Design of a Mott Multiferroic from a Non-Magnetic Polar Metal

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We examine the electronic properties of newly discovered “ferroelectric” metal LiOsO3 combining density-functional and dynamical mean-field theories. We show that the material is close to a Mott transition and that electronic correlations can be tuned to engineer a Mott multiferroic state in 1/1 superlattice of LiOsO3 and LiNbO3. We use electronic structure calculations to predict that the (LiOsO3)1/(LiNbO3)1 superlattice is a type-I multiferroic material with a ferroelectric polarization of 41.2 μC cm⁻², Curie temperature of 927 K, and Néel temperature of 671 K. Our results support a route towards high-temperature multiferroics, i.e., driving non-magnetic polar metals into correlated insulating magnetic states.

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Introduction.—Multiferroics (MF) are a class of insulating materials where two (or more) primary ferroic order parameters, such as a ferroelectric polarization and long-range magnetic order, coexist. Technologically, they offer the possibility to control magnetic polarizations with an electric field for reduced power consumption [1, 2]. Nonetheless, intrinsic room-temperature MF remain largely elusive. This fact may be understood by examining the microscopic origins for the ferroic order which aids in classifying different phases: In Type-I MF, ferroelectricity and magnetism arise from different chemical species with ordering temperatures largely independent of one another and weak magnetoelectric (ME) coupling [3]. The ferroelectric ordering also typically appears at temperatures higher than the magnetic order, and the spontaneous polarization P is large since it is driven by a second-order Jahn-Teller distortion, e.g., BiFeO3 [3, 4]. In Type-II MF, however, magnetic order induces ferroelectricity, which indicates a strong ME coupling between the two order parameters. Nonetheless, P is usually much smaller, e.g., by a factor of 10² as in R-Mn2O3 (R being rare earth) [5]. In a few MFs with high-transition temperatures, i.e., BiFeO3 [6] and Sr1-xBaxMnO3 [7–9], magnetism is caused by Mott physics arising from strong correlations. The interactions localize the spins at high temperature, paving the way for magnetic ordering at room temperature. Materials where this robust magnetism is coupled with ferroelectric distortions are ideal candidates for a room-temperature MFs.

Herein, we propose a design strategy for novel Mott MF phases. It relies on tuning the degree of correlation of the recently discovered class of materials referred to as ‘ferroelectric metals’ with LiOsO3 as the prototypical member [10]. This material is the first undisputed realization of the Anderson-Blount mechanism [11], and challenges the expectation that conduction electrons in metals would screen the electric field induced by polar displacements [10, 12, 13]. Despite robust metallicity, this material shares structural similarities with prototypical insulating ferroelectric oxides, such as LiNbO3 [14, 15]: A R3c crystal structure with acentric cation displacements and distorted OsO6 octahedra [16, 17] and comparable lattice parameters [10, 14]. While the polar displacements in LiNbO3 rely on cross-gap hybridization between p (O) and d (Nb) states [18], in LiOsO3 they are weakly coupled to the states at the Fermi level (E_F), which makes possible the coexistence of an acentric structure and metallicity [16, 19]. In LiOsO3 the empty d manifold of LiNbO3 is replaced by a non-magnetic 5d³ ground state with a half-filled t2g (dxy, dxz, dyz) configuration, which is responsible for the metallic response [16]. However, the strength of the electronic interactions is insufficient to drive a Mott transition in the correlated t2g manifold as revealed by low-temperature resistivity measurements; nonetheless, if it would be possible to enhance the electronic correlations in LiOsO3 and achieve a metal-insulator transition, then a previously unidentified multiferroic material should result.

In this work we explore the feasibility of this approach using a combination of first-principles density functional theory (DFT) plus dynamical mean field theory (DMFT) calculations [20]. We first show that the electronic Coulomb interactions and Hund’s coupling in LiOsO3 make it an ideal candidate for realizing a Mott MF due to the multi-orbital t2g physics. Next, we describe the design of a new multiferroic by control of the electronic structure through atomic scale engineering of a Mott metal-insulator transition (MIT) in an ultrashort period (LiOsO3)1/(LiNbO3)1 superlattice. The insulating and magnetic state is driven by an enhancement of the electronic correlations in LiOsO3 layers owing to the kinetic energy reduction of the t2g orbitals from the superlattice geometry. The ferroelectric properties mainly originate from cooperative Li and O displacements. The multiferroic phase emerges across the MIT, exhibiting a net electric polarization (41.2 μC cm⁻²) and magneti-
zation \([0.9 \mu_B\) per formula unit (f.u.)], with calculated magnetic-ordering and ferroelectric temperatures of 671 K and 927 K, respectively. Our results uncover a promising alternative route to discovery of room-temperature multiferroics: One could search for correlated polar metals near Mott transitions and drive the phases into insulating states, rather than the often-pursued approach of inducing polar displacements in robustly insulating magnets.

