

Quadrupole formation and coupling to magnetic and structural degrees of freedom in the $5d^1$ double perovskites $\text{Ba}_2\text{MgReO}_6$ and $\text{Ba}_2\text{NaOsO}_6$

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(Received 27 February 2026; accepted 29 June 2026; published 10 August 2026)

We investigate the interplay between charge, magnetic, and structural degrees of freedom in the isostructural and isoelectronic $5d^1$ double perovskites $\text{Ba}_2\text{MgReO}_6$ and $\text{Ba}_2\text{NaOsO}_6$. Using first-principles-based electronic structure calculations, we show that both materials exhibit a tendency toward spontaneous quadrupolar order in the cubic paramagnetic phase, which is slightly weaker in $\text{Ba}_2\text{NaOsO}_6$ than in $\text{Ba}_2\text{MgReO}_6$. Our analysis further reveals an intimate coupling between the local magnetic moments and charge quadrupoles, mediated by the strong spin-orbit interaction, that leads to the unusual canted configuration of magnetic moments observed in these systems. When structural degrees of freedom are included, the two materials exhibit pronounced differences. In $\text{Ba}_2\text{MgReO}_6$, the strong coupling to Jahn-Teller distortions stabilizes the antiferroic $Q_{x^2-y^2}$ order, yielding excellent agreement with available experimental data. In contrast, the Jahn-Teller coupling is significantly weaker in $\text{Ba}_2\text{NaOsO}_6$ and appears insufficient to stabilize the antiferroic quadrupolar order. While this is consistent with the absence of any measurable long-range structural distortion above the magnetic transition temperature, it contrasts with experimental results indicating a strong canting of the magnetic moments. Our analysis thus successfully describes the mechanisms shaping the properties of the Re compound while a full quantitative description of the magnetic ground state of $\text{Ba}_2\text{NaOsO}_6$ is still elusive.

DOI: [10.1103/chtv-nvsq](https://doi.org/10.1103/chtv-nvsq)

I. INTRODUCTION

The exploration of exotic states of matter, such as high-temperature superconductivity [1], quantum spin liquids [2], or Mott-insulating states [3], and how such phases emerge from the collective interplay between electronic, magnetic, orbital, and structural degrees of freedom, is a central topic of modern condensed matter physics. Recently, certain complex oxides containing either $4d$ or $5d$ transition metal cations have entered the spotlight. In these materials, the interplay of strong spin-orbit coupling and electronic correlations can give rise to intriguing multipolar orderings, exotic spin textures, and nontrivial topological phases [4–7].

Particularly interesting are B -site-ordered double-perovskite oxides, with the general chemical composition $A_2BB'O_6$, where A and B are nonmagnetic closed-shell ions and B' is a magnetic $4d$ or $5d$ transition metal cation. The high chemical flexibility of these double perovskites, which allows to incorporate many different combinations of ions on the A , B , and B' sites [8], in combination with their simple high-symmetry crystal structure [see Fig. 1(a)], facilitates systematic studies over closely related series of compounds. Indeed, double perovskites have been found to host a variety of exotic quantum states, including symmetry-broken phases

where the order parameter is a higher-order multipole of the charge or magnetization density as well as potential spin liquid or glassy states with no detectable symmetry breaking down to very low temperatures [9–22].

The complexity of the multipolar physics in these materials, involving strong entanglement between spin, orbital, and structural degrees of freedom, poses a significant challenge for the theoretical modeling. Simultaneously, higher-order multipoles are not easily accessible using standard experimental probes, and instead require the application of advanced techniques and often several complementary measurements. Quantitatively predictive first-principles-based calculations are therefore extremely valuable to reveal a possible ordering of higher-order multipoles and elucidate the physical and chemical mechanisms that control their behavior [23–30].

Here, we focus on the two closely related double-perovskites, $\text{Ba}_2\text{MgReO}_6$ and $\text{Ba}_2\text{NaOsO}_6$, containing Re^{6+} and Os^{7+} cations on the B' sites, respectively. Both cations exhibit a nominal $5d^1$ electron configuration, and the octahedral crystal field together with the strong spin-orbit coupling results in a fourfold degenerate $J_{\text{eff}} = 3/2$ ionic ground-state configuration [7]. This degeneracy of their ground-state multiplet makes these systems sensitive to small distortions and prone to spontaneous symmetry breaking. Furthermore, the local magnetic dipole moment is expected to be strongly reduced due to partial cancellation between spin and orbital contributions, and the geometric frustration inherent to the nearest-neighbor interaction on the face-centered cubic lattice formed by the B' cations can lead to a further suppression of conventional antiferromagnetic dipolar order, potentially favoring the emergence of higher-order multipoles.

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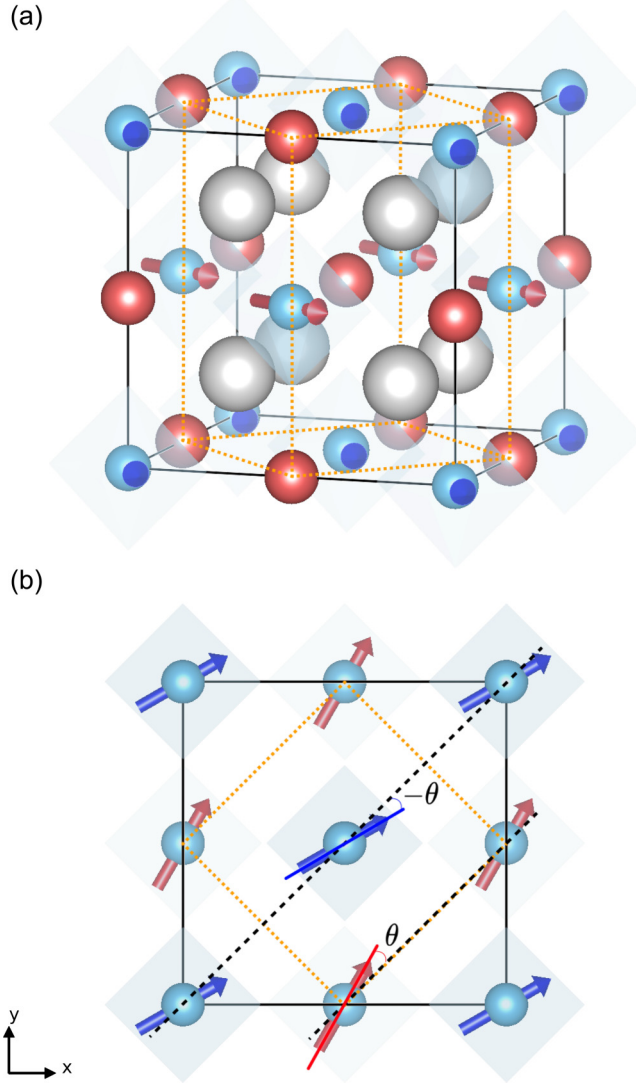


FIG. 1. (a) Three-dimensional view and (b) projection along the z axis of the cubic double perovskite structure ($A_2BB'O_6$), schematically showing the canted ferromagnetic configuration reported for both Ba_2MgReO_6 and Ba_2NaOsO_6 . A ions (nonmagnetic B ions) are shown in gray (red), transition metal ions (B') and their surrounding oxygen octahedra in light blue, and the red and blue arrows indicate the local magnetic moments of the two magnetic sublattices. Thin black and orange dashed lines indicate the conventional cubic and the primitive tetragonal magnetic unit cell, respectively. As shown in panel (b), the local magnetic moments are rotated away from the [110] direction (indicated by the black dashed lines) by an angle $\pm\theta$, with $\theta > 0$ indicating counterclockwise rotation around z . Note that, as shown in panel (a), the B' ions corresponding to blue and red dipole moments are located in different adjacent [001] planes.

Anomalies in the heat capacity of Ba_2MgReO_6 at 33 and 18 K [15,31] suggest that this system undergoes two successive phase transitions, and recent experiments employing both resonant and off-resonant x-ray diffraction revealed that at $T_q = 33$ K the space group symmetry is reduced from $Fm\bar{3}m$ to $P4_2/mnm$. This symmetry lowering has been related to an antiferroic ordering of local $x^2 - y^2$ -type quadrupoles on the Re sites in combination with a ferroic $3z^2 - r^2$ -type

quadrupolar ordering and a small Jahn-Teller distortion of the ReO_6 octahedra [16,19]. The transition at $T_m = 18$ K then corresponds to a noncollinear dipolar magnetic ordering with a net magnetization within a single domain of approximately $0.46\mu_B$ per Re along the [110] direction, but with the local magnetic moments canted away from the [110] direction by an angle θ of about $\pm 40^\circ$ [see Fig. 1(b)], corresponding to an antiferromagnetic component of the order parameter with wave vector along [001] [15,16].

