Interplay between multipolar spin interactions, Jahn-Teller effect, and electronic correlation in a $J_{\text{eff}} = \frac{3}{2}$ insulator

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(Received 28 May 2020; revised 4 February 2021; accepted 19 February 2021; published 1 March 2021)

In this work, we study the complex entanglement between spin interactions, electron correlation, and Jahn-Teller structural instabilities in the 5$d^1$ $J_{\text{eff}} = \frac{3}{2}$ spin-orbit coupled double perovskite Ba$_2$NaOsO$_6$ using first principles approaches. By combining noncollinear magnetic calculations with multipolar pseudospin Hamiltonian analysis and many-body techniques, we elucidate the origin of the observed quadrupolar canted antiferromagnetic order. We show that the noncollinear magnetic order originates from Jahn-Teller distortions due to the cooperation of Heisenberg exchange, quadrupolar spin-spin terms, and both dipolar and multipolar Dzyaloshinskii-Moriya interactions. We find a strong competition between ferromagnetic and antiferromagnetic canted and collinear quadrupolar magnetic phases: the transition from one magnetic order to another can be controlled by the strength of the electronic correlation ($U$) and by the degree of Jahn-Teller distortions.

DOI: 10.1103/PhysRevB.103.104401

I. INTRODUCTION

Double perovskites with strong spin-orbit coupling (SOC) represent a unique playground for the emergence of exotic spin-orbital-lattice entangled phases [1–5]. Structural and orbital frustrations [6], SOC-induced formation of effective J manifolds [7], and relatively strong electronic correlation give rise to a wide range of unusual electronic and magnetic phases including so-called Dirac-Mott insulating states [8,9], multipolar spin interactions [1,2,8], and entangled SOC-Jahn-Teller effects [3,10].

A particularly interesting case is that of 5$d^1$ double perovskites characterized by an effective total angular momentum $J_{\text{eff}} = 3/2$, an example of which is Ba$_2$NaOsO$_6$ (BNOO). BNOO is Dirac-Mott insulator [8,11] with strong SOC and electronic correlation effects [12–14]. Magnetization measurements indicate that below 6.8 K BNOO exhibits weak ferromagnetic interactions and a small ordered spin moment of 0.2 $\mu_B$ [15–18]. Refined NMR analysis confirmed the theoretically predicted canted spin state with two magnetic sublattices [2,19]. In this spin model, depicted in Fig. 1(a), the spins align ferromagnetically within the $xy$ plane with alternating canting angle $\varphi$ in adjacent planes along the $[001]$ axis [see Fig. 1(e)]. As the optimal canting angle extracted from the NMR data, $\varphi_{\text{expt}} = 67^\circ$, is closer to the antiferromagnetic (AFM) limit ($90^\circ$) than to the ferromagnetic (FM) one ($0^\circ$), it is more appropriate to use the jargon canted-antiferromagnetic (c-AFM), rather than c-FM as initially proposed [2,19,20]. The most stunning aspect of BNOO is that this c-AFM phase is associated with a local point symmetry breaking manifested by local deformations of the BO$_6$ octahedra [19,21]. However, x-ray diffraction shows that the cubic symmetry is maintained even at low temperature [16] and no direct evidence of Jahn-Teller (JT) instabilities have been detected by NMR [19,21], even though JT instabilities would be expected in a $d^1$ electronic configuration [6,22] (one of the models proposed in Ref. [19] involves a contraction of the OsO$_6$ octahedra, assimilable to a local $Q_{\text{JT}}$ distortion; see Fig. 1). This apparent violation of the JT theorem [23,24] has been explained by the entanglement of vibronic dynamics with SOC, suggesting the presence of a dynamical Jahn-Teller effect with small static component [3,10] and orbital selective quadrupolar charge ordering [25]. This explains the breaking of local point symmetry and suggests that the canted magnetic ground state of BNOO should be described in terms of the spin-orbital-lattice entangled states involving high-rank spin interactions.

With this study, we aim to clarify the link between JT instabilities and spin couplings by computing the variation of the multipolar interactions due to local structural distortions and explain how this JT-multipolar coupling affects the spin deflection and dictates the formation of the c-AFM ground state. We do so by employing first-principles noncollinear relativistic density functional theory (DFT) [29–31] within the Perdew-Burke-Ernzerhof approximation [32] using the
Slightly lower U or larger JT distortions shift the system to a competing canted-ferromagnetic (c-FM) state.

