Osmates on the verge of a Hund’s-Mott transition: 
The different fates of NaOsO$_3$ and LiOsO$_3$

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In this work, we clarify the origin of the strikingly different spectroscopic properties of the chemically similar compounds NaOsO$_3$ and LiOsO$_3$. Our first-principle many-body analysis demonstrates that the highly sensitive physics of these two materials is controlled by their proximity to an adjacent Hund’s-Mott insulating phase. Small material-specific details hence result in an extremely sharp change of the electronic mobility, explaining the surprisingly different properties of the paramagnetic high-temperature phases of the two compounds.

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Metal-insulator transitions driven by the Coulomb repulsion (Mott transitions) represent one of the most characteristic hallmarks of electronic correlations. A variety of Mott transitions [1] are observed in 3$d$ transition metal oxides (TMO), among which we recall the prototypical case of V$_2$O$_3$[2,3]. Yet, when considering TMOs with heavier transition-metal elements, the impact of correlations gets weakened due to the larger spatial extension of the 4$d$ and 5$d$ electronic orbitals. This may cause correlation effects to become comparable to other physical mechanisms at work, such as spin orbit coupling (SOC) [4,5] and Stoner magnetism.

Aside from specific situations, where an enhancement of correlations can be triggered by the realization of effective \textit{single-orbital} configuration [6,11], one expects systematically weaker many-body effects in the 5$d$ TMOs. One should then observe just mildly renormalized Fermi-liquid properties in these materials, provided that the temperature is high enough to destroy any possible long-range order. However, if a half-filled configuration between nearly degenerate orbitals is realized (e.g. 3 electrons in the $t_{2g}$ orbitals), 4$d$ [12] and even 5$d$ materials may display significant correlation effects. We showcase that the latter scenario is not only an academic problem by demonstrating its actual realization in the elusive physics of two osmates, NaOsO$_3$ and LiOsO$_3$.

We recall that, in general, the presence of $n=3$ electrons in the three $t_{2g}$ orbitals can trigger the formation of very stable high-spin ground states, even if the intraband local Coulomb repulsion is not particularly large. If this happens, the \textit{localizing} strength of the on-site Hund’s exchange coupling ($J$), favoring the onset of a Hund’s-Mott insulating state, gets significantly magnified. As also known, this trend gets reversed for systems with non half-filled $t_{2g}$ orbitals (e.g. $n=2,4$), such that $J$ has a \textit{delocalizing} effect on the ground-state properties (“Janus-faced” nature of the Hund’s coupling [13,14]). The tendency towards metallization for $n=2$ can be ascribed to the competition between two possible localized states [15], a pure Mott state where the double occupancy is minimized and a charge-disproportionated Hund’s insulator, where local spin moment is maximized. In fact, only for $n=3$ the Coulomb repulsion and the Hund’s coupling favor the same insulating state: the Hund’s-Mott insulator, simultaneously associated to a high spin configuration and suppressed charge fluctuations. Thus, in the case of a nominally half-filled $t_{2g}$ configuration both the Hund’s coupling and the local Coulomb repulsion can act cooperatively to suppress the electronic mobility. This also explains why correlation effects fade out extremely quickly, when only slightly moving away from the Hund’s-Mott insulating region $(n=3$ in the $t_{2g}$ orbitals), as observed in the general analysis of Refs. [13] and [16].

The generic trends for 3$d$ and 5$d$ TMOs are summarized in the schematic phase-diagram of Fig. [1]. This shows how the formation of a multi-orbital local spin polarization, mostly driven by the Hund’s exchange, stabilizes the corresponding Mott insulating phases (grey-shadowed zones) for different fillings $(n=2,3)$ of the $t_{2g}$ orbitals. Consistent with the above considerations, the most favorable condition to stabilize or, at least, to approach a Mott phase in the less correlated 5$d$ TMOs is evidently represented by the half-filled $t_{2g}$ configuration.

As the Hund’s-Mott phase is characterized by a high sensitivity with respect to small perturbations (e.g. lifting of the degeneracy of the $t_{2g}$ orbitals, hybridization with the $p$ orbitals of the ligands, etc.), even tiny dif-
ferences in realistic systems may sharply damp correlation effects and strongly modify the physical properties. The pair of (nominally half-filled) osmates, NaOsO$_3$ and LiOsO$_3$, offers a particularly promising playground for observing the physics expected in the proximity of a Hund’s-Mott transition, because in spite of a similar chemical composition the two compounds display quite different physical properties, even in their high-temperature regimes.