In contrast, the case of Ba_2NaOsO_6 appears more complex. Below 6.8 K, this material exhibits a canted magnetic dipolar order similar to Ba_2MgReO_6 , with a canting angle θ of $\pm 67^\circ$ and a net magnetization of $0.2\mu_B$ along the [110] direction [12,32]. However, no deviation from global cubic symmetry or other evidence for long-range quadrupolar order has been found above the magnetic transition temperature [32,33]. Instead, a few kelvin above T_m , the system exhibits signs for a broken local point symmetry, deduced from a splitting of the nuclear magnetic resonance (NMR) spectra, which indicates the emergence of a local electric field gradient around the Na ions, stemming from a local distortion or charge density anisotropy [12–14,34,35]. Recently, it has been proposed that the broken local point symmetry in Ba_2NaOsO_6 is even retained up to at least room temperature, suggesting a dynamical Jahn-Teller scenario without global symmetry breaking [20]. A dynamical Jahn-Teller effect persisting up to temperatures well above T_q has also been suggested for Ba_2MgReO_6 [21,22].

Thus, despite the fact that Ba_2MgReO_6 and Ba_2NaOsO_6 are essentially isostructural and isoelectronic, subtle differences between the two materials seem to affect the possible emergence of a long-range ordered quadrupolar phase.

Several aspects of Ba_2MgReO_6 and Ba_2NaOsO_6 have been addressed previously using first-principles electronic-structure calculations based on density functional theory (DFT) and different extensions of DFT. For Ba_2NaOsO_6 , most studies have examined the interplay between spin-orbit coupling and electronic correlations to clarify the nature of its insulating state [36–38], while Ref. [24] has demonstrated the relevance of multipolar spin interactions and a potential Jahn-Teller distortion for the reported canted magnetic order. Similarly for the case of Ba_2MgReO_6 , previous studies have focused on the influence of spin-orbit coupling on its Mott-insulating character, the emergence of quadrupolar order, and its coupling to magnetic and structural degrees of freedom [19,25,28,30]. In particular, these studies have indicated that a coupling between the quadrupolar order and the structural Jahn-Teller distortion is required to stabilize the experimentally observed antiferroic $x^2 - y^2$ -type order, while, in the absence of such coupling, a ferroic order of t_{2g} -type quadrupoles would be preferred [19,30]. Furthermore, the microscopic model of coupled quadrupolar, dipolar, and vibronic modes presented in Ref. [30] has successfully described the two successive phase transitions at low temperatures.

In the present work, we present a complementary first-principles study, confirming the influence of the Jahn-Teller coupling on the stabilization of the experimentally observed antiferroic quadrupolar order in Ba_2MgReO_6 . Furthermore, we provide a systematic comparison between Ba_2MgReO_6 and Ba_2NaOsO_6 , aiming to identify the origin for their

different behavior. Thereby, we focus specifically on clearly disentangling the coupling between the various degrees of freedom, i.e., electronic quadrupole moments, magnetic dipole moments, and different Jahn-Teller distortions. We find that $\text{Ba}_2\text{NaOsO}_6$ generally exhibits a slightly weaker tendency toward quadrupolar order, and that, in particular, the coupling to the Jahn-Teller modes is significantly weaker than in $\text{Ba}_2\text{MgReO}_6$, and is not able to stabilize the antiferroic quadrupolar order. We also demonstrate an intimate coupling between the direction of the local magnetic moments of the $5d$ transition metal cations and the corresponding local quadrupole, and show that the canting of the magnetic moments away from the ferromagnetic [110] direction is driven by the emergence of an antiferroic component of the local quadrupoles (or vice versa), which rotates the local easy axis away from the global magnetization direction.

Overall, we obtain excellent agreement with available experimental data for $\text{Ba}_2\text{MgReO}_6$. For $\text{Ba}_2\text{NaOsO}_6$, the weaker tendency toward quadrupolar order and the weak coupling to a corresponding Jahn-Teller distortion found in our calculations appear consistent with the absence of any long-range ordered quadrupolar and Jahn-Teller distorted phase above the magnetic ordering temperature. On the other hand, based on our analysis of the correspondence between antiferroic quadrupolar order and the canting of the local magnetic moments, the lack of stabilization of such an antiferroic quadrupolar order in our calculations appears to contradict the reported canting of the magnetic moments away from the [110] direction, based on the analysis of NMR spectra [12]. Further research is needed to resolve this remaining discrepancy.

II. METHODS AND COMPUTATIONAL DETAILS

A. Constraining quadrupole moments and magnetic dipoles

The quadrupole moment corresponding to an electron density $n(\vec{r})$ around a specific site I can be defined as $Q_{ij}^I = \int d^3r r_i r_j n(\vec{r})$, with r_i a Cartesian component of the distance vector relative to the chosen site. Since Q_{ij}^I is by definition a totally symmetric tensor, it can be decomposed into its trace and a symmetric traceless part, which form one- and five-dimensional irreducible representations under arbitrary rotations, respectively. The components of the latter can be labeled as Q_t^I , with $t \in \{xy, yz, 3z^2 - r^2, xz, x^2 - y^2\}$.

Expressing the electron density in terms of the density matrix with respect to a suitably chosen atomic-orbital-like basis (labeled by the usual angular momentum and spin quantum numbers, l , m , and s) allows to write the components Q_t^I as follows:

$$Q_t^I = \sum_{lm, l'm'} \mu_{lm, l'm'}^{2,t} \rho_{l'm', lm}^I, \quad (1)$$

where we use the same notation as in Ref. [39] to express the matrix elements of the charge-multipole operators with rank k , $\mu_{lm, l'm'}^{k,t}$ [40,41], while $\rho_{l'm', lm}^I = \sum_s \rho_{l'm's, lms}^I$ represents the angular part of the density matrix. We note that this definition is completely equivalent to the definition of general spherical multipole tensors, $w_t^{kpr, I}$, described in Refs. [40,41] and used, e.g., in Ref. [25], where for charge multipoles $p = 0$ and $r = k$, such that $Q_t^I = w_t^{202, I}$. Since for the materials considered

here, the dominant contribution to the charge quadrupoles arises from the d orbitals, we further restrict our analysis to $l = l' = 2$.

To constrain the local charge quadrupoles, we use the method introduced in Refs. [39,42]. Thereby, the energy as function of local quadrupoles is obtained by adding a linear form of the constraint to the DFT (or DFT + U) energy using the method of Lagrange multipliers, and then minimizing the resulting functional with respect to the density and the Lagrange multiplier:

$$E[\{\tilde{Q}_t^I\}] = \min_{\rho(\vec{r}), s_t^I} \left(E_0[\rho(\vec{r})] - \sum_{I,t} s_t^I (Q_t^I[\rho(\vec{r})] - \tilde{Q}_t^I) \right). \quad (2)$$

Here, $\tilde{Q}_t^I$ denote the specific values to which the quadrupoles are constrained, s_t^I are the corresponding Lagrange multipliers, and $\rho(\vec{r}) = n(\vec{r}) + \vec{\sigma} \cdot \vec{m}(\vec{r})$ is the full spin density, which describes both the electronic charge and spin density of the system, with $\vec{\sigma}$ representing the vector of Pauli matrices. The constraint results in an orbital-dependent local potential shift added to the usual Kohn-Sham potential, which induces a deformation of the electron density around the atom according to the corresponding multipole component. To obtain a specific value, $\tilde{Q}_t^I$, the corresponding Lagrange multiplier, s_t^I , which represents the amplitude of the local potential shift, has to be adjusted self-consistently. Alternatively, one can drop this minimization with respect to s_t^I and simply vary the strength of the potential shift within a suitable range to obtain properties as a function of the local quadrupole moments [39]. In all our calculations, the constraint is applied to only one specific quadrupolar component at a time, allowing the remaining components to relax freely.

