahmed and Gehring [81], validating their results and our simulation approach. Two phases of the Ahmed and

Gehring phase diagram are of particular interest, which we call *collinear* and *C-type* (phases 1 and 5 using the notation of Ahmed and Gehring). Collinear is a ferro-orbital model with parallel axes of elongation, and C-type consists of alternating stacked elongations within a single plane with identical stacking perpendicular to that plane [Fig. 1(a)]. These are of interest because they have been reported experimentally. We henceforth only study these two phases for perovskites. The next step was to test whether, for $T \ll 1$, adding a dynamic JT magnitude with the $E_{\text{single-ion}}$ term would enable the recovery of these two phases.

Figure 3 shows cross-sections of the final perovskite supercell for the C-type ordering (where $J_1 = 1$ and $J_2 = -0.1$), indicating successful convergence with the expected orbital order; energy and mean JT magnitude $\langle \rho \rangle$ with iteration are shown in Fig. S12 in the Supplemental Material [26]. Figure S11 in the Supplemental Material [26] shows the corresponding information for the collinear case. In both cases, the dynamic ρ model can reproduce the phase diagram given by the static ρ model [81].

We next consider the variable-temperature behavior of these orbital orderings. We performed simulations, with simulated annealing, at a series of temperatures up to $T = 30$, for both the collinear and C-type (J_1, J_2) configurations. Figure 4 shows the mean energy and $\langle \rho \rangle$ for the final 10% of iterations in the simulations as a function of temperature, for both cases. We see that, as temperature increases, there is a transition, which can be seen best in the heat capacity data (Fig. 4), where heat capacity is the variance in E_{total} divided by T^2 . Here, $\langle \rho \rangle$ decreases with heating, with the rate of decrease being low on approach to the transition, and then a rapid decrease before settling at around $\langle \rho \rangle \approx 0.8$. We have tested the resilience of this finding against varying cell size (Figs. S13 and S14 in the Supplemental Material [26]) with little impact on results. We use representative points in the center of the collinear

