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## Design of heteroanionic MoON exhibiting a Peierls metal-insulator transition

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Using a first-principles approach, we design the heteroanionic oxynitride MoON to exhibit a first-order isosymmetric thermally-activated Peierls-type metal-insulator transition (MIT). We identify a ground state insulating phase ( $\alpha$ -MoON) with monoclinic Pc symmetry and a metastable high temperature metallic phase ( $\beta$ -MoON) of equivalent symmetry. We find that ordered fac-MoO<sub>3</sub>N<sub>3</sub> octahedra with edge- and corner-connectivity stabilize the twisted Mo–Mo dimers present in the  $\alpha$  phase, which activate the MIT through electron localization within the  $4d a_{1g}$  manifold. By analyzing the temperature dependence of the soft zone-boundary instability driving the MIT, we estimate an ordering temperature  $T_{\rm MIT} \sim 900$  K. Our work shows that electronic transitions can be designed by exploiting multiple anions, and heteroanionic materials could offer new insights into the microscopic electron-lattice interactions governing unresolved transitions in homoanionic oxides.

Introduction. Transition metal oxides are widely studied for their diverse electronic properties and symmetrybreaking phase transitions—features governed by the frontier orbital structures of the active cations sustained by geometries of the oxide-anion sublattices [1-4]. Both changes to the underlying atomic structure and the strength of electron-electron interactions microscopically underpin whether metal-insulator transitions (MITs) occur within these materials. On the one hand, cation dimerization, as in  $d^1$  Peierls oxides such as  $AO_2$  rutile compounds (A = V, Nb, and Ta), is essential to thermallydriven MITs. Although electronic correlations play an important role in  $VO_2$  [5, 6], studies show they play a lesser (if any) role in binary Mo- and Ta-based compounds [7]. On the other hand, changes in the anion-sublattice geometry are pivotal to altering the orbital structure and opening band gaps in ternary oxides [8], as exemplified by  $BO_6$  octahedral rotations in  $ABO_3$  perovskite doped rareearth titanates and vanadates [9–11]. MITs may also arise due to  $BO_6$  breathing distortion, sometimes referred to as charge-ordering, facilitated by intersite Coulomb interactions, e.g., in perovskite nickelates and ferrites [12–15]. Alternatively when correlation and lattice energetics are comparable, MITs may result from symmetry-preserving distortions of the anion sublattice [16].

In this Letter, we exploit the chemistry of the anion sublattice to both enforce orbital-filling instabilities on the cation and provide asymmetric bond geometries to induce a symmetry-preserving MIT. The differing anion, rather than cation, chemistries are used to go beyond dilute doping for carrier-density control; we use them to drive reduced symmetries, providing an avenue to activate lattice-mediated electronic transitions and trigger a steric structural instability. This emerging concept is utilized in heteroanionic materials [17], compounds where the anion sublattice involves two or more species, to achieve a range of properties, but is rarely practiced for MIT materials discovery [18]. To that end, we design heteroanionic MoON to host a Peierls-driven MIT; we predict an insulating monoclinic ground state ( $\alpha$ -MoON), which emerges from a metastable metallic phase ( $\beta$ -MoON). We show that

the  $\beta \rightarrow \alpha$  MIT occurs at  $T_{\text{MIT}} \sim 900$  K and that ordered heteroleptic MoO<sub>3</sub>N<sub>3</sub> octahedra in  $\alpha$ -MoON are crucial in stabilizing the monoclinic lattice with twisted Mo-Mo dimers and a semiconducting gap.

Design from Homoanionic Compounds. Conceptually, molybdenum oxynitride may be derived from two homoanionic rutile-structured materials as  $MoO_2(d^2) + MoN_2(d^0) \rightarrow 2MoON(d^1)$ , whereby exchange of the oxide  $(O^{2-})$  anion for nitride  $(N^{3-})$  allows us to retain the  $d^1$  configuration that is prone to an electronic degeneracy under octahedral symmetry. Note that the +4 and +6 oxidation states of Mo are the most favorable, hence increasing the likelihood of a valence instability for molybdenum oxynitride. Ordering of the O and N also affords control over the unit cell size, which is important to the Mott-Peierls transitions in binary  $d^1$  compounds [19].