Apart from constraining the local quadrupoles, we also perform calculations where we constrain the directions of the local spin moments, in order to monitor the energy and other properties as function of the canting angle θ [see Fig. 1(b)] and also to simulate a disordered paramagnetic state. Here, we use the well-established method of adding a penalty term to the DFT + U energy, which corresponds to adding a quadratic form of the constraint to the energy functional [43]:

$$E = E_0[\rho(\vec{r})] + \sum_I \lambda [\vec{S}_I - \hat{S}_I^0 (\hat{S}_I^0 \cdot \vec{S}_I)]^2. \quad (3)$$

Here, $\vec{S}_I = \vec{S}_I[\rho(\vec{r})]$ is the local spin moment at site I and $\hat{S}_I^0$ is a unit vector pointing along the direction along which $\vec{S}_I$ is constrained. The parameter λ in Eq. (3) determines the strength of the constraint, and has to be chosen such that the corresponding penalty energy remains negligible compared to the energy scale of interest.

B. Computational details

We perform DFT + U calculations, with spin-orbit coupling always included, within the projector-augmented-wave (PAW) framework using the Vienna *Ab Initio* Simulation Package (VASP) [44,45] based on the exchange-correlation energy functional of Perdew-Burke-Ernzerhof (PBE) [46]. We use the simplified rotational invariant formulation of DFT + U first proposed by Dudarev *et al.* [47], where the local interaction is parametrized by a single parameter U_{eff} . A plane-wave cutoff energy of 600 eV is used in all calculations.

tions, which ensures convergence of the quadrupoles within a tolerance of 10^{-3} .

Most of our calculations are performed for the perfectly cubic structure with $Fm\bar{3}m$ space group symmetry using experimental structural data obtained at room temperature in Ref. [16] for $\text{Ba}_2\text{MgReO}_6$ and Ref. [33] for $\text{Ba}_2\text{NaOsO}_6$. The corresponding parameters are listed in Table I of Sec. III C.

Calculations for the magnetically ordered state are performed using a minimal unit cell containing two transition metal cations that allows for a canting of the magnetic moments between the two sublattices according to the experimentally observed magnetic structure shown in Fig. 1. The simple tetragonal Bravais lattice vectors of this cell correspond to a $1/\sqrt{2} \times 1/\sqrt{2} \times 1$ cell with respect to the conventional cubic cell of the underlying face-centered cubic lattice. In this case, we use a Γ -centered $8 \times 8 \times 6$ $\vec{k}$ grid, and converge the total energy to a tolerance of at least 10^{-8} eV. For the cases where structural relaxations are performed, all force components are converged to values smaller than 10^{-3} eV/Å.

To simulate the paramagnetic state, we employ a supercell approach with the individual local magnetic moments frozen along random directions. The random orientation of the (spin) magnetic moments leads to a random local symmetry breaking that, in principle, can allow for the development of local quadrupoles, while simultaneously, for a large enough supercell, the cubic symmetry can be retained by averaging over all sites. The validity of this static approach to the paramagnetic state depends on the time scale of the property of interest relative to that of the dynamics of the magnetic moment directions (see, e.g., Ref. [48] for a more detailed discussion). Here, we make the reasonable assumption that the dynamics of the charge quadrupoles, representing a purely electronic degree of freedom, is either faster or similar to that of the local magnetic moments, so that the quadrupole moments can essentially adjust immediately to the given magnetic dipole configuration, and thus a static approximation is applicable.

Specifically, we use a $2 \times 2 \times 2$ supercell of the basic magnetic cell, containing 16 B' sites, analogous to what was used in a previous study [25]. We then assign random magnetic moment directions to each transition metal cation, with the additional condition that the total initial magnetization of the cell, calculated assuming the same length for each moment along the chosen direction, is below a tolerance threshold of $0.001\mu_B$. In this case, we use a $3 \times 3 \times 2$ Γ -centered $\vec{k}$ -point grid, and the total energy is converged to an accuracy better than 10^{-5} eV. Achieving better convergence is challenging due to the complexity of the noncollinear magnetic configurations, the large supercell, and the two different constraints (one on the local charge quadrupoles and one on the spin moments). Nevertheless, we verified that the local charge quadrupoles are well converged at this level of precision, and, since the energy scale of interest is almost 3 orders of magnitude larger than our convergence threshold, a better convergence is not required.

To further ensure that our results are independent of a specific configuration with random magnetic moment directions (given the limited size of our supercell), we always generate four different paramagnetic configurations, and then

average over these four calculations to obtain our final results [48]. Note that we apply quadrupolar potential shifts of the same magnitude, $|s_i|$, to all transition metal sites in the unit cell with relative signs according to either a ferroic or an antiferroic arrangement. For each individual paramagnetic configuration, we thus obtain the total energy, $E(s_i)$, and a sign-weighted local quadrupole moment $Q_i(s_i)$, defined by averaging the local quadrupole moments across all sites, multiplied with the sign of the applied local shift. To obtain $E(Q_i)$, we then fit an even sixth-order polynomial to all data points, $\{E(s_i), Q_i(s_i)\}$, obtained for the individual paramagnetic configurations. Alternatively, we first average all total energies and cell-averaged local quadrupoles for a given s_i over all four paramagnetic configurations and then perform the polynomial fit for $E(Q_i)$ on these preaveraged data points. Both procedures lead to almost identical results, with the data presented in Sec. III A corresponding to the latter procedure.

Finally, we have also estimated the effective Hubbard parameter, U_{eff} , for both $\text{Ba}_2\text{MgReO}_6$ and $\text{Ba}_2\text{NaOsO}_6$ using the linear-response-theory-based approach suggested in Ref. [49], using finite difference calculations to obtain the site-resolved charge susceptibilities. For this analysis, we use a $2 \times 2 \times 2$ supercell defined relative to the conventional cubic unit cell of the face-centered cubic lattice (each containing four transition metal ions), a $2 \times 2 \times 2$ Γ -centered $\vec{k}$ grid, and a convergence threshold for the total energy of 10^{-8} eV. We initialize the magnetic moments in a ferromagnetic configuration with magnetization along the [110] direction, and use $U_{\text{eff}} = 0$ for these calculations; i.e., we do not iterate U_{eff} to self-consistency.

We obtain similar values for both materials, $U_{\text{eff}} = 1.31$ eV for $\text{Ba}_2\text{MgReO}_6$ and $U_{\text{eff}} = 1.25$ eV for $\text{Ba}_2\text{NaOsO}_6$. These values are comparable to the value $U_{\text{eff}} = 1.8$ eV used in Ref. [25] for $\text{Ba}_2\text{MgReO}_6$, which results in a band gap of ~ 0.2 eV, in agreement with the thermal activation energy deduced from electrical resistivity measurements [15]. In contrast, these values are significantly smaller compared to $U_{\text{eff}} = 3.4$ eV used for $\text{Ba}_2\text{NaOsO}_6$ in Ref. [24] based on a very simple tight-binding and point-charge estimation in Ref. [32].

In view of the general conceptual uncertainties in the exact definition of the effective Hubbard parameter, and the missing self-consistency with respect to U_{eff} , we consider our calculated values for U_{eff} only as rough but nevertheless very instructive estimates. Thus, in order to allow for a better comparison with Ref. [25], we use $U_{\text{eff}} = 1.8$ eV for both materials, except where otherwise noted.

III. RESULTS

A. Emergence of quadrupolar order in the cubic paramagnetic phase

Our first goal is to establish whether the two materials indeed exhibit a tendency for spontaneous quadrupolar order, even in the absence of dipolar magnetic order and any structural symmetry lowering.