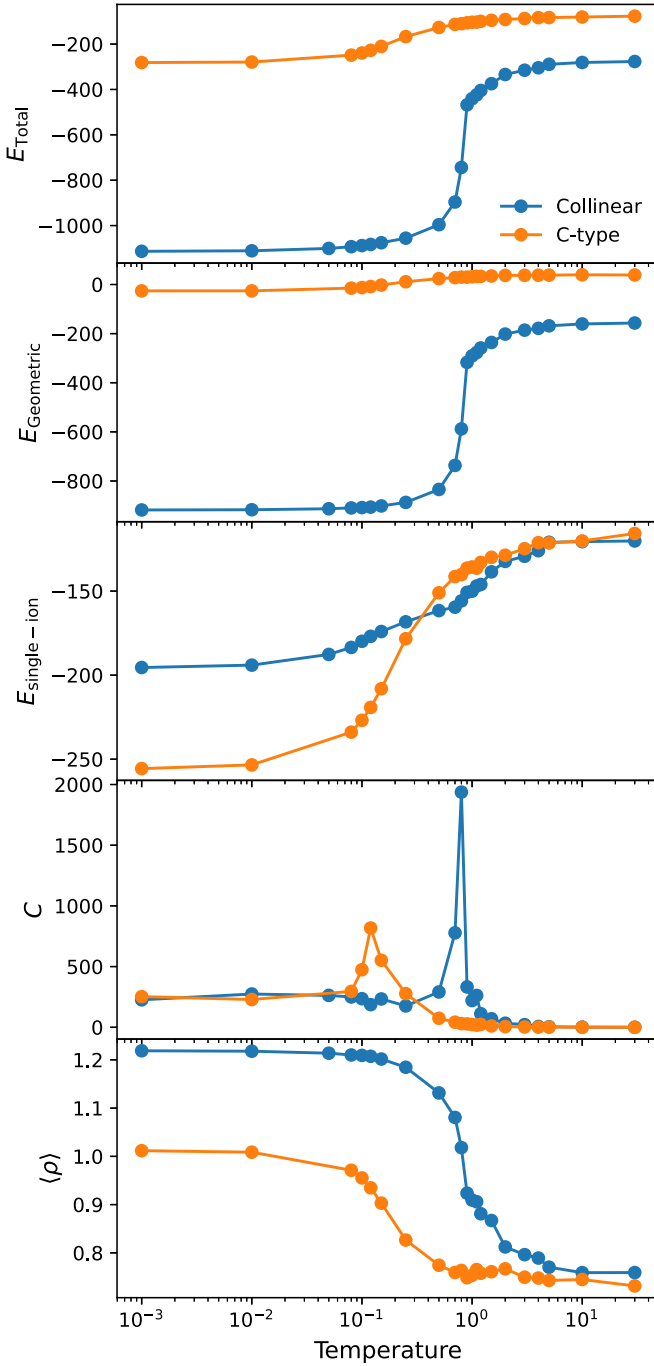


FIG. 4. The mean energy terms E_{total} , $E_{\text{geometric}}$ [Eq. (3)], and $E_{\text{single-ion}}$ [Eq. (2)]; heat capacity C ; and mean $\langle \rho \rangle$ averaged over the final 10% of iterations in Monte Carlo simulations, as a function of temperature for the collinear and C-type orbital orderings in an $8 \times 8 \times 8$ perovskite lattice. The Monte Carlo simulations ran for 10^7 iterations in total at each temperature. This figure is reproduced on a nonlogarithmic temperature scale in Fig. S21 in the Supplemental Material [26].

and C-type phases in (J_1, J_2) space, but in Sec. S7 in the Supplemental Material [26], we show that our findings are qualitatively consistent at the boundaries of these regions in phase space. The finding that $\langle \rho \rangle$ decreases on heating even in the low-temperature regime approximately corresponds to

experimental observations from diffraction on LaMnO_3 that $d\rho/dT < 0$, although KCuF_3 exhibits the opposite trend [78].

A convergence of $\langle \rho \rangle \rightarrow 0.8$ at high temperatures appears consistent with the experimental reports (from pair distribution function and EXAFS) of JT-like octahedral distortion at high temperatures, if we interpret it as the system remaining close to the enthalpic minimum imposed by Eq. (2). However, when we plot histograms of ρ in the final configuration (Fig. 5), we see that the distribution at high temperature does not resemble the distribution at low temperature, which would be the signature of an order-disorder transition. Instead, we see $N(\rho)$ appears invariant with the magnitude, which suggests that, rather than a persistence of JT distortions, the system is merely dynamically exploring the available phase space of possible values of ρ , which is consistent with the recent theoretical study of LaMnO_3 [84]. These findings could be interpreted more in terms of a displacive transition than an order-disorder transition, although the invariance in $N(\rho)$ with ρ indicates that, if there is a free-energy minimum at the origin in $E_g(Q_2, Q_3)$ phase space, it is not significantly more stable than other regions of the phase space.

IV. RESULTS: LAYERED NICKELATE

We next simulated the layered nickelates. Here, we rely on the axiom that interlayer effects are negligible due to the alternating AO_6 octahedral layers ($A = \text{Li}, \text{Na}$) and consider only single layers. As with the perovskites, we first performed Monte Carlo simulations for the static ρ case where all sites begin JT distorted, with $P_{\text{switch}} = 0$, and the Hamiltonian consisting solely of the $E_{\text{geometric}}^{\text{nickelate}}$ term (i.e., $\alpha = \beta = 0$), with $T \ll 1$. An example of a converged layer configuration is shown in Fig. 6. We see the emergence of ordered collinear domains, as reported from diffraction studies on NaNiO_2 [29,30,32,33] and stoichiometric LiNiO_2 [39]. The boundary between these domains resembles the zigzag ordering which has been proposed as a possible ground state for LiNiO_2 on the basis of DFT studies [44,87]. Defects then occur when two or three domains intersect. Such defects involve either overbonded (no JT axes) or underbonded (multiple JT axes) oxygen anions and resemble the dimer or even trimer models proposed by Chung *et al.* [37] (Figs. S3(e) and S3(h) in the Supplemental Material [26]) which DFT calculations have found to be highly unstable [87]. This domain effect, in contrast, does not seem to be important for the perovskites, likely because they can relieve frustration by stacking patterns along c , which reduces the likelihood of frustrated interactions.