Using density functional theory (DFT) calculations [20], we first investigate MoO<sub>2</sub> and MoN<sub>2</sub> in the hypothetical rutile structure, with space group  $P4_2/mnm$ , exhibited by known  $d^1$  oxides at high temperatures [5, 21, 22]. This structure consists of equally spaced Mo cations coordinated by 6 anions, forming one-dimensional chains of distorted edge-shared octahedra along the tetragonal caxis (Fig. 1). These corner-connected chains form a threedimensional structure, designated as  $^3_{\infty}$ [MoO<sub>6/3'</sub>], where the anions exhibit a trigonal planar coordination (3').

We find that rutile-structured MoO<sub>2</sub> exhibits a smaller axial ratio (c/a = 0.549) than VO<sub>2</sub> (c/a = 0.626) [23], with a Mo-Mo distance of 2.69 Å and MoO<sub>6</sub> octahedra elongated along the O-O bonds orthogonal to the [001] chain direction. These features enhance the metal-metal  $\sigma$ -bonding across the shared octahedral edge, which cause the  $t_{2g}$  orbitals to split into  $a_{1g}$  states, mediated by  $\sigma$ - $d_{xy}$ overlap of neighboring Mo atoms, and  $e_g^{\pi}$  states, derived from Mo  $d_{xz}$  and  $d_{yz}$  orbitals interacting with oxygen [24]. The result is that the dispersive  $a_{1g}$  band overlaps with the  $e_g^{\pi}$  states [20]. Consequently, we find a nonmagnetic (S =0) metallic phase with the two Mo *d*-electrons delocalized over the  $a_{1g}$  and  $e_g^{\pi}$  manifolds (Fig. 1a).

Experimentally, MoO<sub>2</sub> is isostructural to insulating VO<sub>2</sub> with space group  $P2_1/c$  and Mo-Mo dimers [25, 26].



FIG. 1. (a) Total densities-of-states (DOS) for homoanionic  $MoO_2$  and  $MoN_2$  in the (inset) rutile and monoclinic structures. Orbital resolved DOS for (b) monoclinic  $MoO_2$ , indicating metallicity persists despite Mo-Mo dimerization and splitting of the 4d orbital symmetries, and (c) rutile  $MoN_2$ .

Our relaxed structure exhibits a Mo-Mo distance of 2.43 Å and c/a = 0.550, in good agreement with experiment [24] and the observation that axial ratios c/a > 0.625 (< 0.625) favor (distorted) rutile structures [19]. The Mo-Mo dimerization splits the  $a_{1g}$  rutile states into bonding  $(a_{1g})$ and antibonding  $(a_{1g}^*)$  combinations such that one electron per Mo site is localized in the  $a_{1g}$  bonding state while the other is itinerant in the  $e_g^{\pi}$  band (Fig. 1b). In contrast to insulating  $d^1$  VO<sub>2</sub> with an observed V-V distance of 2.52 Å and c/a = 0.635, monoclinic  $d^2$  MoO<sub>2</sub> remains metallic despite shorter Mo-Mo distances.

Rutile-structured MoN<sub>2</sub> exhibits a larger axial ratio, c/a = 0.607, and MoN<sub>6</sub> octahedra compressed along the N-N bonds orthogonal to the [001] chain direction due to stronger orbital hybridization. Although MoN<sub>2</sub> is nominally  $d^0$ , we find it is semimetallic due to the broad bandwidth of the nonbonding N 2p states and N 2p-Mo  $4d\pi$  hybridization (Fig. 1c). At the DFT+U level, an onsite Coulomb repulsion of  $U(Mo, 4d) \leq 4 \text{ eV}$  also does not open a gap [20].