We thus fix the crystal structure to the experimentally observed cubic $Fm\bar{3}m$ structures and simulate the paramagnetic state by using supercells with random orientation of the local magnetic dipole moments and no net magnetization, as described in Sec. II B. For each paramagnetic configuration,

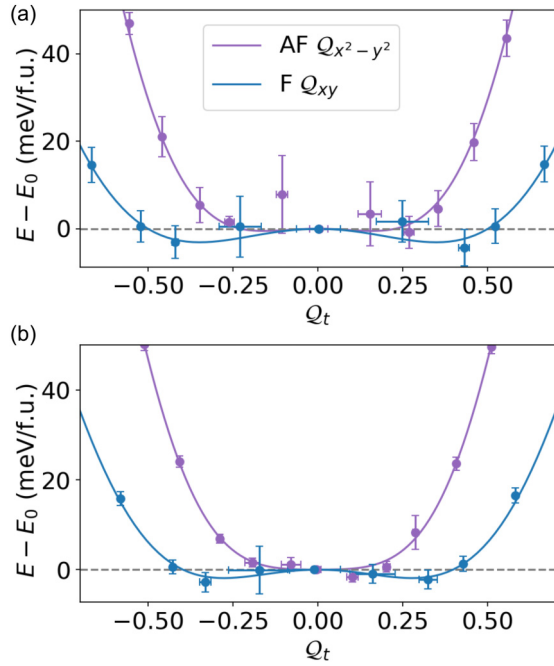


FIG. 2. Energy as function of the local quadrupole moment, Q_t , for FQ-xy order (blue) and AFQ- $x^2 - y^2$ order (purple) for structurally cubic $\text{Ba}_2\text{MgReO}_6$ [panel (a)] and $\text{Ba}_2\text{NaOsO}_6$ [panel (b)] in the paramagnetic case. Error bars indicate the standard deviation of the energies and local quadrupoles over the different paramagnetic configurations with the same value for the constraint s_t .

we explore the energy landscape for different quadrupolar orders by applying a constraint on a specific component of the local quadrupoles on the $5d$ transition metal cations [39], with relative signs on the different sites arranged according to either ferroic or antiferroic order, while all other multipolar components are free to relax. We then vary the strength of the constraint to obtain the energy as a function of the size of the average local quadrupole moment. Specifically, we consider a ferroic ordering of xy -quadrupoles (FQ-xy order, symmetry-equivalent to FQ-xz and FQ-yz), and an antiferroic ordering of $x^2 - y^2$ -quadrupoles with alternating signs of the quadrupoles along the z direction (AFQ- $x^2 - y^2$ order). The latter is consistent with the symmetry-lowering observed in $\text{Ba}_2\text{MgReO}_6$ below T_q [16,19] and is also the ground-state order predicted by the model of Ref. [9]. On the other hand, different complementary first-principles-based approaches in fact predict the FQ-xy order to be more favorable for $\text{Ba}_2\text{MgReO}_6$ in the absence of any structural distortion [19,30].

The calculated quadrupolar energy landscapes for both $\text{Ba}_2\text{MgReO}_6$ and $\text{Ba}_2\text{NaOsO}_6$, obtained from appropriate averaging as described in Sec. II B, are shown in Fig. 2. Both materials exhibit rather similar behavior and, most strikingly, both systems are unstable with respect to a spontaneous FQ-xy-type quadrupolar order. The corresponding energy curves exhibit a characteristic “double well” shape, with an energy lowering of about 3 meV/formula unit (f.u.) for $\text{Ba}_2\text{MgReO}_6$ and 2 meV/f.u. for $\text{Ba}_2\text{NaOsO}_6$ relative to the cubic non-quadrupolar state. In contrast, the energy associated with the AFQ- $x^2 - y^2$ order exhibits only a very shallow minimum of about 0.5 meV/f.u. for $\text{Ba}_2\text{MgReO}_6$ and no minimum away

from $Q_t = 0$ for $\text{Ba}_2\text{NaOsO}_6$, even though the energy landscape is notably flat in this region. We have verified that the penalty energy arising from the magnetic constraint in Eq. (2) is at least one order of magnitude smaller than these energy differences associated with the spontaneous quadrupolar order. We also note that both AFQ- $x^2 - y^2$ and FQ-xy orders allow for an additional secondary FQ- $3z^2 - r^2$ order appearing alongside the imposed quadrupole component, whereas all other quadrupolar components are negligible or zero on average. A potential energy-lowering associated with the formation of these $3z^2 - r^2$ quadrupoles is thus implicitly included in this data.

Our findings clearly show that, in the absence of any structural distortions or magnetic dipolar order, an FQ-xy order is preferred over an AFQ- $x^2 - y^2$ order, in line with previous reports for $\text{Ba}_2\text{MgReO}_6$ using complementary first-principles-based methods [19,30]. This is different from what was obtained from the purely electronic model presented in Ref. [9], which incorporated only a single simplified quadrupolar intersite interaction. On the other hand, the energy lowering of 3 meV/f.u. we obtain for FQ-xy order in $\text{Ba}_2\text{MgReO}_6$ is in very good quantitative agreement with the energy gain obtained from the more general electronic multipolar intersite exchange interactions calculated in Ref. [30].

The differences between the two materials are somewhat subtle, but overall the tendency for spontaneous quadrupolar order is consistently weaker in $\text{Ba}_2\text{NaOsO}_6$ compared to $\text{Ba}_2\text{MgReO}_6$, represented by the smaller energy gain for FQ-xy order, the smaller magnitude of the corresponding Q_t , and the absence of an energy minimum for AFQ- $x^2 - y^2$ order in $\text{Ba}_2\text{NaOsO}_6$. While these quantitative differences are small, they clearly indicate a weaker tendency for quadrupolar order in $\text{Ba}_2\text{NaOsO}_6$, consistent with the absence of any long-range ordered quadrupolar order or structural Jahn-Teller distortion above T_m .

Finally, we note that the relatively large error bars in Fig. 2, in particular, for small $|Q_t|$, result from large variations of the individual local quadrupole moments in the paramagnetic configurations, which suggests a rather strong influence of the specific local symmetry breaking through the quasirandom orientation of the local magnetic dipole moments. Indeed, if we switch off spin-orbit coupling in these calculations, the variation of the local quadrupoles in the $Q_t \approx 0$ region is significantly reduced. This demonstrates the strong coupling between quadrupole and magnetic dipole moments, mediated by the spin-orbit coupling, which is further analyzed in the next section.

B. Coupling between charge quadrupoles and magnetic dipoles

Next, we investigate the coupling between the quadrupolar order and the magnetic dipolar order. For this, we perform analogous calculations of the energy as function of the two relevant quadrupolar order parameters as in the previous section, but now with unconstrained magnetic moments. Thus, while the magnetic moments are initialized to a collinear ferromagnetic configuration with magnetization along $[110]$, i.e., the experimentally observed magnetization direction [15,16], the moment directions are free to relax in the subsequent calculation.

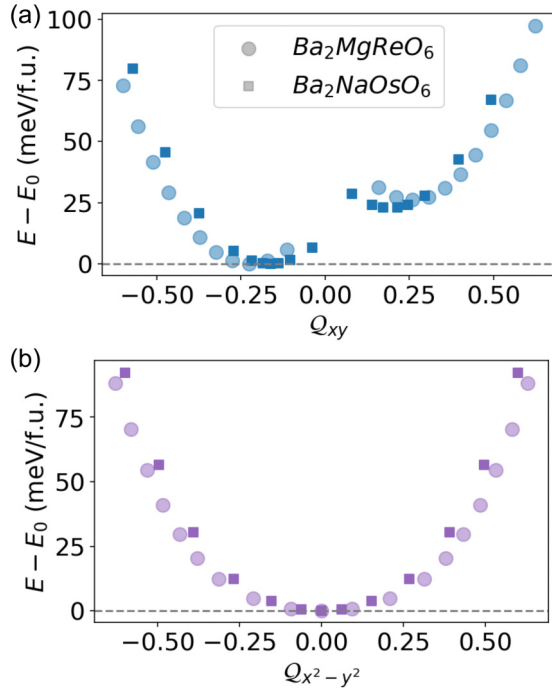


FIG. 3. Energy as function of the local quadrupole moments for Ba_2MgReO_6 (circles) and Ba_2NaOsO_6 (squares) for the ferromagnetic case with net magnetization along [110] and (a) FQ-xy order or (b) AFQ- $x^2 - y^2$ order.

A magnetization along [110] reduces the magnetic space group symmetry to $Im'm'm$. Nevertheless, we still fix the crystal structure to the experimentally observed perfectly cubic $Fm\bar{3}m$ symmetry, in order to separate the effect of the magnetic symmetry breaking from that of any structural distortion.