For $T \ll 1$, we see this behavior is preserved when working with the dynamic ρ and nonzero $E_{\text{single-ion}}$ term, with K_{oxy} arbitrarily large (i.e., 10^{10}). From here, we iteratively increase temperature and evaluate the changes in $\langle \rho \rangle$, as shown in Fig. 7. As with the perovskites, the heat capacity C shows that an ordering transition occurs, above which there is local disorder. We see that, keeping K_{oxy} arbitrarily large, as $T \gg 1$, $\langle \rho \rangle \rightarrow 0.4$, much lower than the perovskite case. Figure 5 shows histograms of ρ at low and high temperatures, with most Ni sites exhibiting a large JT distortion at low T (except a few Ni sites which occur at the boundary between domains), and Ni sites at high temperatures exhibiting no preference for

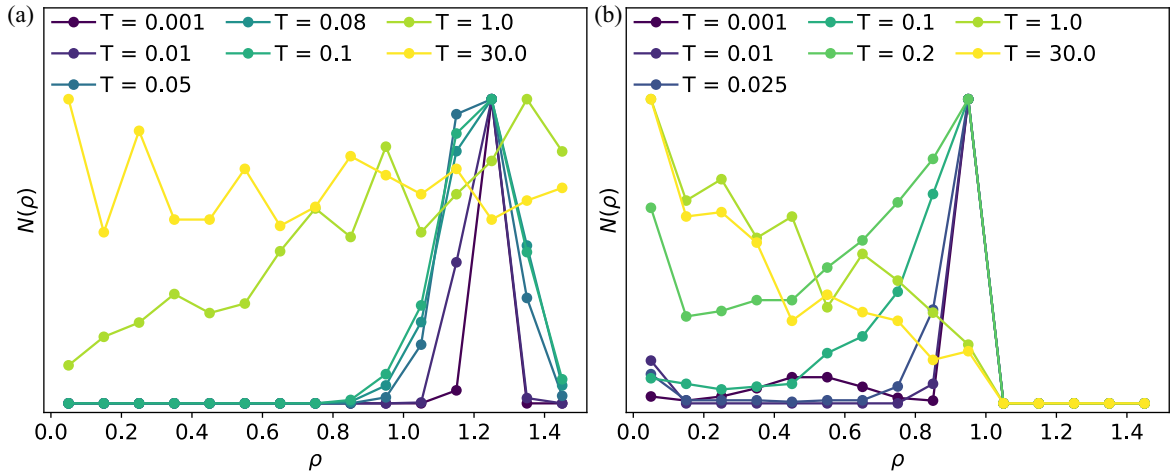


FIG. 5. Histograms of ρ for the final (a) $8 \times 8 \times 8$ perovskite collinear ordered supercell and (b) 10×30 nickelate layer with $K_{\text{oxy}} = 10^{10}$, after 10^7 iterations with simulated annealing. For other configurations, see Figs. S15–S19 in the Supplemental Material [26].

JT distortion, with the highest distribution of sites occurring at low ρ . This suggests that the preference for large ρ and JT distortions vanishes on the 2D nickelate lattice, which is displacive-like behavior. Although our simulations for the perovskites were broadly consistent with a similar conclusion, there clearly exist differences between these two cases: (1) the significantly reduced $\langle \rho \rangle$ at high T for the nickelate as compared with the perovskite case [Fig. 8] and (2) the decreasing $N(\rho)$ with ρ for the nickelate case compared with the approximate invariance of $N(\rho)$ with ρ in the perovskite case [Fig. 5].