Structure Assessment. By implementing a heteroanionic composition from  $MoO_2$  and  $MoN_2$  components, MoON should exhibit analogous rutile-monoclinic polymorphism and Mo-Mo dimerization. Because molybdenum oxynitrides are typically synthesized through nitrogenation of  $MoO_3$ , their structures are poorly defined [27– 31]. Therefore, we surveyed 85 prototype AB<sub>2</sub> and A<sub>2</sub>B structures to identify ordered low-energy MoON variants. We then filtered to 14 candidate MoON structure-types based on Mo-O and Mo-N bond lengths, ionic radii, and charge states, and occupied suitable Mo cation sites followed by O/N on coordinating anionic sites. All possible anion order configurations were then enumerated as in Ref. 32, followed by full DFT geometric optimization [20].

Fig. 2a shows the ground state energies for MoON by structure type. All configurations are nonmagnetic. The most energetically favorable structures are variations of distorted rutile, maintaining 1D chains of edgesharing octahedra with the expected coordination, *i.e.*,  $AB_2 = {}^{3}_{\infty}[AB_{6/3'}]$ , in addition to distorted bonding environments and cell shapes. Additional symmetry breaking occurs to the prototype space groups owing to the presence of the ordered anions:  $B \rightarrow B$  and B', such that  $MoON = {}^{3}_{\infty}[MoO_{3/3'}N_{3/3'}]$ , whereby each Mo cation is coordinated by three oxide and nitride anions. This ordering both allows all metal atoms to exhibit a  $d^1$  configuration while maintaining a c/a axial ratio close to the structurestability boundary (c/a = 0.625) [19].

Structure of MoON Polymorphs. We focus on two MoON phases derived from structures of the TcO<sub>2</sub>- [33] and MoO<sub>2</sub>-type [2], both of which exhibit monoclinic Pcsymmetry with fac-anion order (Fig. 2a, inset). The former is predicted to be the ground state for MoON (Fig. 2a, starred); hereafter, referred to as  $\alpha$ -MoON (see Table S1 of 20). The  $\alpha$ -MoON structure exhibits Mo-Mo dimers, reflected by the alternation of short and long Mo-Mo bond distances (Fig. 2b). The Mo atoms also exhibit antiparallel displacements perpendicular to the edge-sharing MoO<sub>3</sub>N<sub>3</sub> chains and the Mo-Mo bonds, which facilitates dimer formation while minimizing strain costs from deviations in ideal Mo-O and Mo-N bond lengths.

The MoO<sub>2</sub>-type structure, designated as  $\beta$ -MoON, is 80 meV/f.u. ( $\approx 928$  K) higher in energy than the  $\alpha$  phase to which it is similar; however, the Mo-Mo dimers are absent. All Mo-Mo distances are equal (2.91 Å), ensuring metallic behavior [20]. We also obtain an axial ratio of 0.609, which is close to the critical value c/a = 0.625. Additionally, the alternating Mo displacements present in the  $\alpha$  phase, are forbidden by symmetry in the  $\beta$  phase, *i.e.*, all Mo-Mo bonds are collinear with the [100] direction (monoclinic setting). The Mo cations are displaced from the center of each O<sub>3</sub>N<sub>3</sub> octahedra toward the nitride face as a result of the *fac* configuration of the O<sub>3</sub>N<sub>3</sub> octahedra, which is stabilized by the difference in orbital hybridization [34]. Indeed, the Mo-N bond lengths (average of 1.98 Å) are shorter than the Mo-O bond lengths (2.05 Å).