Figure 3(a) depicts the energy landscapes obtained for FQ-xy order for both materials, which exhibit two minima for both positive and negative $Q_{xy} \neq 0$. This resembles, to some extent, the double well obtained for the paramagnetic case. However, due to the symmetry reduction resulting from the magnetic order, the two minima for $Q_{xy} \neq 0$ are now unequal, with the global minimum at $Q_{xy} \approx -0.2$. We note that the significant energy difference between the two minima results solely from the strong spin-orbit coupling. Specifically, the presence of a magnetization along [110] breaks the fourfold symmetry around the z axis. Consequently, a 90° rotation around z , which changes the sign of the Q_{xy} quadrupole, is no longer a symmetry operation, and the states with $\pm Q_{xy}$ become inequivalent. This also means that rotating the magnetization by 90° into the $[\bar{1}\bar{1}0]$ direction switches the two energy minima such that the deeper minimum is now observed for $Q_{xy} \approx +0.2$ (we verified this in our calculations). On the other hand, a reversal of the magnetization by 180° does not affect the quadrupolar energy landscape, since Q_{xy} is invariant under this operation. The lower energy observed for negative Q_{xy} and magnetization along [110] means that the electrons around the Re and Os cations prefer to accumulate perpendicular to the axis of magnetization.

We note that the $Im'm'm$ symmetry resulting from the presence of a magnetization along [110] allows for a ferroically ordered Q_{xy} (and $Q_{3z^2-r^2}$) quadrupole moment to emerge

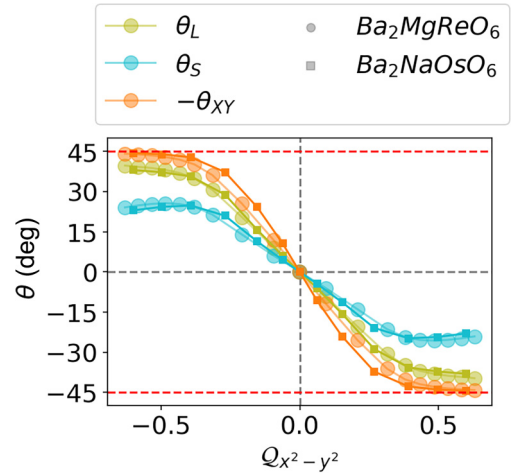


FIG. 4. Evolution of canting angles of the local orbital (green) and spin (blue) moments as a function of the local $Q_{x^2-y^2}$ component for an imposed AFQ- $x^2 - y^2$ order, together with the angle $- \theta_{XY}$ (orange) indicating the rotation of the total local quadrupole moment.

without any further symmetry lowering. Thus, the state with $Q_{xy} = 0$ does not correspond to an extremum of the total energy, and the minimum for $Q_{xy} \approx -0.2$ corresponds to a calculation with unconstrained quadrupoles.

Figure 3(b) shows analogous results for the AFQ- $x^2 - y^2$ order. It can be seen that emergence of this type of quadrupolar order is now energetically unfavorable for both materials, even though, similar to the paramagnetic case, the energy surface around $Q_{x^2-y^2} \approx 0$ is rather flat and cannot be fitted well with a simple quadratic parabolic behavior. Note that the sign of the local $Q_{x^2-y^2}$ moments can be reversed, e.g., by a mirror operation perpendicular to [110], which is still a symmetry operation within $Im'm'm$, and thus the energy in Fig. 3(b) is symmetric with respect to $\pm Q_{x^2-y^2}$.

Another important feature that can be seen from both panels in Fig. 3 is that the tendency toward quadrupole formation appears consistently slightly weaker for Ba_2NaOsO_6 than for Ba_2MgReO_6 , similar to what is observed for the paramagnetic case in Sec. III A. Specifically, in Fig. 3(a), the energy minimum for Ba_2NaOsO_6 appears for smaller $|Q_{xy}|$ than for Ba_2MgReO_6 , and in Fig. 3(b), one can recognize a slightly higher stiffness of the energy landscape for Ba_2NaOsO_6 .

These results demonstrate that in the cubic structure, and with net magnetization along [110], an FQ-xy order spontaneously occurs, while the experimentally observed AFQ- $x^2 - y^2$ configuration is energetically unfavorable.

We further observe that, while the local magnetic moments remain perfectly aligned along the [110] direction for the FQ-xy order, constraining a nonzero AFQ- $x^2 - y^2$ order leads to an antiferromagnetic canting of the Re/Os magnetic moments within the x - y plane away from the net magnetization direction, consistent with the canting observed experimentally in the lowest temperature phase of Ba_2MgReO_6 (cf. Fig. 1). The canting angles θ_S and θ_L , corresponding to the local spin and orbital moments, respectively, as function of the imposed $Q_{x^2-y^2}$ moment are shown in Fig. 4. In addition, together with the increasing local $Q_{x^2-y^2}$ quadrupole, the corresponding Q_{xy} moment is gradually reduced, until it eventually vanishes for

$|\mathcal{Q}_{x^2-y^2}| \gtrsim 0.5$. This gradual change from a $\mathcal{Q}_{xy}$ to a $\mathcal{Q}_{x^2-y^2}$ quadrupole can also be described as a rotation of the local quadrupole by 45° as shown in the following.

Defining quadrupoles $\mathcal{Q}_{XY}(\theta)$ and $\mathcal{Q}_{X^2-Y^2}(\theta)$ within a local coordinate system X - Y that is rotated by an angle θ around the z axis relative to our global coordinate system, the corresponding transformation of the quadrupole moments can be expressed as

$$\begin{pmatrix} \mathcal{Q}_{XY}(\theta) \\ \mathcal{Q}_{X^2-Y^2}(\theta) \end{pmatrix} = \begin{pmatrix} \cos 2\theta & -\sin 2\theta \\ \sin 2\theta & \cos 2\theta \end{pmatrix} \begin{pmatrix} \mathcal{Q}_{xy} \\ \mathcal{Q}_{x^2-y^2} \end{pmatrix}. \quad (4)$$

Thus, the angle defining the orientation of a coordinate system where $\mathcal{Q}_{X^2-Y^2} = 0$, i.e., describing the rotation of a local $\mathcal{Q}_{XY}$ quadrupole, is given by $\theta_{XY} = \frac{1}{2} \arctan(-\frac{\mathcal{Q}_{x^2-y^2}}{\mathcal{Q}_{xy}})$.

In Fig. 4, we also plot $-\theta_{XY}$ along with the canting angles of the spin and orbital moment. It can be seen that, in particular, the canting of the orbital moment closely follows, with opposite sign, the rotation defined by $-\theta_{XY}$. This makes sense, since the orientation of the local quadrupole reflects the occupation of the local d orbitals, which also sets the local single-ion anisotropy determining the preferred direction of the orbital moment. The observation that the orbital moment rotates opposite to the local quadrupole means that while, for the collinear ferromagnetic configuration, the axis of electron accumulation is oriented perpendicular to the magnetization direction, it becomes aligned with the local orbital moment for the maximally canted antiferroic configuration, i.e., for $\theta = \pm 45^\circ$, corresponding to a 90° angle between the two sublattices. The local spin moment follows the local orbital moment due to the strong spin-orbit coupling, but the fact that the canting of the spin moment is weaker than that of the orbital moment indicates a competition with the intersite spin-spin symmetric exchange favoring a collinear alignment, which leads to an unusual noncollinearity between the local spin and orbital moments. We also note that in these results there is no discernible difference between the two materials.

The same coupling between local magnetic and quadrupole moments can also be observed by constraining the spin moments instead of the quadrupoles. Figure 5 shows the evolution of the quadrupoles obtained from a set of calculations where we constrain the directions of the spin moments to a specific canting angle θ_S . Increasing θ_S leads to a gradual suppression of $\mathcal{Q}_{xy}$ and the emergence of an increasing AFQ- $x^2 - y^2$ component. We also plot the value of $\mathcal{Q}_{XY}(-\theta_S)$, defined according to Eq. (4), in a local coordinate system that rotates opposite to θ_S . Since, to a very good approximation, $\mathcal{Q}_{XY}(-\theta_S)$ remains constant for increasing spin canting, this shows that the spin canting results in an essentially rigid rotation of the charge anisotropy around the transition metal sites opposite to that of the spin moment. We also note that in these calculations the local orbital moments always remain nearly parallel to the local spin moments. The observation that the local quadrupole moments (and the local orbital moments) remain aligned with the spin moments also indicates that the quadrupolar intersite coupling, which prefers a FQ- xy alignment, is relatively weak compared to the spin-orbit coupling. Finally, it is important to note that the energy for the configurations with a constrained canting angle $\theta_S \neq 0$ is always higher than that of the collinear configuration with $\theta_S = 0$, indicating that the collinear ferromagnetic state with