In Ref. [34], we presented a mathematical proof that JT disorder in layered nickelates has subextensive configurational entropy and argued that this drives the displacive behavior

in layered nickelates. One of the axioms of this proof is that oxygen underbonding is unfeasible, and so multiple axes of JT elongation do not point at the same oxygen; this is equivalent to our choice in these Monte Carlo simulations to set $K_{\text{oxy}} \rightarrow \infty$. In Fig. 7, we also show the temperature dependence of $\langle \rho \rangle$ if we reduce the magnitude of K_{oxy} (while retaining $K_{\text{oxy}} > 0$), i.e., resulting in scenarios such as the trimer or dimer JT ordering being energetically unfavorable but not totally unfeasible as for the $K_{\text{oxy}} \rightarrow \infty$ case. This results in $\langle \rho \rangle$ converging to a much higher value, similar to the case for the perovskites, and with distributions of ρ exhibiting no preference for particular ρ values (Fig. S15 in the Supplemental Material [26]). Despite the simplicity of the model, this suggests that the oxygen underbonding penalty can strongly influence the high-temperature ρ distribution by restricting the configurational entropy of orbitally disordered states. Within this framework, lattice geometry therefore provides a mechanism for producing different high-temperature JT behavior in different model systems.

V. CONCLUSIONS

In this study, we successfully extended the Monte Carlo model of Ahmed and Gehring [81,85,86] to include variable JT distortion amplitudes, enabling us to retain the simplicity of the Ahmed and Gehring model while allowing for the possibility that JT distortions may vanish locally at high temperature. The results of this approach are qualitatively consistent with both experimental evidence for persistence of JT-like distortion modes above JT transitions in perovskites [65,67] (which, in our simulations, manifests as a high $\langle \rho \rangle$) and recent computational results which have suggested that the high-temperature state of JT-distorted perovskites is not characterized by well-defined JT-distorted octahedra [84] but rather a dynamic sampling of the (Q_2, Q_3) phase space. More generally, these results show that allowing amplitude fluctuations qualitatively alters the high-temperature behavior of Potts-like JT models.

Despite our finding that our variable-amplitude model does not show persistent JT distortions at high temperature, there

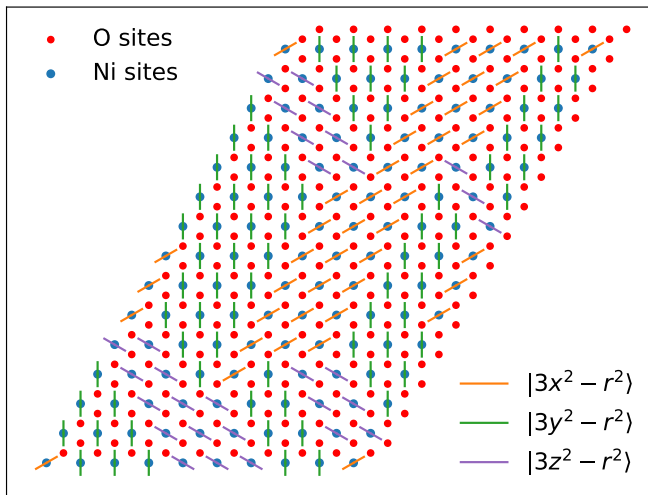


FIG. 6. An example converged configuration of a 10×15 layered nickelate. This simulation used a static ρ ($P_{\text{switch}} = 0$; $\alpha = \beta = 0$) model, with $K_{\text{oxy}} = 10^{10}$ and $T = 0.001$ after simulated annealing (with $T_{\text{max}} = 10$), and was run for 10^6 iterations. Collinear domains can be seen, often bound by defects of overbonded (no JT axes) or underbonded (multiple JT axes) oxygen anions, indicating that this is a local—but not global—energy minimum.