The fac-anionic order, for which equivalent anions occupy neighboring sites among octahedral faces allowing maximal Mo-anion  $\pi$ -hybridization [17], is pervasive in heteranionic materials and important for the stability of  $\alpha$ -MoON. First, it reduces the symmetry of the corresponding homoanionic compounds:  $P4_2/mnm \rightarrow Pc$  and  $P2_1/c \rightarrow Pc$  due to the  $4e \rightarrow 2a$  Wyckoff orbit splitting, which allows the isosymmetric monoclinic polymorphism and Mo-Mo dimerization without symmetry breaking. Second, the fac-MoO<sub>3</sub>N<sub>3</sub> with a local Mo d<sup>1</sup> configuration is considerably more stable than alternative isomers



FIG. 2. (a) Energies for competing polymorphs of MoON relative to the ground state  $\alpha$ -MoON (starred).  $\beta$ -MoON is the next lowest-energy polymorph (magenta bar). In all cases, the lowest energy anion order is represented. (inset) The *fac*-MoO<sub>3</sub>N<sub>3</sub> octahedra consist of O (red) and N (yellow) anions on opposite faces. Mo-O and Mo-N bonds lengths are given (in units of Å). (b) A slice of the  $\alpha$ - and  $\beta$ -MoON structures, illustrating the edge- and corner-connectivity of the MoO<sub>3</sub>N<sub>3</sub> octahedra, with the Mo-Mo distances and dimer twist angle ( $\varphi$ ) defined. Orange arrows indicate the direction of the Mo displacements across the  $\beta \rightarrow \alpha$  transition. (Anion displacements omitted for clarity). (c) Total (gray) and atom-projected DOS of  $\alpha$ -MoON.

[20]. Other arrangements are higher in energy, even lying above  $\beta$ -MoON, since they do not bring a kinetic energy gain from gap formation. The anionic ordering energy scale is comparable to the charge gap (0.30 eV) that opens in the  $\alpha$ -phase (Fig. 2c), with differences in energy up to 0.24 eV/f.u. In contrast, changes in  $\beta$ -MoON are relatively smaller (Fig. 2a, inset), indicating a strong interaction between the Mo-Mo dimers and anion order. Last, fac-order enables c/a = 0.609, proximate to the inherent rutile-structure instability, whereas alternative arrangements give  $c/a \leq 0.590$ .

Phase Stability. The  $\beta$ -MoON phonon dispersions reveal that the structure is unstable (Fig. 3a). An instability appears at the C point  $(k = \frac{1}{2}, \frac{1}{2}, 0)$  with frequency  $\nu = 66.4i \,\mathrm{cm}^{-1}$  (Cm symmetry) and two unstable phonons occur at the Y point  $(k = \frac{1}{2}, 0, 0)$  with  $\nu_1 = 48.4i \,\mathrm{cm}^{-1}$  and  $\nu_2 = 40.0i \,\mathrm{cm}^{-1}$ , both giving Pc symmetry. In addition, there exists a small surface in momentum space about  $\Gamma$  for which there is a dynamical instability (maximum frequency  $15.3i \,\mathrm{cm}^{-1}$ ) that is not due to numerical issues, but arises from mixing of an optical (octahedral rotation) with an acoustic mode [35].

Condensing the instability at C leads to nearly no energetic gain and the formation of a metastable, semimetallic phase (Cm symmetry) with weak Mo-Mo dimers (0.027Å) and negligible twisting ( $\varphi \approx 1^{\circ}$ ). For that reason, we do not discuss it further. Both Y modes lead to the formation of strong Mo-Mo dimerization along the [100] direction; however, the equilibrium mode distortions differ in the degree of dimer twist  $\varphi$ , 175.3° vs 177.7° relative to the secondary displacements present, which is important to the MIT in homoanionic  $VO_2$  [36]. This behavior is reflected in the different energetic gains upon distortion relative to  $\beta$ -MoON. Indeed, increasing the  $\nu_1$ -distortion amplitude leads to a larger energy gain, corresponding to shorter Mo-Mo distances in the dimer, than that obtained with the distortion vector from  $\nu_2$  (Fig. 3b, filled symbols). Furthermore, condensing  $\nu_1$  followed by full

structure relaxation results in the insulating  $\alpha$ -MoON ground state (Fig. 3b), for which our lattice dynamical calculations find all real frequencies indicating dynamical stability at 0 K [20], whereas condensing  $\nu_2$  leads to a semimetallic Pc phase with weaker dimerization (Mo-Mo = 2.864 Å). Moreover,  $\alpha$ -MoON is thermodynamically stable with respect to all known Mo-O, Mo-N, and O-N binary compounds; it is 80 meV atom<sup>-1</sup> below the ternary convex hull [20], indicating it is robust to phase decomposition.