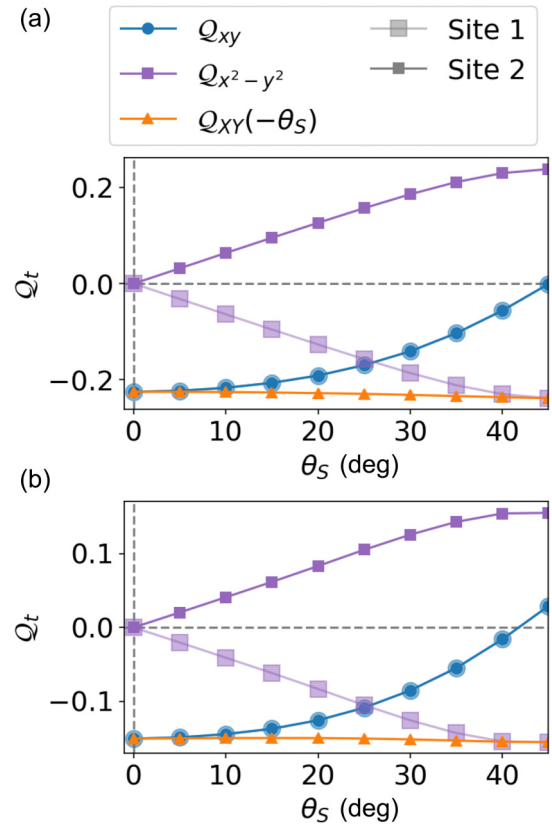


FIG. 5. Evolution of the local quadrupole components $\mathcal{Q}_{xy}$ and $\mathcal{Q}_{x^2-y^2}$ (defined in the global coordinate system) on the two B' sites in the unit cell as a function of the canting angle θ_S between the spin moments (defined on site 1) and the $[110]$ direction for (a) $\text{Ba}_2\text{MgReO}_6$ and (b) $\text{Ba}_2\text{NaOsO}_6$. $\mathcal{Q}_{XY}(-\theta_S)$ represents the xy -type quadrupole (on site 1) defined in a local coordinate system that is rotated in the opposite direction as the local spin moment, calculated according to Eq. (4).

magnetization along $[110]$ is the most favorable magnetic configuration for both materials, at least in the cubic structure and with magnetic moments confined to the x - y plane.

These results are consistent with Ref. [25], which already showed that the AFQ- $x^2 - y^2$ component in $\text{Ba}_2\text{MgReO}_6$ is zero for the cubic structure with collinear magnetic moments along $[110]$, but becomes nonzero when a spin canting is enforced. Here, we extend and complete this picture by considering all relevant quadrupole components, showing how the canting is related to a rotation of the local quadrupole, addressing the corresponding energetics, and also considering $\text{Ba}_2\text{NaOsO}_6$ as a closely related material.

The observation that the orientation of the orbital and also the spin moments closely follow the orientation of the local quadrupoles and vice versa indicates a strong local coupling between these quantities. Therefore, the coupling between the quadrupoles (encoding the anisotropy of the electron distribution around the B' atoms) and the orbital moments essentially represents a single-ion anisotropy, with orbital and spin moments then coupled via the strong spin-orbit coupling. Our results thus suggest that the canting of the magnetic moments is in fact driven by the AFQ- $x^2 - y^2$ order through this local coupling. In contrast, Ref. [24] attributed the canting of the mag-

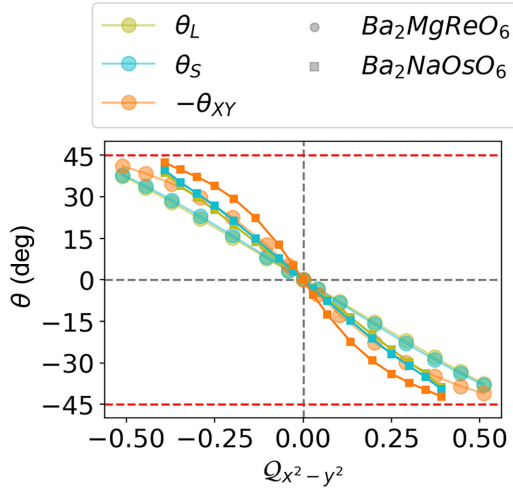


FIG. 6. Evolution of the local quadrupolar angle $-\theta_{XY}$ (orange), and the angles θ_L (green) and θ_S (blue), describing the orientation of the local orbital and spin moments, respectively, as a function of the $Q_{x^2-y^2}$ component of the local quadrupole for an imposed FQ- $x^2 - y^2$ order.

netic moments to intersite antisymmetric exchange. However, this suggestion was based on fitting a model containing only intersite interactions and no local couplings to the total energy as function of θ_S obtained from DFT calculations, which, in principle, contain both local and intersite interactions.

To address a potential effect of antisymmetric exchange, which is symmetry-allowed for nonzero AFQ- $x^2 - y^2$ order, we perform additional calculations where we impose a FQ- $x^2 - y^2$ order instead of the corresponding AFQ order. This FQ- $x^2 - y^2$ order preserves the inversion symmetry between neighboring B' sites, which means that antisymmetric exchange remains symmetry-forbidden. Analogously to the calculations corresponding to Fig. 4, we initialize the magnetic moments along the [110] direction, but they are free to relax to any direction during the calculation.

As shown in Fig. 6, also in this case the orientation of the orbital and spin moments closely follows the rotation of the local quadrupole described by $-\theta_{XY}$. Note that here the magnetic dipole moments stay perfectly collinear, with the same orientation on both B' sites in the unit cell, and thus the angles θ_S and θ_L merely describe a rotation of the spin and orbital moments relative to the [110] direction and not a canting between the magnetic sublattices. Thus, Fig. 6 shows that the magnetic moments rotate toward the x (y) direction for positive (negative) $Q_{x^2-y^2}$. Given the clear similarity between Figs. 4 and 6, and noting that intersite antisymmetric exchange is symmetry-allowed only in the first case, this strongly suggests that the quadrupolar single-ion anisotropy is indeed the dominant mechanism determining the orientation of the local spin and orbital moments in both cases, and is, in principle, on its own sufficient to establish the canted configuration observed experimentally.

C. Coupling to the structural Jahn-Teller distortion

Up to now, we have only considered purely electronic coupling between the charge multipoles and magnetic dipoles,

while the atomic positions were fixed to the perfectly cubic room-temperature structures. We have seen that both $\text{Ba}_2\text{MgReO}_6$ and $\text{Ba}_2\text{NaOsO}_6$ exhibit a tendency toward spontaneous quadrupolar order, and that the canting of the local magnetic dipoles away from the [110] direction is related to the AFQ- $x^2 - y^2$ order, which, however, is not energetically favorable. We have also seen that the tendency toward quadrupolar order is weaker in $\text{Ba}_2\text{NaOsO}_6$ compared to $\text{Ba}_2\text{MgReO}_6$, but that these quantitative differences are small and that qualitatively both materials behave very similar.

We now explore how the coupling between electronic and structural degrees of freedom affects the quadrupolar and magnetic dipolar order in $\text{Ba}_2\text{MgReO}_6$ and $\text{Ba}_2\text{NaOsO}_6$. We note that previous work, using different first-principles-based computational approaches, has already demonstrated that the coupling to the structural distortion is crucial to stabilize the experimentally observed AFQ- $x^2 - y^2$ order in $\text{Ba}_2\text{MgReO}_6$ [19,30].

We perform full structural relaxations for both materials starting from the reported Jahn-Teller-distorted low-temperature structure of $\text{Ba}_2\text{MgReO}_6$ [16]. Table I summarizes the relevant parameters of all relaxed and experimental structures, together with the local charge quadrupoles and the magnetic spin and orbital dipole moments calculated for each structure. The distortion of the oxygen octahedra around Re and Os is characterized by the collective modes, Q_1 - Q_6 , using Van Vleck notation according to Ref. [50], with all modes defined relative to the corresponding cubic $Fm\bar{3}m$ structures. We also include data calculated for the experimental cubic structures obtained without confining the magnetic moments to the x - y plane. In this case, the lowest energy state corresponds to a collinear ferromagnetic configuration with magnetization along the [111] direction, and a ferroic ordering of t_{2g} -type quadrupoles with $Q_{yz} = Q_{xz} = Q_{xy}$.