**Calculation Details.**—We perform first-principles DFT calculations within local-density approximation (LDA) + Hubbard \(U\) method as implemented in the Vienna \textit{Ab initio} Simulation Package (VASP) \cite{21} with the projector augmented wave (PAW) approach and a 600 eV plane wave cutoff with a 5\(\times\)7\(\times\)7 \(k\)-point mesh. We relax the volume and atomic positions (forces <0.1 meV \(\text{Å}^{-1}\)) using Gaussian smearing (20 meV width) for the Brillouin zone (BZ) integrations. We perform LDA+DMFT calculations including local Coulomb interactions parameterized by the \(U\) and the Hund’s coupling \(J_h\) starting from Wannier orbitals constructed from the LDA bands \cite{22} using an energy range spanned by the full \(d\) manifold. The impurity model is solved using Exact Diagonalization (ED) with a parallel Arnoldi algorithm \cite{23, 24}.

**Correlations in LiOsO\(_3\).**—We first examine the effect of the interactions on the metallic state of LiOsO\(_3\) and determine the critical values for a Mott transition \(U_t\) in the paramagnetic and antiferromagnetic (AFM) phases using LDA+DMFT. The criterion for a Mott-Hubbard transition is frequently associated with the ratio between the bandwidth \((W)\) and the interaction strength \(U\), so that the Mott transition occurs for \(U_c\) of the order of \(W\). In a multiband Hubbard model with \(M\) orbitals, \(U_c\) is enhanced by orbital fluctuations, \(i.e., \, U_c \sim \sqrt{M}W,\) \cite{25} and it is influenced by the Hund’s coupling \(J_h\). Indeed, at half-filling, \(U_c\) is reduced by an enhancement of \(J_h\) \cite{26}.

In the following, we show this precisely the situation in LiOsO\(_3\) \cite{16}. Due to the energy separation between \(t_{2g}\) and \(e_g\) orbitals in the spectral density of state of LiOsO\(_3\) around the Fermi level, we resort to using a model for the \(t_{2g}\) levels only \cite{16}. Owing to the symmetry breaking in bulk LiOsO\(_3\), the orbitals in the \(d\) manifold are also permitted to mix, which lifts the degeneracy of \(t_{2g}\) orbitals with two of states remaining degenerate.

Fig. 1 shows the orbital resolved quasiparticle weight \((Z)\) of the occupied orbitals as a function of \(U\) for two different values of \(J_h\) for paramagnetic LiOsO\(_3\) in the experimental structure (see top panels). \(Z\) measures the metallic character of the system, and it evolves from \(Z=1\) for a non-interacting metal to \(Z=0\) for a Mott insulator. Upon increasing the value of \(J_h\), the critical value of \(U\) required to reach the Mott state \((Z=0)\) is shifted to larger values of \(U\) \cite{26}.

In the correlated regime, we anticipate electron localization will lead to long-range magnetic order of the localized spins. Spin-polarized LDA+DMFT calculations, initialized with a \(G\)-type AFM structure (every spin on an Os cation is antiparallel to all its neighbors), reveal that the local magnetic moment rapidly saturates to the atomic value \(S = 3/2\). A finite magnetization also develops at intermediate \(U\) in the metallic state (Fig. 1, lower panels). The MIT, marked by vertical arrows, occurs for a weaker coupling in the AFM than in the paramagnetic state.

**Design of a Mott Multiferroic.**—The LDA+DMFT calculations reveal that a simultaneous Mott and magnetic state could be engineered in LiOsO\(_3\) by reducing the electronic kinetic energy. One avenue to control and decrease the kinetic energy relies on heterostructuring and interleaving two perovskites together to form a coherent superlattice, whereby an isostructural insulator would restrict the electron hopping due to the reduction in available channels \cite{27–29}. Such geometries can be achieved in practice using oxide molecular-beam epitaxy or pulsed-laser deposition methods \cite{30, 31}.