II. RESULTS AND DISCUSSION

We start by comparing the dependence of the energy on the canting angle for the JT-distorted and JT-quenched (undistorted) phases in Fig. 2, obtained by changing stepwise the canting angle \( \phi \) from the FM (\( \phi = 0^\circ \)) to the AFM (\( \phi = 90^\circ \)) limits. The JT structure exhibits two minima, a lower c-AFM ground state found at \( \phi = 66^\circ \), in excellent agreement with experiment (67° [19]) and a c-FM phase just 0.05 meV/u.c. higher in energy. Conversely, the undistorted structure shows a clear minimum for a parallel spin alignment followed by an AFM state. The size of the spin (\( m_s \)) and orbital (\( m_o \)) moments are essentially the same in both structures (\( m_s \approx 0.8 \mu_B \) and \( m_o \approx 0.6 \mu_B \)). In the ground-state JT-distorted structure, the resulting net ordered moment is 0.23\( \mu_B \), in very good agreement with measurements (0.2\( \mu_B \)) [16,19]. These results clearly indicate that the JT effect is essential to stabilize the observed canted ground state.

To decipher the role of JT distortions on the spin deflection, we have extracted the intersite spin interactions by fitting the canting energies curves with a pseudospin Hamiltonian in the general multipolar form [49,50]:

\[
H_{ij} = \sum_{k,K} \sum_{Q,K} I_{kk}^{OQ} O_k^{(i)} O_K^{(j)},
\]

where \( i, j \) are the site indexes, \( I_{kk}^{OQ} \) are the coupling constants, and \( O_k^{(i)}(j) \) and \( O_K^{(i)}(j) \) are the multipolar tensor operators of rank \( K \) and \( K' \), with \( K \leq 2J_i, Q = -K, \ldots, K, K' \leq 2J_i, Q' = -K', \ldots, K' \). The multipolar operators \( O \) are estimated within the mean-field approximation, i.e., \( O(J_i)O(J_j) \approx \langle O(J_i)O(J_j) \rangle - \langle O(J_i) \rangle \langle O(J_j) \rangle \). After applying symmetry properties of pseudovectors and multipolar operators for the \( \Gamma_1 \) state [151] as well as crystal symmetry, we obtained the following fitting formula which expresses the magnetic energy as a function of the canting angle \( \phi \) (the derivation is given in the SM [27]):

\[
E(\theta) = A_1 \cos(2\phi) + A_2 \cos(4\phi) + A_3 \cos(6\phi),
\]

\[
+ B_1 \sin(2\phi) + B_2 \sin(4\phi).
\]

To validate the DFT mapping and decode the specific type of spin couplings at play, we have performed a direct calculation of the intersite interactions using the FT-HI method proposed by Pournovskii [40] and ED [41], taking the undistorted phase as a reference (FT-HI and ED cannot be applied to the JT-distorted phase). All possible on-site fluctuations within the paramagnetic ground state of a shell, encoded by the corresponding multipole moments \( O_k^{(i)}(J_i) \), are included; all relevant intersite couplings can thus be extracted. In the present case of the \( J_{\text{eff}} = \frac{3}{2} \) shell of Os, those are all intersite interactions between dipole, quadrupole, and octupole moments that are permitted by the symmetry. With the effective Hamiltonian thus obtained, we evaluated the dependence of zero-temperature total energy versus \( \phi \); the spin-spin coupling parameters \( A_i \) are subsequently extracted by fitting it to the form (2).
The fitting curves follow very well the first-principles data for both the distorted and undistorted phases as shown in Figs. 2(a) and 2(b). The optimal fitting parameters and the corresponding FT-HI and ED results are collected in Table I, where each coefficient is associated with the specific type of dipolar or multipolar couplings. Both phases exhibit relatively large quadrupole-quadrupole (q-q) couplings and non-negligible octupole-octupole (o-o) interactions. The inclusion of o-o terms in the JT phase is essential to shift the minimum from 70° to 66°, whereas the formation of the two competing canted minima is mostly governed by the q-q term A2. We also note that DM interactions, embedded in coefficients B1 and B2, are inoperative in the undistorted phase (not allowed by symmetry), but the breaking of the local symmetry caused by the JT effect activates the DM channel, which is mainly responsible for stabilizing the canted phases. Our data indicate that besides the standard first-order d-d DM interaction, an additional second-order d-d DM coupling emerges involving both q-q and d-o terms. This type of interaction can be classified as multipolar DM interaction, namely an antisymmetric DM exchange among multipolar tensors.