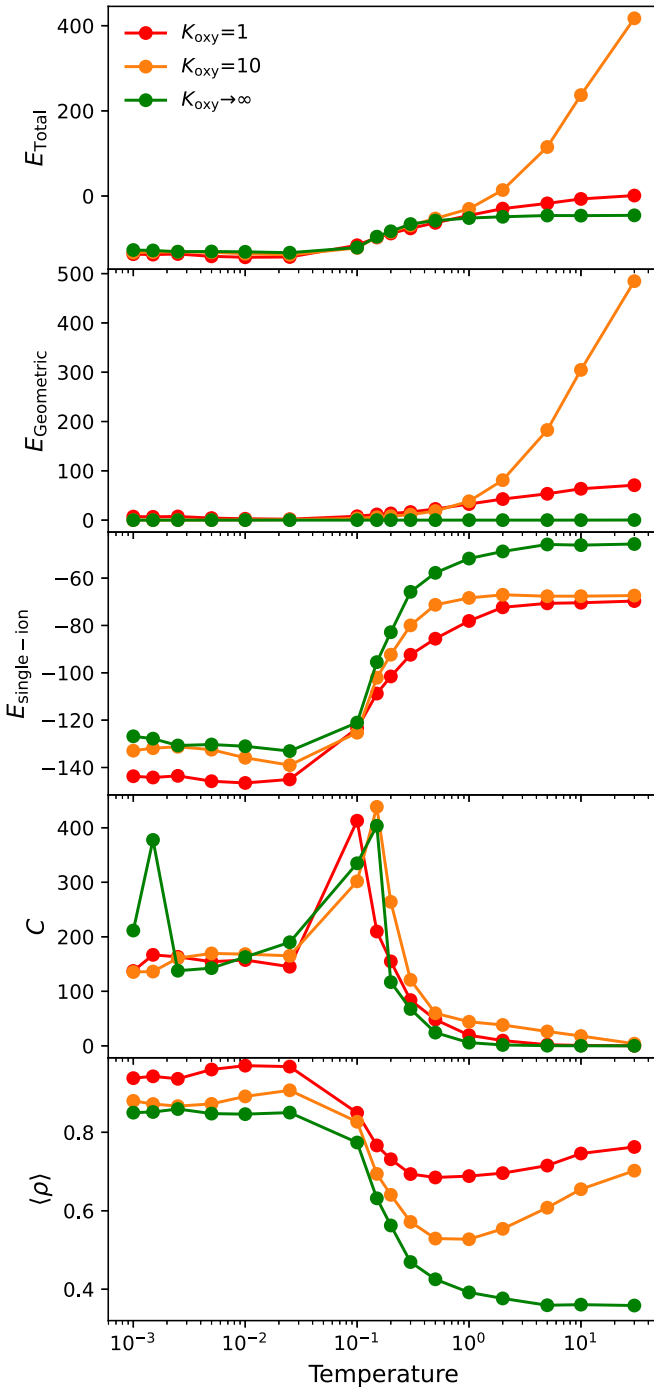


FIG. 7. The mean energy terms E_{total} , $E_{\text{geometric}}$ [Eq. (5)], and $E_{\text{single-ion}}$ [Eq. (2)]; heat capacity C ; and mean $\langle \rho \rangle$ averaged over the final 10% of iterations in Monte Carlo simulations, as a function of temperature for the 10×30 nickelate lattice. The Monte Carlo simulations ran for 10^7 iterations in total at each temperature. We present these results as a function of the strength of the oxygen underbonding penalty K_{oxy} . This is plotted on a nonlogarithmic temperature scale in Fig. S22 in the Supplemental Material [26].

are clearly differences between the two systems due to the geometry of the lattice. We reported that the converged $\langle \rho \rangle$ of the perovskite lattices is much higher (~ 0.8) than the nickelate lattice (~ 0.4) at high temperature [Fig. 8], and as