Owing to the chemical and structural compatibility of LiOsO\(_3\) with LiNbO\(_3\), with a lattice mismatch of 3.2\%, we devise an ultrashort period perovskite superlattice of \((\text{LiOsO}_3)_{1}/(\text{LiNbO}_3)_{1}\) as illustrated in panel (a) of Fig. 2. The superlattice is constructed by beginning from the \(R3c\) crystal structure of LiOsO\(_3\) (LiNbO\(_3\)) and imposing a layered order along the \([110]\) direction in the rhombohedral setting, which is equivalent to a \(1/1\) period LiOsO\(_3\)/LiNbO\(_3\) grown along the pseudocubic (pc) \([001]\) direction \cite{32}. The geometry in Fig. 2 is also different from a superlattice constructed along the \([101]_{pc}\) direction (c.f., Ref. 33), which is likely more challenging to realize experimentally. Following full relaxation of the superlattice, we find the cation order results in a symmetry reduction to the polar space group \(Pc\) with out-of-phase Os\(_6\) and Nb\(_6\) octahedral rotations, \(i.e.,\, a^+b^-b^-\) tilt pattern...
There is some spectral weight transfer in the vicinity of $E_F$ among the Os orbitals, which are sensitive to the electron correlation strength as shown in Fig. 1. We now explore the effect of electronic correlations by means of LSDA+$U$ calculations at different values of $U_{\text{eff}} = U - J_h$. An accurate value of the Hubbard $U$ is unknown for perovskite osmates, but it is expected to be comparable to that of NaOsO$_3$ [35] and double perovskite Sr$_2$CrOsO$_6$ [36] for which a correct description of the electronic properties are obtained with $U$ values of 1.0 and 2.0 eV, respectively. Note that the differences from various implementations of the LDA+$U$ scheme for bulk LiOsO$_3$ were found to be minor [16], and are anticipated to also be insignificant for the superlattice.

Electronic Properties.—Fig. 2 shows the LDA electronic density of states (DOS) for the LiOsO$_3$/LiNbO$_3$ superlattice (d), compared with LiOsO$_3$ (b) and LiNbO$_3$ (c) using the LDA-optimized atomic structures. The results for LiOsO$_3$ (Fig. 2b) highlight the metallic character of the former, where the weight at the Fermi level ($E_F$) mainly comes from Os 5d states which show strong admixture from the O 2p states. In contrast, LiNbO$_3$ is a band insulator, with the O 2p states forming the valence band and Nb 4d states at the conduction band minimum, separated by a gap of 3.28 eV (Fig. 2c). In the superlattice, we find essentially no charge transfer between Os and Nb:

\[ \text{LiOsO}_3/\text{LiNbO}_3 \]

We note that when SOI are excluded in the calculations (Fig. 3, solid lines), the MIT occurs at a further reduced correlation strength ($U_c \sim 0.5$ eV), and the magnetic moment only slightly increases. Such behaviors are also observed in bulk LiOsO$_3$ [16].

Ferroelectric Polarization.—We now apply a group the-
We use the energy difference between the high-symmetry within LSDA+U calculations that produce the Pc ground state. We use a fictitious $P2_1/c$ centrosymmetric phase (where polar displacements are switched off) as the reference phase from which the symmetry-adapted mode displacements are obtained as different irreducible representations (irreps) of the $P2_1/c$ space group operators [39]. We find the loss of inversion symmetry mainly derives from cooperative Li and O displacements in the (101) mirror plane of the Pc phase. Moreover, we find anti-polar displacements along the $b$-axis which result in no net polarization. All polar displacements are described by a distortion vector that corresponds to the irrep $\Gamma_2$ along the [101]-direction of the $Pc$ structure (Fig. 4). These displacements are consistent with the acentric Li and O ionic displacements identified to be responsible for lifting inversion symmetry in bulk LiOsO$_3$ [10, 13] and across the ferroelectric transition in LiNbO$_3$ [40].

We now compute the ferroelectric polarization in LiOsO$_3$/LiNbO$_3$ using the Berry’s phase approach [41] within LSDA+U ($U_c = 0.5$ eV). The spontaneous electric polarization of the $Pc$ phase is $32.3 \mu$C cm$^{-2}$ and $25.5 \mu$C cm$^{-2}$ along the [100]-direction, $i.e.$, along the pseudo-cubic [001] superlattice repeat direction and [001]-directions, respectively. (Note that the [101]-direction in LiOsO$_3$/LiNbO$_3$ corresponds to the polar [111]-direction in LiNbO$_3$.) Together this yields a net polarization along the [101]-direction of $41.2 \mu$C cm$^{-2}$. These values are also robust to SOI, with a change of less than 15% to value of the total polarization. Following the recipe of Ref. 42, we use the energy difference between the high-symmetry ($P2_1/c$) and low-symmetry ($Pc$) to obtain a ferroelectric Curie temperature of 927 K for the superlattice. This value is close to the extrapolated transition temperature for LiNbO$_3$ (>1,400 K) [43], and far exceeds that of bulk LiOsO$_3$ where inversion symmetry is lost near 140 K [10].

