

# Orbital-Quenching-Induced Magnetism in $\text{Ba}_2\text{NaOsO}_6$

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The double perovskite  $\text{Ba}_2\text{NaOsO}_6$  with heptavalent Os ( $d^1$ ) is observed to remain in the ideal cubic structure despite single occupation of the  $t_{2g}$  orbitals, even in the ferromagnetically ordered phase below 6.8 K. Analysis based on an *ab initio* tight-binding dispersion, spin-orbit coupling, Hund's coupling, and strong Coulomb repulsion shows that the magnetic  $\text{OsO}_6$  cluster is near a momentless condition due to spin and orbital compensation. Quenching (hybridization) then drives the emergence of magnetism. An on-site Coulomb repulsion  $U > U_c = 1.1$  eV is necessary to produce the observed (Mott) insulating phase.

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Orbital physics in transition metal oxides has attracted a good deal of attention for three decades, with a good deal of activity focused on coupling to spin, charge, and lattice degrees of freedom in  $d^1$  systems. The  $d^1$  configuration is typically found in the early 3d transition metals (TMs), *i.e.* titanates and vanadates, and the associated phenomena – often revolving around the tendency to orbitally order – are remarkably rich. The  $d^1$  configuration can also occur in the mid- to late-5d TM ions, which are distinguished also by unusually high formal valence states.

Unless fully itinerant, partially filled  $d$  shells lead to non-spherical ions that often are accommodated by orbital ordering (OO), that is, ordered alignment of the filled orbitals[1] in the manner that minimizes strain, electronic, and magnetic energies. An outcome is that OO has been identified as the driving mechanism in symmetry-breaking structural and magnetic transitions,[2] and can also be coupled to magnetism and charge order, the Mott insulating  $d^1$  perovskite  $\text{YTiO}_3$  being a well studied example.[3] Very different behavior is shown by the  $d^1$  system  $\text{LaTiO}_3$  which has a structural distortion although evidence of OO has been difficult to obtain. A prominent explanation is that orbital fluctuations dominate, leading to a disordered *orbital liquid* ground state.[4, 5]

$\text{Ba}_2\text{NaOsO}_6$  (BNOO) is an example of a heptavalent osmium compound ( $d^1$  if formal valence is meaningful; we demonstrate below that it is) showing unusual behavior. It is a double perovskite structure ferromagnetic insulator[6, 7] ( $T_C = 6.8$  K) with a single 5d electron in the  $t_{2g}$  complex that orders magnetically, yet it shows no evidence of orbital order that would destroy its cubic symmetry. On the other hand,  $\text{La}_2\text{NaOsO}_6$  with high-spin  $d^3$  Os configuration with nominally cubic symmetry is observed to be highly distorted,[8] which is ascribed to misfit arising from the small cation radius. The question of spin ordering may also be delicate, since

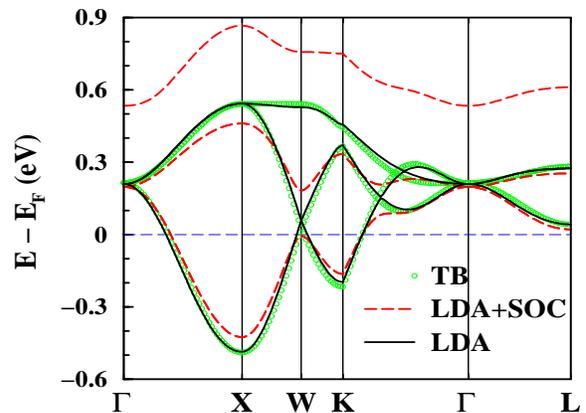


FIG. 1: (color online) Nonmagnetic Os  $t_{2g}$  band structure in LDA, tight-binding (TB) representation, and LDA+SOC, relative to the Fermi level  $E_F$ . In LDA, the top of the  $t_{2g}$  manifold is very flat near the  $\Gamma$  point and along the  $X$ - $W$  line, resulting in very sharp peaks just above  $E_F$  in the density of states (see Fig. 2). From LDA+SOC, the spin-orbit coupling constant  $\xi$  is 0.30 eV.

isostructural and isovalent  $\text{Ba}_2\text{LiOsO}_6$  (BLOO) orders *antiferromagnetically* in spite of a very similar Curie-Weiss susceptibility.[6]