Last, the instability near  $\Gamma$ , k = (0.03, 0, 0), further distorts the octahedra through twisting of the Mo-Mo dimers away from the linear 1D chains through a CaCl<sub>2</sub>type distortion (rotations of O<sub>3</sub>N<sub>3</sub> octahedra). When it is combined with the displacements for  $\nu_1$  and  $\nu_2$  (Fig. 3b, open symbols), we find it leads to greater stability of the  $\alpha$ -like *Pc* phases over  $\beta$ -MoON, because its permits further splitting of the  $a_{1q}$ - and  $e_q^{\pi}$ -derived bands.

Metal-Insulator Transition.  $\beta$ -MoON is a polar metal [37] owing to its Pc symmetry and partial filling of the  $4d a_{1g}$  and  $e_g^{\pi}$  bands by one itinerant electron per Mo site (Fig. 3c and Ref. 20). We find that weaker splitting of the  $a_{1g}$  and  $e_g^{\pi}$  bands occurs in  $\beta$ -MoON compared to rutile-structured MoO<sub>2</sub> due to reduced Mo-Mo bonding, reflected by the 2.91 Å (2.69 Å) Mo-Mo distances in  $\beta$ -MoON (rutile MoO<sub>2</sub>). In contrast,  $\alpha$ -MoON is semiconducting with a 0.30 eV indirect band gap (Fig. 2c and Fig. 3g). The gap arises from both the formation of Mo-Mo dimers and their twisting, consistent with the displacive  $\nu_1$  mode at Y and the long wavelength instability near  $\Gamma$  (Fig. 3a). We note that we are not arguing for a purely displacive nature of the MIT, but rather that the character of the displacive instabilities account for the microsopic degrees-of-freedom active in the transition; order/disorder effects are examined later. For that reason, we choose to computationally modulate the Mo-Mo dimerization length and twist angle rather than use solely the eigendisplacements obtained from our phonon calculations



FIG. 3. (a) Phonon dispersion curves of  $\beta$ -MoON at 0 K. (b) The filled (open) symbols indicate the normalized energy gain with Y-mode eigendisplacement amplitude (combined with the instability near  $\Gamma$ ). (c) Electronic band structure of the  $\beta$ -MoON phase. (d)-(f) Evolution in the  $\beta$ -MoON band dispersions as a function of the Mo-Mo distances (Å) and twisting distortions ( $\varphi$ ) exhibited by the  $\alpha$ -MoON phase. (g) Electronic band structure for the  $\alpha$ -MoON phase. Note that the structure used in (e) corresponds to the energy minimum of  $\nu_1$  (filled symbols) in (c). The Fermi level is set to 0 eV.

to assess the band-structure response (Fig. 3d-g).

First, upon moderate dimerization (Fig. 3d), band crossings along the  $\Gamma - Y$  (dimer) direction at approximate half fillings are immediately removed, consistent with the formation of  $a_{1q}$  bonding (and antibonding) states that shift to lower (higher) energy; yet, a semimetallic state persists with flat bands at the Fermi level and band crossings in other portions of the Brillouin zone. Fig. 3e shows that the addition of Mo-Mo twisting leads to a larger separation in the  $a_{1q}$  and  $e_q^{\pi}$  bands at both  $\Gamma$  and along  $\Gamma - \mathbf{E}$  (dimer twist direction). Subsequent integer band filling occurs as  $\varphi$  increases (Fig. 3f). Mo-Mo dimers of 2.70 Å are thus sufficient to completely open the band gap in the direction of the 1D chains provided the dimers are also twisted. Spontaneous lattice strain, which accompanies these displacements active in the  $\beta \rightarrow \alpha$  transition, contribute to the gap opening but are not the primary factor since the Laue class is preserved in the process. Upon further dimerization and reaching  $\alpha$ -MoON (Fig. 3g), the valence bandwidth increases from enhanced  $\sigma$ - $d_{xy}$  orbital overlap to form a singlet state. Thus, the charge excitation gap depends on the Mo-Mo interaction strength controlled by both the dimer separation and twisting angle across