**Magnetic Ordering Temperature.**—Our DMFT calculations indicate that when the superlattice material enters in the Mott state the magnetic moment is $\sim 3 \mu_B$, corresponding to a high-spin $S = 3/2$ state. We now estimate the Néel temperature for LiOsO$_3$/LiNbO$_3$ by extracting the exchange interaction constants from spin-polarized DFT energies computed at $U_c$ without SOI following the approach in Ref. 44. Assuming that the magnetism arises by ordering such localized spins, we obtain intra- and inter-plane Os–Os exchange magnetic couplings of $-5.6$ meV and $-0.2$ meV respectively, where a negative interaction indicate AFM exchange. From these values and without Anderson’s renormalization [45], we estimate a Néel temperature of 671 K for the LiOsO$_3$/LiNbO$_3$ superlattice, which makes the material a correlation-induced room-temperature multiferroic.

**Conclusions.**—We used a LDA+DMFT approach to study the electronic properties of the “ferroelectric” metal LiOsO$_3$. A detailed understanding of the electronic structure of LiOsO$_3$ shows that a reduction of the kinetic energy can drive the system into a Mott insulating state. We use this concept to propose a strategy to design multiferroic materials by constructing a superlattice with the uncorrelated polar LiNbO$_3$ dielectric. On the basis of LSDA+U calculations we show that the ultra-short period LiOsO$_3$/LiNbO$_3$ superlattice should be a type-I room-temperature Mott multiferroic with a large 41.2 $\mu$C cm$^{-2}$ electric polarization.

The large ferroelectric displacements from the LiNbO$_3$ layers facilitate the high ferroelectric ordering temperature in the LiOsO$_3$/LiNbO$_3$ heterostructure as observed from the similarity in the Curie temperature of the superlattice with that of LiNbO$_3$. In this case LiOsO$_3$/LiNbO$_3$ would behave as a paramagnetic Mott ferroelectric at high temperatures and transition into Mott multiferroic below the Néel temperature, which is predicted to be well-above room temperature. Because the exchange interactions of Os are mediated by the coordinating O ligands, which are essential to and produce the ferroelectric distortion, a strong ME coupling is anticipated as in Sr$_{1-x}$Ba$_x$MnO$_3$ [7–9]. We hope this work motivates the synthesis of new artificial multiferroics, and the adds to the growing discussion of new applications where noncentrosymmetric metals and ferroelectric materials may be united.

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Supplementary Materials

[1] H. T. Stokes and D. M. Hatch, "FINDSYM: Program for Identifying the Space Group Symmetry of a Crystal," J. Appl. Cryst. 38, 237-238 (2005), ISOTROPY Software Suite, http://iso.byu.edu.
TABLE I. Calculated crystallographic parameters for $R3c$ LiOsO$_3$ using LDA functional.

| Atom | Wyck. Site | $x$  | $y$  | $z$   |
|------|------------|------|------|-------|
| Li   | 6$a$       | 0    | 0    | 0.61117 |
| Os   | 6$b$       | 0    | 0    | 0.32084 |
| O    | 18$b$      | -0.00388 | 0.36259 | 0.06825 |

$R3c$  
$a = b = 4.9399$ Å, $c = 13.3019$ Å  
$\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$

TABLE II. Calculated crystallographic parameters for $R3c$ LiNbO$_3$ using LDA functional.

| Atom | Wyck. Site | $x$  | $y$  | $z$   |
|------|------------|------|------|-------|
| Li   | 6$a$       | 0    | 0    | 0.61517 |
| Nb   | 6$b$       | 0    | 0    | 0.33169 |
| O    | 18$b$      | -0.01367 | 0.35987 | 0.06330 |

$R3c$  
$a = b = 5.1052$ Å, $c = 13.7472$ Å  
$\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$

TABLE III. Calculated crystallographic parameters for $Pc$ Li$_2$NbOsO$_6$ using the LDA functional.