The question of formal valence, and identification of several material constants, can be identified from first principles local density approximation (LDA) calculations using two all-electron full-potential electronic methods of FPLO and Wien2k.[9–12] The Fermi level  $E_F$  lies in the  $t_{2g}$  bands, confirming the heptavalent nature of the Os ion. A crystal (ligand) field splitting of almost 5 eV separates the centroids of the  $e_g$  and  $t_{2g}$  bands, reflecting the unusually strong  $5d - 2p$  hybridization, and a gap of roughly 1.5 eV separates the  $t_{2g}$  bands from the O  $2p$ -dominated  $\text{OsO}_6$  cluster orbitals, with gaps separating various degenerate molecular orbitals.[13, 14]

Several complications must be taken into account to obtain a realistic picture of the electronic struc-

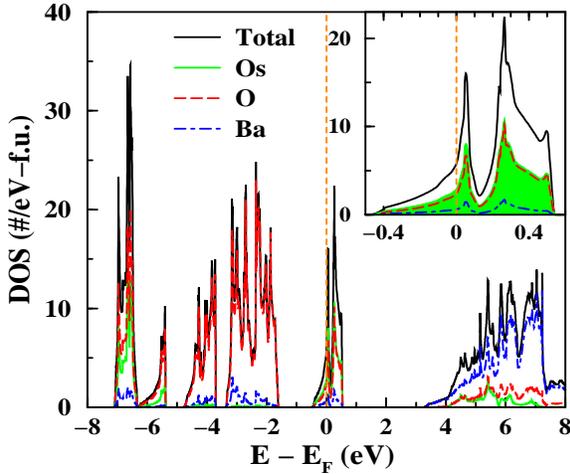


FIG. 2: (color online) Total and atom-projected densities of states (DOS) per formula unit for nonmagnetic state in LDA. The vertical dashed line indicates the Fermi energy. Inset: Blowup near  $E_F$ . It displays that contribution of six oxygens is nearly similar with Os character in the  $t_{2g}$  manifold. As a result, it is anticipated that the oxygens significantly contribute to magnetic moment.

ture. (i) The strong hybridization of Os  $5d$  orbitals with O  $2p$  states, which has ramifications here beyond the usual ones in oxides. (ii) Strong spin-orbit coupling (SOC) on the Os site has serious consequences. (iii) Hund's (exchange) coupling effectively selects the occupied orbital. (iv) Intra-cluster Coulomb repulsion, which is the obvious suspect for a magnetic insulating state in an open shell system. Finally, quantum fluctuations may also play an important role.

The unusual aspects of BNOO then are: a Mott insulating state based on a localized  $d^1$  ion that nonetheless retains a cubic environment, and a small ordered moment in a 3D system where fluctuation effects typically are minor. It is most instructive to consider the various aspects of the electronic structure consecutively. We proceed in a different manner from Xiang and Whangbo[15] in their study of the behavior of BNOO.

*Isolated  $t_{2g}$  bands: cluster orbitals.* The  $t_{2g}$  bands, with bandwidth  $W=1.05$  eV, form a self-contained system for the purpose of understanding the low energy, low temperature physics. The three bands can be fit accurately to three first neighbor  $d-d$  hopping parameters (in meV)  $t_\sigma = -121, t_\pi = 64, t_\delta = 24$  meV, with on-site energy  $\varepsilon = 202$ . For BLOO  $\varepsilon = 208, t_\sigma = -131$  are the only changes. Note that  $t_\delta$  is necessary to give the excellent fit shown in Fig. 1. The corresponding total and atom-decomposed density of states (DOS) are pictured in Fig. 2, which reveals the isolation of the  $t_{2g}$  bands. As pointed out

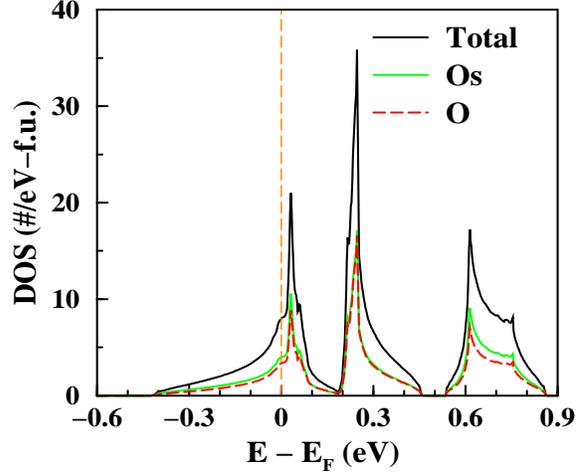


FIG. 3: (color online) Total and atom-projected DOS per formula unit, with spin-orbit coupling included. Oxygen contribution is 50% throughout the bands. The two lower bands are distinct, and nearly disjoint, leading roughly to a half-filled single-band configuration.

by Erickson *et al.*[7] the overlap takes place between O  $2p_\pi$  orbitals on neighboring  $\text{OsO}_6$  octahedra. The Fermi level lies 0.5 eV (one electron) up into the bands. The DOS shown in Fig. 2 is highly non-symmetric, with 2/3 of the weight lying in the upper half of the bands.