After clarifying the essential features of the c-AFM ground state, we move now to the analysis of the competition between the c-AFM and c-FM phases and how this competition is controlled by the strength of U and the degree of JT mode Q1. Being almost degenerate in energy, it is expected that small perturbations could change the relative stability of these two phases, providing insights on the mechanism favoring one or the other spin ordering. To explore this possibility, we have computed the canting energies for different values of the relative JT distortion Q1 (from the fully distorted structure, here identified as Q1 = 1 to the undistorted Q1 = 0 limit) and U (from 3.4 to 2.4 eV). The results, displayed in Fig. 3, indicate that both degrees of freedom act on the spin deflection and can trigger a magnetic transition from the c-AFM to c-FM.

By decreasing U, the c-AFM phase is progressively destabilized in favor of the c-FM phase which becomes the global minimum. A further decrease of U washes out completely the AFM canting. Similarly, reducing Q1 acts on the canting angle by inverting the stability of the two canted minima and drives the systems toward the collinear limits as Q1 approaches 0. In order to explore the combined action of JT effect and electronic correlation, we have repeated similar calculations and constructed a complete magnetic phase diagram as a function of Q1 and U, displayed in Fig. 3(c). The phase diagram shows three different phases characterized by specific value of the canting angle: (i) a FM phase which is favored in the limit of vanishing JT distortion and small U, (ii) a c-FM phase emerges beyond a small critical JT distortion in the whole considered U regime, and finally (iii) the c-AFM phase, corresponding to the experimentally observed ground state, which covers the top portion of the phase diagram and is favored by increasing the JT mode and U. For Q1 = 1, the c-AFM phase represents the ground state for U larger than 3.1 eV.

The interplay between Q1 and U affects the exchange couplings. The transition from one phase to the other can be rationalized by inspecting the variation of the spin-spin interactions upon U and Q1 shown in Fig. 4. First, we note that the tendency to move toward a FM-type canting is mostly triggered by the steep decrease of the d-d interaction

![Image](https://www.pnas.org/content/early/2021/04/30/2021171196.full.pdf)

**FIG. 2.** Dependence of the energy on the canting angle and spin-spin interaction matrix. (a) Calculated DFT+U+SOC φ dependent energies for the optimized JT-distorted phase (circles) and corresponding fitting curve obtained using Eq. (2). The fitting curves obtained by removing the A1 (o-o), the A2 (q-q), and A2-A2-B2 (q-q and o-o) coefficients are also displayed. (b) Comparison between DFT, FT-HI, and ED canting energies for the undistorted (Q1 = 0) phase. (c) FT-HI interaction matrix showing the nonzero and nonconstant mean values of the tensor operators \( \langle O \rangle \) in the pseudospin eigenbasis [see Eq. (1)] summed over the out-of plane interacting bonds (see SM for details [27]). To guarantee a quantitatively consistent comparison between DFT and FT-HI, the DFT FM-AFM energy difference is aligned to that obtained by FT-HI (see SM for details [27]).