FIG. 4. (a) Finite temperature phonon dispersion curves of  $\beta$ -MoON. (b) Radial distribution function g(r) obtained from our finite temperature AIMD calculations. The short Mo-Mo distances in the  $\alpha$  and  $\beta$  phases are indicated by vertical lines.

a shared MoO<sub>3</sub>N<sub>3</sub> edge, making it sensitive to the local MoO<sub>3-x</sub>N<sub>3+x</sub> coordination [20]. With extreme anion disorder, e.g., whereby homoleptic octahedra form  $(x = \pm 3)$ , Mo sites with  $4d^n (n > 1)$  configurations can result, leading to  $e_g^{\pi}$  band occupation and persistent metallicity in the presence of Mo-Mo dimers. A finite number of non-fac configurations with homoleptic octahedra could lead to a percolative component to the MIT; however, such units are rare in oxyfluorides [17]. Furthermore, the addition of the Coulomb repulsion in our calculations does not change the MIT scenario [20].

Finite-Temperature Effects. Although  $\beta$ -MoON is dynamically unstable at 0 K, thermal vibrations should provide sufficient anharmonic interactions to stabilize it at finite temperatures. Indeed, our calculated anharmonic phonon dispersion curves at 300 K and 500 K show that formerly unstable 0 K modes at the C and Y points are stable, although instabilities near the zone center persist (Fig. 4a). A clear trend of decreasing imaginary character, which may be further assisted by changes in cell shape or volume not considered here, occurs with increasing temperature for those modes near  $\Gamma$  [20]. Moreover, the radial distribution functions, g(r) in Fig. 4b, obtained from our ab initio molecular dynamics (AIMD) simulations, reveal that the Mo-Mo dimerization decreases upon heating. It is completely lost at  $T \ge 900$  K, suggesting stabilization of  $\beta$ -MoON. At intermediate temperatures, we observe a finite density of dimers indicating an order-disorder component to the MIT as the displacive modes condense to achieve long-range order with decreasing temperatures. The MIT temperature scale is also consistent with our analysis of the Gibbs free energies of the  $\alpha$  and  $\beta$  phases [20], which shows that  $\beta$ -MoON is thermodynamically stable above 900 K and close to  $T_{\rm MIT} \approx 928 \, {\rm K}$  predicted with a Boltzmann approximation. Thus, we predict a thermally-induced isosymmetric transition near 900 K.

Summary. We propose targeted synthesis of MoON through either ammonolysis reactions with homoanionic compounds or oxidation of MoN<sub>2</sub> thin films following growth with subsequent transport or optical measurements to assess the predicted Peierls MIT occurring near 900 K. The  $\beta \rightarrow \alpha$  transition is characterized by the

formation of twisted Mo dimers, which lift band degeneracies and crossings to form a singlet state in the 4d $a_{1g}$ -derived bands. This electronic configuration and the coupled lattice instability are enabled by the multiple oxide and nitride anions arranged in a *fac* configuration, which enable the  $d^1$  band filling and critical axial ratio.

Our work shows how studies of heteroanionic materials enable better understanding of complex transitions and anion-exchange could be applied to newly-discovered compounds exhibiting transitions in which electron correlation, Jahn-Teller effects, and metal-metal bonding compete, e.g., iron oxides (Fe<sub>4</sub>O<sub>5</sub>) [38], hollandite-type vanadates and manganates [39, 40], and perovskite ferroelectrics [41]. Heteroanionic chemistries could also be exploited to design and deliver topological and quantum materials platforms [42, 43] for future (opto)electronics.

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