As analyzed in some detail by Singh and coworkers[13, 14] in the context of pentavalent Ru in  $\text{Sr}_2\text{YRuO}_6$  which also contains a closed shell ion ( $\text{Y}^{3+}$ ) in one of the cation sites, the  $\text{OsO}_6$  unit should be approached as an isolated cluster. The Os  $t_{2g}$  states generalize to cluster orbitals with the Os  $5d_{xy}$  state (say) bonded to the  $p_\pi$  orbitals lying in the  $x - y$  plane. We calculate that half of the density of the  $t_{2g}$  bands lies on Os, the other half distributed amongst four  $p_\pi$  orbitals, and the cluster orbital (with symmetric partners  $\mathcal{D}_{xz}, \mathcal{D}_{yz}$ ) is

$$\mathcal{D}_{xy} \approx \sqrt{\frac{1}{2}}d_{xy} + \sqrt{\frac{1}{8}}\sum_{j=1}^4 p_{\pi,j}. \quad (1)$$

This cluster orbital aspect is central to the following analysis.

*Tendency toward magnetism.* Paramagnetic BNOO is not unstable to ferromagnetism but is on the verge of being so; for an  $8 \times 8 \times 8$   $k$  mesh or finer, the magnetic moment that is obtained on coarser meshes vanishes. Thus the Stoner interaction constant within LDA is  $I_{st} = 1/N(E_F) = 0.35$  eV [The Fermi level density of states  $N(E_F) = 2.88$  states/eV per spin]. As for the SOC strength (below), it is important that this parameter is not evaluated from the Os atomic potential alone, because the relevant

local (molecular) orbital is only half Os  $5d$  and  $I_{st}$  is reduced accordingly.] The Hund's (exchange) splitting for a fully polarized  $d^1$  orbital is  $\mathcal{J}_H \approx I_{st} = 0.35$  eV, which is much smaller than the bandwidth but comparable to the SOC strength (see below).

*Spin-orbit coupling.* It has been known for fifty years[16–18] that the  $t_{2g}$  complex can be mapped onto an angular momentum  $\vec{L} \rightarrow -\vec{L}$  with  $\mathcal{L}=1$ , so within these bands the SOC operator becomes  $-\xi\vec{L} \cdot \vec{S}$  with  $\xi > 0$ . The basis  $\{\mathcal{D}_{xy}, \mathcal{D}_{yz}, \mathcal{D}_{zx}\}$  can be transformed to  $|0\rangle \rightarrow \mathcal{D}_{xy}$ ;  $|\pm 1\rangle \rightarrow \mathcal{D}_{zx} \pm i\mathcal{D}_{yz}$ , where the integer denotes the angular momentum projection  $m_{\mathcal{L}}$  onto  $\hat{z}$ . The negative sign leads to an inverted spectrum, with the  $J = \frac{3}{2}$  quartet at  $-\xi/2$  and the  $J = \frac{1}{2}$  doublet at  $+\xi$ . The calculated splitting at  $k=0$  gives a large SOC  $\xi=0.30$  eV, so large it splits off the entire upper  $J=1/2$  band as is clear from Fig. 1.

The DOS with SOC included is displayed in Fig. 3. In addition to the split-off upper  $J = \frac{1}{2}$  band, the lower two bands are nearly disjoint, being bound together only by the degeneracy within the  $J = \frac{3}{2}$  states at zero momentum(Fig. 1). As a result, the problem of the Mott insulating state does not rigorously reduce to a single band problem though it may be effectively single band. As a result of the mapping  $\vec{L} \rightarrow -\vec{L}$  within the  $t_{2g}$  states of interest, the total angular momentum is  $\vec{J} = \vec{S} - \vec{L}$  ( $J = \frac{1}{2}, \frac{3}{2}$ ), the magnetic moment is  $\vec{M} = \mu_B(2\vec{S} - \vec{L})$ , and the  $g$ -factor is  $g_J = \frac{3}{2} - \frac{5}{8J(J+1)}$ . In this isolated cluster limit, the r.m.s. moment  $(\vec{M}^2)^{1/2}$  is small ( $1 \mu_B$ ) for  $J = \frac{1}{2}$  but is larger ( $\sqrt{7}\mu_B$ ) in the  $J = \frac{3}{2}$  ground state.