Focusing first on the results obtained for $\text{Ba}_2\text{MgReO}_6$, we find that the relaxed structure shows very good agreement with the reported low-temperature experimental structure from Ref. [16] (and also with the relaxed structure from Ref. [25], not shown in Table I), except for a slight overestimation of the calculated cell volume typical for the PBE functional. Consequently, the calculated quadrupoles and magnetic dipoles are also very similar to those obtained for the experimental $P4/mnm$ structure. Most importantly, the coupling between electronic and structural degrees of freedom now stabilizes an AFQ- $x^2 - y^2$ quadrupolar component and a corresponding Q_2 Jahn-Teller distortion, which now becomes energetically more favorable than the ferroic ordering of t_{2g} -type quadrupoles in the cubic structure. The stabilization of the AFQ- $x^2 - y^2$ order (and the AF- Q_2 Jahn-Teller distortion) is also accompanied by an AF canting of the magnetic moments away from the [110] direction, consistent with the analysis of the coupling between charge quadrupoles and magnetic dipoles presented in Sec. III B. The Q_{xy} and $Q_{x^2-y^2}$ quadrupoles correspond to a “quadrupolar angle,” θ_{XY} , of approximately -28° , while orbital and spin moments are canted by about 25° and 18° , respectively, relative to the [110] direction, indicating again a competition between the local easy magnetic axis set by the quadrupoles (now energetically stabilized by the Jahn-Teller distortion), the spin-orbit coupling, and the intersite symmetric spin exchange. This degree of canting is

TABLE I. Experimental and relaxed structural parameters for $\text{Ba}_2\text{MgReO}_6$ and $\text{Ba}_2\text{NaOsO}_6$, together with the local charge quadrupoles, Q_i , the angle θ_{XY} , magnetic spin and orbital dipoles, $\vec{S}$ and $\vec{L}$, absolute value of the total magnetic moment, $|\vec{M}|$, the corresponding canting angles, θ_S , θ_L , θ_M , and the energy differences, ΔE , obtained for the corresponding structures using the specified values for U_{eff} . The different structures are characterized by their unit cell volumes (per 2 f.u.), the ratio of out-of-plane and in-plane lattice parameters, $c/\sqrt{2}a$, the volume ratio of the BO_6 and $\text{B}'\text{O}_6$ octahedra, Q_{ratio} , and the (inversion symmetric) distortion modes of the ReO_6 octahedra, Q_1 - Q_6 , using the Van Vleck notation according to [50] and defined relative to the corresponding cubic $Fm\bar{3}m$ structure. Quantities that order antiferroically across the two B' sites in the cell are labeled with “(AF)”. The last column (labeled “ θ_S constrained”) contains results of a relaxation with constrained θ_S (see main text for details).

Structure	$\text{Ba}_2\text{MgReO}_6$			$\text{Ba}_2\text{NaOsO}_6$			
	$Fm\bar{3}m$ [16]	$P4_2/mnm$ [16]	Relaxed	$Fm\bar{3}m$ [33]	Relaxed	Relaxed	Relaxed (θ_S constr.)
U_{eff} (eV)	1.8	1.8	1.8	1.8	1.8	3.4	3.4
Vol. ($\text{\AA}^3$)	263.78	263.78	274.87	283.97	293.60	292.98	293.05
$c/\sqrt{2}a$	1.000	1.001	1.002	1.000	1.000	1.000	0.996
Q_{ratio}	1.322	1.323	1.305	1.723	1.715	1.733	1.734
ΔE (eV/f.u.)	0.146	0.148	0.000	0.118	0.000	0.000	0.008
Jahn-Teller modes							
Q_1 ($\text{\AA}$)	0.000	-0.001	0.076	0.000	0.055	0.043	0.043
Q_2 ($\text{\AA}$) (AF)	0.000	-0.044	-0.036	0.000	0.000	0.000	-0.018
Q_3 ($\text{\AA}$)	0.000	0.010	0.002	0.000	0.000	0.000	-0.010
Q_4 ($\text{\AA}$)	0.000	0.000	0.000	0.000	-0.012	0.014	0.000
Q_5 ($\text{\AA}$)	0.000	0.000	0.000	0.000	-0.012	0.014	0.000
Q_6 ($\text{\AA}$)	0.000	0.000	0.019	0.000	0.012	0.014	-0.019
Charge quadrupoles							
$Q_{x^2-y^2}$ (AF)	0.000	-0.248	-0.208	0.000	0.000	0.000	-0.135
Q_{z^2}	0.000	0.043	0.010	0.000	-0.001	0.000	-0.065
Q_{yz}	-0.126	0.000	0.001	-0.088	0.091	-0.111	0.000
Q_{xz}	-0.126	0.000	0.001	-0.088	0.091	-0.111	0.000
Q_{xy}	-0.126	-0.078	-0.142	-0.088	-0.092	-0.111	0.143
θ_{XY} (deg)	-	-36.3	-27.8	-	-	-	-68.3
Spin moments							
S_x (μ_B)	-0.449	-0.283	-0.341	-0.375	-0.379	-0.415	0.245
S_y (μ_B)	-0.449	-0.673	-0.678	-0.375	-0.379	-0.415	-0.608
S_z (μ_B)	-0.449	0.001	0.003	-0.375	0.376	-0.416	0.000
θ_S (deg)	-	22.2	18.3	-	-	-	67.0
Orbital moments							
L_x (μ_B)	0.151	0.050	0.085	0.114	0.119	0.140	-0.095
L_y (μ_B)	0.151	0.226	0.236	0.114	0.118	0.140	0.214
L_z (μ_B)	0.151	0.000	-0.001	0.115	-0.118	0.140	0.000
θ_L (deg)	-	32.5	25.1	-	-	-	68.9
Total magnetic moments							
$ \vec{M} $ (μ_B)	0.516	0.504	0.511	0.451	0.450	0.477	0.421
θ_M (deg)	-	17.5	14.9	-	-	-	65.8

consistent with the previous first-principles study of Ref. [25]. Defining the total magnetic moment simply as $\vec{M} = \vec{S} + \vec{L}$ (note that here $\vec{S}$ and $\vec{L}$ are defined in μ_B) results in a canting angle of about 15° for $\vec{M}$, which is significantly smaller than the experimentally reported value of 40° [15]. However, we note that this angle has merely been estimated from the discrepancy between the observed magnetization of $0.46\mu_B$ per Re and an assumed local magnetic moment of $0.6\mu_B$. Indeed, our calculated $\vec{M}$ corresponds to a net magnetization of $0.49\mu_B$ per Re along [110] and is thus in excellent agreement with the experimentally measured magnetization.

We now turn to the results obtained for $\text{Ba}_2\text{NaOsO}_6$. To allow for a better comparison with Ref. [24], where a value of $U_{\text{eff}} = 3.4$ eV has been used, we perform relaxations for both $U_{\text{eff}} = 1.8$ eV and $U_{\text{eff}} = 3.4$ eV. As seen from Table I, the initialized AF- Q_2 Jahn-Teller distortion is not stable in $\text{Ba}_2\text{NaOsO}_6$ for both values of U_{eff} , and the system relaxes to a state with a ferroic ordering of t_{2g} -type quadrupoles, a small (ferroic) trigonal distortion of the OsO_6 octahedra, corresponding to $|Q_4| = |Q_5| = |Q_6| \neq 0$, and a collinear ferromagnetic order with magnetization along a [111]-type direction. (Note that magnetization directions of $[\bar{1}\bar{1}1]$ and $[\bar{1}\bar{1}\bar{1}]$ only represent different but equivalent domain states.)

This state is, in principle, equivalent to the electronic and magnetic ground state obtained for the cubic structure (for both $\text{Ba}_2\text{NaOsO}_6$ and $\text{Ba}_2\text{MgReO}_6$), but with the additional appearance of the t_{2g} -type Jahn-Teller modes, consistent with the symmetry lowering stemming from the magnetic and quadrupolar order. The resulting trigonal distortion of the OsO_6 octahedra corresponds to the ground state of a d^1 ion in an isolated octahedron coupled to t_{2g} -like distortion modes, the so-called $t \otimes T$ problem, in the presence of zero or finite spin-orbit coupling [51,52]. Finally, we point out that the corresponding unit cell volume and the relative size of the BO_6 and $\text{B}'\text{O}_6$ octahedra agree very well with the experimental data for the cubic structure (for both values of U_{eff}), again with the usual PBE overestimation of the total volume.