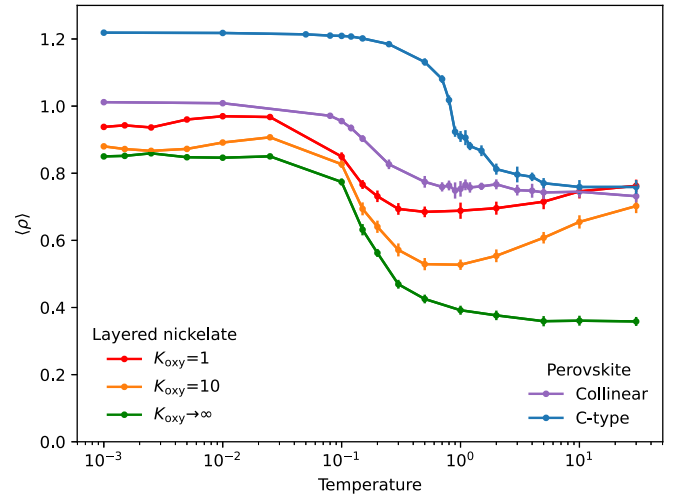


FIG. 8. $\langle \rho \rangle$ with temperature, comparing phase 1 (collinear) and phase 5 (C-type) perovskite ordering with layered nickelates for various K_{oxy} . The corresponding figure with nonlogarithmic temperature scaling is in Fig. S23 in the Supplemental Material [26].

shown in Fig. 5, the number distribution of distortion magnitudes appears invariant with ρ for the perovskite case but decreases as ρ increases for the nickelate case. This is likely a consequence of the subextensivity of configurational entropy of disordered octahedral elongations on the nickelate lattice, as previously reported [34]. If this were to occur in real systems, it would likely manifest experimentally in a larger skewness for the first metal-oxygen peak in the experimental pair distribution function for perovskites like LaMnO_3 , as compared with nickelates like NaNiO_2 . This may be a factor in the historic attribution of order-disorder behavior to the JT transitions in the perovskites.

In addition to the layered nickelates and perovskites studied in this work, the model presented here may be applied to other JT-distorted systems of interest. For instance, spinels, double perovskites, and Prussian Blue analogs all exhibit cJT distortions. Authors of future work should investigate these systems and benchmark findings against local probe experiments such as total scattering and EXAFS. Another useful direction would be to apply the more complex anharmonic vibrational Hamiltonian developed by Radin *et al.* [82] to perovskite systems such as LaMnO_3 to better understand the recent developments in our understanding of these systems.

ACKNOWLEDGMENTS

The authors thank James M. A. Steele, Nicola D. Kelly, and Amber Visser at the University of Cambridge and Annalena R. Genreith-Schriever at RWTH Aachen University for useful comments. A.L.G. acknowledges funding from UKRI through a Frontier Research Grant EP/Z534031/1 and the Royal Society through the Faraday Discovery Fellowship fund, provided by DSIT.

DATA AVAILABILITY

The data that support the findings of this article are openly available [94], embargo periods may apply.

APPENDIX: SIMULATED ANNEALING

In the simulated annealing procedure, temperature is initialized at $T_0 = \max(T_{\max}, 10T_{\text{target}})$, where T_{target} is the target temperature of the run, and $T_{\max} \gg 1$. At each iteration i out of a total number of iterations n , the temperature T_i is

given by

$$T_i = \begin{cases} T_0 \left(\frac{T_{\text{target}}}{T_0} \right)^{\frac{i}{n_{\text{sa}}-1}} & \text{if } i < n_{\text{sa}}, \\ T_{\text{target}} & \text{if } i \geq n_{\text{sa}}, \end{cases} \quad (\text{A1})$$

where $n_{\text{sa}} = 0.8n$ is rounded down to the nearest integer.

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