At the band structure level, there remains only the Hund's exchange splitting  $H_{ex} = -\mathcal{J}_H S_z$  due to the Os moment, and this interaction lifts all degeneracies. The lowest state at  $k=0$  is

$$|m_{\mathcal{L}} m_S\rangle = | + 1 \uparrow \rangle \propto [|\mathcal{D}_{zx} + i\mathcal{D}_{yz}\rangle \uparrow]. \quad (2)$$

but the dispersion leads to overlapping bands and metallicity, so intra-cluster interaction effects are required to describe the observed insulating character.

*Intra-molecular repulsion: the Mott insulating state.* For a lattice of  $d^1$  ions in  $t_{2g}$  orbitals, an on-site Hubbard repulsion of no more than  $U \sim W$  should lead to a Mott insulating state. To model this insulating state we initially applied the correlated band LDA+U method, using  $J=1$  eV (whose value seemed immaterial) and varying  $U$ . Since the initial interest was to look for an orbitally ordered solution, the full rotationally-invariant form of interaction implemented in Wien2k was used. A Mott insulating state was not obtained for any reasonable value of  $U$ . At  $U=4$  eV  $\approx 4W$  the increasing exchange splitting leads only to a half metallic state.

This deficiency of the LDA+U method, as conventionally applied to atomic orbitals, to produce the expected Mott insulating state is a situation we have observed previously in a  $4d$  oxide. The problem can be cast not as a failure of the method *per se*, but rather of the application to an extended *cluster* orbital system by applying the orbital shifts solely to the Os  $5d$  atomic function, rather than the entire molecular orbital. Since only 50% of the  $\mathcal{D}$  orbital's charge is Os  $5d$ , no state with integer  $5d$  occupation number can arise, whereas in the LDA+U method integer occupation is necessary to obtain the insulating state.

*Full correlated electronic structure.* To model the observed ferromagnetic Mott-insulating phase realistically, we use the TB Hamiltonian (Wannier representation) for the orthonormal cluster orbitals, including SOC interaction  $H_{SOC}$ , Hund's (exchange) interaction  $H_{ex}$ , and correlation interaction  $H_U$

$$H = H_0 + \xi\vec{L} \cdot \vec{S} - \mathcal{J}_H \hat{S}_z + H_U. \quad (3)$$

As mentioned above, Hund's exchange lowers the pure spin up  $| + 1 \uparrow \rangle$  member of the lower spin-orbit quartet, making it the orbital to occupy to achieve the lowest energy. Then Coulomb repulsion lowers this occupied state by  $\sim U$  with respect to the others. We find that a critical (minimum) value of  $U_c = 1.1$  eV is required to produce the Mott insulating state. This critical value is significantly less than those that have been suggested[7, 15] as applicable to BNOO, which reaffirms Coulomb repulsion on top of strong SOC as the mechanism underlying the insulating state, as well as compensation of the moment as we now describe.

The  $| + 1 \uparrow \rangle$  state is pure-spin and pure-orbital moment, but kinetic hopping mixes it with other states. In this state the  $z$ -component of the moment  $\langle M_z \rangle = \langle + 1 \uparrow | (2S_z - \mathcal{L}_z) | + 1 \uparrow \rangle \equiv 0$  is compensated precisely, making BNOO a transition metal analog of the case of the  $\text{Sm}^{3+} d^5$  ion[19] where  $L = 2S$  and  $M_z \sim 0$ : the ion/cluster is magnetic ( $J \neq 0$ ) but there is nearly vanishing total moment for a fixed direction of spin. After taking account of the mixing in of other states by the kinetic hopping, the spin and orbital moments each depend strongly on the value of  $U$  (Table I) while the cancellation remains near-complete. This cancellation is a nontrivial effect, since appreciable mixing in of the  $|0 \downarrow\rangle$  state degrades the spin moment without affecting the orbital moment.