| Spin-spin interactions (in meV) as derived from DFT, FT-HI, and ED approaches for the undistorted Q1 = 0 FM phase and corresponding DFT values for the fully distorted c-AFM phase. | Coefficients | FT-HI | ED | DFT | |---|---|---|---|---|---| | A1 | d-d | 0.84 | 0.39 | | q-q | -0.03 | 0.00 | | o-o | -1.32 | -1.25 | | A2 | q-q | -0.40 | -0.48 | -0.66 | | A3 | o-o | -0.21 | | | B1 | DM d-d | 0 | 0 | 0 | | B2 | DM q-q, d-o | 0 | 0 | 0 | }
embedded in the exchange coefficient $A_1$, which changes sign rather quickly when $U$ or $\tilde{Q}_1$ are reduced, thereby driving the AFM-to-FM transition. We note that coefficients $A_3$ and $B_2$, besides being relatively small, remain essentially unaffected by tuning $U$ at the optimized JT distorted structure, implying that the o-o character is mostly linked to the structural instabilities. This is confirmed by the observation that $A_3$ is rapidly diminished with decreasing $\tilde{Q}_1$, thus revealing a direct link between o-o interaction and structural distortion. The JT distortion is therefore a determinant factor for the onset of the dipolar and multipoles DM interactions expressed by the coefficient $B_1$ and $B_2$, respectively. Similar to the multipolar DM component, the dipolar one ($B_1$), which is zero by symmetry in the undistorted limit, also rapidly increases versus $\tilde{Q}_1$ and reaches a large value in the fully JT-distorted phase ($B_1 = -0.99$ meV). Finally, from the trend of $A_2$, we infer that q-q interactions become stronger with decreasing $\tilde{Q}_1$ and are responsible for the preservation of the two minima in the undistorted phase. Conversely, reducing $U$ leads to a linear reduction of $A_2$, which contributes to the disruption of the large-$\phi$ minimum. The above analysis can give insights on the role of dynamical JT effects in BNOO that should be manifested by two types of magnetic fluctuations: FM fluctuations, controlled by the changes in $A_1$, and canted-FM to canted-AFM fluctuations governed by the variation of $B_1$.

III. SUMMARY AND CONCLUSIONS

In conclusion, by combining many-body effective Hamiltonians with material-specific DFT-based descriptions, we have decoded the complex entanglement between structural frustration and electronic correlation in the spin-orbit coupled and spin-canted double perovskite BNOO. We show that this exotic magnetic order originates from the anomalous Dzyaloshinskii-Morya interactions generated by JT distortions and elucidate the direct effect of $U$ and JT on the spin-spin interactions. This work contributes to recent study of atypical multipolar orderings in relativistic oxides [52,53] with a transparent analysis that helps to show the intricate physics at play in this class of materials.

To study the cross coupling between spin exchange interaction, Jahn-Teller distortions, and electronic correlation, we have integrated three different schemes: magnetically constrained noncollinear DFT+$U$, DMFT in the Hubbard-I approximation (FT-HI) combined with the magnetic force theorem, and exact diagonalization. Since the direct computation of spin exchanges at FT-HI and ED for JT-distorted structures is at present not possible, we have first verified the validity of the DFT+$U$ data for the undistorted phase by comparing the spin exchanges extracted from DFT+$U$ total energies with those calculated explicitly at FT-HI and ED level [Fig. 2(b)]. In DFT+$U$, the spin interactions are estimated by fitting the total energy curves obtained at different canting angles (via magnetically constrained calculations) with the spin Hamiltonian given in Eq. (2) (derived in the SM [27]). After normalizing the DFT+$U$ data to the FT-HI/ED values (see SM [27] for further details), we have then addressed the JT-induced modifications at DFT+$U$ level, by performing a series of calculation stepwise from the ideal undistorted phase to the fully distorted real structure [Figs. 3(a) and 3(b)]. In order to account for the role of electron-electron correlation and construct the phase diagram displayed in Fig. 3(c), these calculations have been conducted for different values of $U$, from 2.4 to 3.4 eV.

In studying the JT distortion, we have followed the Van Vleck notation for the definition of the main JT distortions $Q_1$, $Q_2$, and $Q_3$. Since the value of $Q_1$ is significantly larger than the corresponding $Q_2$ and $Q_3$ values (see SM [27]), we have considered the variation of the the spin interactions as a
function of the JT parameter $\hat{Q}_1$, defined as the ratio between $\hat{Q}_1$ for the interpolated structure and the corresponding value for the optimal one. Additional details can be found in the SM [27], which includes Refs. [54–61].

ACKNOWLEDGMENTS

We gratefully acknowledge the helpful discussions with V. Mitrovic. C.F. thanks S. Streltsov for useful insights on the Jahn-Teller effect. D.F.M. acknowledges support from the Vienna Doctoral School in Physics and the University of Bologna (Thesis Abroad Scholarship). L.V.P. acknowledges the support by the European Research Council Grant No. ERC-319286-QMAC and is grateful to the computer team at CPHT for support. B.H.K. was supported by a KIAS Individual Grant (No. CG068701) at Korea Institute for Advanced Study. The computational results were achieved by using the Vienna Scientific Cluster (VSC).

[60] L. V. Purovskii (private communication).