| Atom | Wyck. Site | $x$  | $y$  | $z$   |
|------|------------|------|------|-------|
| Li1  | 2$a$       | 0.27896 | 0.25751 | 0.45909 |
| Li2  | 2$a$       | 0.78342 | 0.74972 | -0.07013 |
| Nb   | 2$a$       | -0.00633 | 0.25287 | 0.00169 |
| Os   | 2$a$       | 0.49713 | 0.75123 | 0.53150 |
| O1   | 2$a$       | 0.23965 | 0.12376 | 0.02510 |
| O2   | 2$a$       | 0.73578 | 0.60514 | 0.54599 |
| O3   | 2$a$       | -0.09599 | 0.05685 | 0.71217 |
| O4   | 2$a$       | 0.41768 | 0.54538 | 0.23192 |
| O5   | 2$a$       | 0.04578 | 0.58866 | 0.85929 |
| O6   | 2$a$       | 0.54412 | 0.04168 | 0.32305 |

$Pc$  
$a = b = 7.35270$ Å, $b = 5.02739$ Å, $c = 5.36541$ Å  
$\alpha = \gamma = 90^\circ$, $\beta = 95.109^\circ$

TABLE IV. Calculated crystallographic parameters for $Pc$ Li$_2$NbOsO$_6$ without monoclinic angle using the LDA functional.

| Atom | Wyck. Site | $x$  | $y$  | $z$   |
|------|------------|------|------|-------|
| Li1  | 2$a$       | 0.27310 | 0.26765 | 0.47516 |
| Li2  | 2$a$       | 0.78081 | 0.75357 | -0.05429 |
| Nb   | 2$a$       | -0.00421 | 0.25110 | 0.00188 |
| Os   | 2$a$       | 0.49815 | 0.75234 | 0.52637 |
| O1   | 2$a$       | 0.24071 | 0.12246 | 0.01238 |
| O2   | 2$a$       | 0.73609 | 0.60651 | 0.54411 |
| O3   | 2$a$       | -0.09326 | 0.05556 | 0.71992 |
| O4   | 2$a$       | 0.41773 | 0.53696 | 0.24015 |
| O5   | 2$a$       | 0.04603 | 0.58671 | 0.85024 |
| O6   | 2$a$       | 0.54504 | 0.03169 | 0.30376 |

$Pc$  
$a = b = 7.35884$ Å, $b = 5.03159$ Å, $c = 5.36980$ Å  
$\alpha = \beta = \gamma = 90^\circ$
TABLE V. Calculated crystallographic parameters for $Pc$ Li$_2$NbOsO$_6$ without monoclinic angle using the LSDA+ $U$ with $U\_c=0.5$ eV.

| Atom   | Wyck. Site | $x$     | $y$     | $z$     |
|--------|------------|---------|---------|---------|
| Li1    | 2a         | 0.27431 | 0.26460 | 0.47149 |
| Li2    | 2a         | 0.77680 | 0.75646 | -0.05271|
| Nb     | 2a         | -0.00460| 0.25150 | 0.00212 |
| Os     | 2a         | 0.49708 | 0.75063 | 0.52604 |
| O1     | 2a         | 0.24114 | 0.12241 | 0.01487 |
| O2     | 2a         | 0.73596 | 0.60719 | 0.54175 |
| O3     | 2a         | -0.09280| 0.05536 | 0.72002 |
| O4     | 2a         | 0.41875 | 0.54274 | 0.23604 |
| O5     | 2a         | 0.04702 | 0.58598 | 0.84961 |
| O6     | 2a         | 0.54653 | 0.03942 | 0.31046 |

$Pc$ 

$a = 7.35714$ Å, $b = 5.03042$ Å, $c = 5.36865$ Å

$\alpha = \beta = \gamma = 90^\circ$

FIG. 5. (Color online) Resolved 5$d$ $t_{2g}$ states of Os for (a) LiOsO$_3$ and (b) Li$_2$NbOsO$_6$ within LDA. The bandwidth of the $d_{xy}$ orbitals for bulk LiOsO$_3$ and Li$_2$NbOsO$_6$ are the same while in the superlattice the $d_{xz}$ and $d_{yz}$ orbitals have a reduced bandwidth.
FIG. 6. (Color online) Superlattice construction: (a) Starting from the \( \textit{R}3\text{c} \) crystal structure of LiNbO\(_3\) in the hexagonal setting with 30 atoms, (b) we transform to the rhombohedral setting with 10 atoms. (c) Next we double the cell with the transformation matrix and (d) substitute a NbO\(_2\) layer with OsO\(_2\) layer. (e) We identify the new space group \( \textit{Pc} \) with FINDSYM \cite{1} and finally (f) we set the monoclinic angle to 90\(^\circ\).