*Discussion.* This near-pure spin state is unexpected, given the strong SOC which is largely regarded as mixing (*not* separating) spin and orbital moments, nevertheless it is an occurrence that has recently been anticipated.[20] At the level of description of the Hamiltonian Eq. 3 in mean field approx-

TABLE I: Values of spin, orbital, and total moments versus the value of  $U$ , within the correlated  $t_{2g}$  shell of BNOO. Increasing the hopping  $t$  parameters (by 50-100%) reduces the individual moments but hardly changes the net moment.

| $U$ | $M_S$ | $M_L$  | $M_{tot}$ |
|-----|-------|--------|-----------|
| 1.1 | 0.714 | -0.717 | -0.003    |
| 1.5 | 0.909 | -0.866 | +0.043    |
| 2.0 | 0.976 | -0.935 | +0.041    |

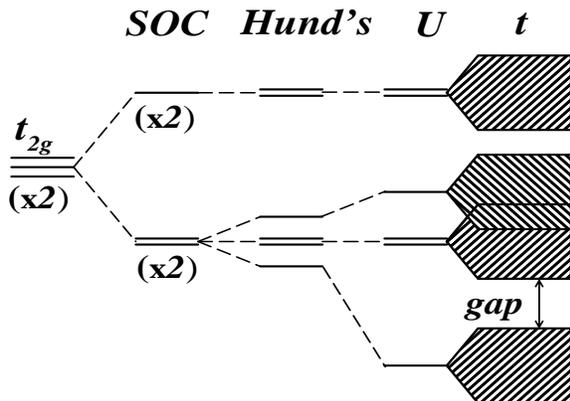


FIG. 4: Evolution (schematic) of the  $t_{2g}$  energies from isolated  $3 \times 2$ -fold degenerate for the isolated ion (in its cubic environment), through SOC, Hund's coupling, Coulomb repulsion  $U$ , and finally dispersion due to hopping  $t$ . The occupied band has pure spin-orbital  $|+1 \uparrow\rangle$  character until intercluster hopping is included.

imation, we have a Curie-Weiss moment  $\langle M^2 \rangle^{1/2} = \sqrt{7} \mu_B$  and an ordered FM moment of  $\approx 0.04 \mu_B$ , which is only nonzero due to quenching. The agreement with the observed values (near 0.7 and 0.2  $\mu_B$ , respectively) in absolute terms is not good, however one would expect a small moment of 0.2  $\mu_B$  to be difficult to reproduce in a first principles manner. The degree of collinearity of  $\vec{S}$  and  $\vec{L}$ , which finally determines the moment, is sensitive to the environment. The magnitude of collinearity,  $\vec{L} \cdot \vec{S} / (\|S\| \|L\|)$ , is

only 40% in the  $J = \frac{3}{2}$  manifold anyway. Adding a crystalline anisotropy term  $\gamma \mathcal{L}_z^2$  decreases it rapidly, by a further 35% for  $\gamma = \xi$  and by 60% for  $\gamma = 2\xi$  (this is orbital moment quenching). The quantum fluctuations are thus quite sensitive to the environment.

The matter of quantitative agreement is actually a broader question:  $\text{Ba}_2\text{CaOsO}_6$  (BCOO) with one more electron and  $S=1$  and a cubic crystal structure is more conventional, yet it has a Curie-Weiss moment[21] of 1.61  $\mu_B$  that is also far below the spin-only value of 2.83  $\mu_B$ . The Re-based  $d^1$  double perovskites  $\text{Sr}_2\text{XReO}_6$ ,  $X = \text{Mg}$  and  $\text{Ca}$ , on the other hand, experience much smaller SOC and have moments equal to the spin only values and display structural distortions as the conventional picture would suggest. This distinction supports the involvement of strong spin-orbit coupling in both the small moment and the “restoration” of cubic symmetry in the heptavalent osmates BNOO and BLOO.

The small ordered moment was one of the principle questions about BNOO. From the point of view presented here, a small ordered moment is *expected* and the question becomes rather: why is it as large as observed? The magnetic order issue is a challenging and delicate question. Spin coupling proceeds through three distinct hopping processes  $t_\sigma, t_\pi, t_\delta$  between anisotropic  $\mathcal{D}_{xz} + i\mathcal{D}_{yz}$  orbitals, and the behavior of the Curie-Weiss susceptibility reflects a net antiferromagnetic coupling. Such coupling is strongly frustrated on an fcc lattice, and FM ordering is one way to relieve the frustration. The large quantum fluctuations suggest an orbital liquid picture may be appropriate. The related osmates BLOO and BCOO, unlike BNOO, both manage to order antiferromagnetically, indicating that geometrical frustration and/or competing couplings are prominent in this structure. The surviving cubic symmetry of the Os  $d^1$  ion requires further study, but frustration and large spin-orbital fluctuation seem to be implicated.

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