The absence of a stable AF- Q_2 Jahn-Teller distortion and a resulting canting of the magnetic moments in $\text{Ba}_2\text{NaOsO}_6$ might appear at odds with results of previous first-principles calculations presented in Ref. [24]. However, we note that in the structural relaxations of Ref. [24], the spin moments have been constrained to the experimentally reported canting angle of 67° . Therefore, Table I also contains our results of completely analogous relaxations with θ_S constrained to 67° (performed only for $U_{\text{eff}} = 3.4 \text{ eV}$). The resulting structure agrees well with that of Ref. [24], and one can see that in this case the AF- Q_2 distortion indeed remains stable, even though the resulting amplitude is only about half of that obtained for $\text{Ba}_2\text{MgReO}_6$.

The fact that constraining a nonzero spin canting stabilizes an AF- Q_2 Jahn-Teller distortion is fully consistent with our results presented in Fig. 5, where constraining θ_S induces an $\text{AFQ-}x^2 - y^2$ order in the cubic structure. If the structural degrees of freedom are allowed to relax, such an $\text{AFQ-}x^2 - y^2$ order will then produce a corresponding AF- Q_2 Jahn-Teller distortion, due to a bilinear coupling between the local quadrupole and Jahn-Teller mode (see, e.g., Ref. [30]). However, as shown by our unconstrained relaxations, the spin canting and associated AF- Q_2 Jahn-Teller distortion is not energetically stable for $\text{Ba}_2\text{NaOsO}_6$, even for a value of U_{eff} significantly exceeding the value calculated from linear response theory (cf. Sec. IIB).

Thus, the results of our structural relaxations indicate that the coupling to the Jahn-Teller distortion is significantly weaker in $\text{Ba}_2\text{NaOsO}_6$ compared to $\text{Ba}_2\text{MgReO}_6$. In principle, this appears to be consistent with the absence of any experimentally resolvable Jahn-Teller distortion above T_m in $\text{Ba}_2\text{NaOsO}_6$. Even though our fully relaxed structure exhibits a small trigonal Jahn-Teller distortion, this distortion is rather subtle. The distortion corresponds to oxygen displacements smaller than $0.01 \text{ \AA}$, and the trigonal distortion of the lattice vectors is less than 0.005° . Furthermore, the presence of magnetic long-range order in the corresponding calculations might even lead to an overestimation of the corresponding distortion. On the other hand, the absence of a stable $\text{AFQ-}x^2 - y^2$ order and a corresponding AF- Q_2 Jahn-Teller distortion in the relaxed structure also results in an absence of any canting between the magnetic moments, which appears to be in contradiction to experimental observation based on the analysis of NMR spectra [12].

IV. SUMMARY AND CONCLUSIONS

In this work, we have addressed the possible emergence of quadrupolar order and its coupling to magnetic dipolar order and structural Jahn-Teller distortions for two closely related $5d^1$ double perovskites, $\text{Ba}_2\text{MgReO}_6$ and $\text{Ba}_2\text{NaOsO}_6$. We have shown that both materials exhibit a tendency for spontaneous quadrupolar order even in the completely undistorted, perfectly cubic structure, and even in the absence of any magnetic dipolar order. In this case, a ferroic ordering of t_{2g} -type quadrupoles, e.g., FQ- xy order, is energetically more favorable than a potential $\text{AFQ-}x^2 - y^2$ order for both systems, and the overall tendency toward quadrupolar order is slightly weaker for $\text{Ba}_2\text{NaOsO}_6$ than for $\text{Ba}_2\text{MgReO}_6$. The preference for FQ- xy -type order in the absence of any structural distortion is consistent with several previous first-principles-based studies for $\text{Ba}_2\text{MgReO}_6$ [19,30] and confirms that a coupling to the structural Jahn-Teller distortion has to be taken into account to explain the experimentally observed low-temperature phase.

For the magnetically ordered case with net magnetization along [110], we have demonstrated an intimate coupling between the local quadrupoles and the local magnetic dipoles. Even though FQ- xy order is still energetically preferred over $\text{AFQ-}x^2 - y^2$ order in the absence of any structural distortion, the gradual introduction of a nonzero $\text{AFQ-}x^2 - y^2$ component, equivalent to an alternating rotation of the local charge anisotropy around the z axis, leads to a corresponding canting of the magnetic dipoles away from the net magnetization direction. Therefore, the orbital moments follow the local easy axis set by the quadrupole almost rigidly, while the spin moments “lag behind,” indicating a competition between the strong spin-orbit coupling, which tends to align the spin and orbital moments, and the usual symmetric intersite spin exchange, which prefers a collinear alignment of spins on neighboring sites. Conversely, an enforced canting of the spin moments also leads to a corresponding alternating rotation of the local quadrupole or, equivalently, an induced $\text{AFQ-}x^2 - y^2$ component.

We note that an equivalent coupling between the canting of the spin moment and the local charge quadrupoles has also been observed in Ref. [25] for $\text{Ba}_2\text{MgReO}_6$, albeit calculated for the distorted $P4_2/mnm$ structure. In that case, due to the presence of the corresponding Jahn-Teller distortion, the $\text{AFQ-}x^2 - y^2$ component persists along the whole range of explored canting angles, due to the strong bilinear coupling between quadrupoles and Jahn-Teller distortion, but nevertheless a similar rotation of the total local quadrupole (described by both $Q_{x^2-y^2}$ and Q_{xy} components) as function of the spin canting can be observed. A coupling between quadrupoles and local magnetic dipoles is also consistent with the coupling between the spin canting and local Jahn-Teller distortion observed in first-principles calculations for $\text{Ba}_2\text{NaOsO}_6$ in Ref. [24], considering that imposing a Jahn-Teller distortion on the $\text{B}'\text{O}_6$ octahedra will inevitably also generate a corresponding local quadrupole component (and vice versa).

Finally, considering also small distortions of the cubic structure, we again confirm the energetic stabilization of the $\text{AFQ-}x^2 - y^2$ by the simultaneous emergence of a corresponding AF- Q_2 Jahn-Teller mode for $\text{Ba}_2\text{MgReO}_6$, consistent with

the experimentally observed low-temperature phase. In addition, we obtain excellent quantitative agreement with the corresponding experimental data, both for the degree of structural distortion and the net magnetization. For $\text{Ba}_2\text{NaOsO}_6$, the coupling to the structural distortion is significantly weaker and is not sufficient to stabilize an antiferroic order of local quadrupoles or a corresponding Jahn-Teller distortion. While this is consistent with the absence of any long-range-ordered distorted phase above T_m in $\text{Ba}_2\text{NaOsO}_6$, it appears to be at odds with the reported canted magnetic order below T_m , since, according to our analysis (and Refs. [24,25]), such a canting should be tied to an antiferroic quadrupolar order, which, however, appears energetically unfavorable in our calculations.

Further research is required to resolve this remaining discrepancy for $\text{Ba}_2\text{NaOsO}_6$. We note that, while there is no reason why the PBE + U approach used in our work should be more suitable for $\text{Ba}_2\text{MgReO}_6$ than for $\text{Ba}_2\text{NaOsO}_6$, the small volume overestimation inherent in the PBE functional could, in principle, introduce some systematic deviations in the corresponding results. It would also be instructive to investigate whether correlation effects beyond the static DFT + U approximation used here could affect the complex properties of these systems, by performing calculations for both materials, e.g., within DFT plus dynamical mean-field theory [53].

In summary, by systematically comparing results for two isoelectronic and isostructural $5d^1$ double perovskites, we have elucidated the mechanisms that govern the emergence of their symmetry-broken low-temperature phases with strongly coupled quadrupolar, magnetic dipolar, and structural degrees of freedom. Our work can thus serve as reference for future studies of other $5d^1$ double perovskites, and also provides a well-defined starting point for future studies relating the observed trends to differences in the underlying structural or electronic parameters (e.g., unit cell volume, B - B' size ratio, intersite hopping, degree of d - p hybridization, etc.).

ACKNOWLEDGMENTS

This work was supported by ETH Zürich. Calculations were performed on the Euler cluster of ETH Zürich and the Eiger cluster at the Swiss National Supercomputing Center (Project ID s1304). We further acknowledge the use of the VESTA software package for structural visualizations [54].

DATA AVAILABILITY

The data that support the findings of this article are openly available in Ref. [55].

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