In particular, for the orthorhombic perovskite NaOsO$_3$ terahertz and infrared spectroscopy [17] have revealed the presence of a high temperature ($T$) metallic state with relatively good Fermi liquid properties. Upon cooling, a MIT is accompanied by the emergence of a long-range ($G$-type) antiferromagnetic order at $T = T_N \sim 410$K [18]. The physics below $T_N$ initially was interpreted as that of the elusive Slater insulating state [19] and later better defined in terms of a spin-fluctuation-driven Lifshitz transition [20][22]. Hence, both the high-$T$ metallic phase of NaOsO$_3$ and its antiferromagnetic behavior below $T_N$, appear compatible with a weakly correlated scenario.

In contrast, the rhombohedral LiOsO$_3$ does not exhibit any magnetic ordering at low-$T$, but instead features a phase-transition to a non-centrosymmetric structure for $T < T_c = 140$ K [24]. The essential difference emerging in comparison to NaOsO$_3$ is, that upon raising the temperature, the optical spectra of LiOsO$_3$ very rapidly lose any sign of metallic coherence [24]. The Drude peak is even replaced by a slight low-frequency downturn already at $T = 300$ K. In fact, the temperature trend of the infrared spectra observed for LiOsO$_3$ resembles surprisingly well that of undoped V$_2$O$_3$ [25], the prototypical 3$d$ TMO on the verge of a Mott MIT [19].

Given the very similar energy scales (width of the conduction bands, effective size of the screened electronic interaction) and the (half-filled) electronic configuration of the two materials, one of the few plausible explanations for the sharp contrast between the high-$T$ spectral properties of NaOsO$_3$ and LiOsO$_3$ would be their proximity to a Hund’s-Mott insulating phase as depicted in Fig. [1].

To demonstrate that this scenario indeed applies, we perform state-of-the-art ab-initio many-body calculations on an equal footing for both compounds, exploiting the density functional theory (DFT) [27][28] merged with dynamical mean field theory (DMFT) [29]. The DMFT calculations have been performed for the Wannier-projected $t_{2g}$ orbitals of Os [30] considering the full Coulomb (screened) interaction on Os, calculated by means of the constrained random phase approximation (cRPA) for both compounds [26]. Aside from specific bandstructure details, the main energy scales in the two materials are quite similar. The $t_{2g}$ bandwidths are 3.9 eV (NaOsO$_3$) and 3.5 eV (LiOsO$_3$); the local orbital splittings of the $t_{2g}$ manifold are about 150 meV and 250 meV, while the averaged intra-orbital Coulomb repulsion $U$ is 2.25 eV and 2.35 eV and the averaged local Hund’s exchange coupling $J$ is 0.24 eV and 0.25 eV for NaOsO$_3$ and LiOsO$_3$ respectively [26]. We have also verified that the atomic SOC, which is of similar magnitude ($\sim 0.3$ eV) in NaOsO$_3$ and LiOsO$_3$, does not alter the DMFT results in the paramagnetic phases of the two osmates.

The corresponding multi-orbital Hamiltonian, which we solved in DMFT by means of the w2dynamics package [31], reads

$$H = \sum_{k\sigma m} H_{lm}(k) c_{k\sigma}^\dagger c_{km\sigma} + \sum_{r\sigma' \Gamma} U_{\Gamma} c_{r\Gamma \sigma}^\dagger c_{r\Gamma \sigma'} c_{r\Gamma \sigma'}^\dagger c_{r\Gamma \sigma} \tag{1}$$

where $l, m, n, o$ are the $t_{2g}$ orbital indices, $k$ denotes the fermionic momentum, $r$ the lattice site and $\sigma, \sigma'$ the spin. Here $H_{lm}(k)$ and $U_{\Gamma}$ represent the single particle part and the local interaction of the low-energy Hamiltonian for the subspace of the $t_{2g}$ Os orbitals. As usual, the best quantitative agreement with experimental trends is obtained for slightly enhanced cRPA values, here about 8% for both compounds [26], which is within the accuracy of cRPA estimated by the more accurate constrained functional renormalization group procedure [32][33]. The (full
the most metallic of the two stable DMFT solutions of LiOsO$_3$ and LiOsO$_3$. Dashed lines (left panel) refer to paramagnetic calculations below the $T_N$ of NaOsO$_3$, while the dotted line (right panel) marks the most metallic of the two stable DMFT solutions of LiOsO$_3$ found at $T = 276$ K. Inset: Values of the averaged intra- and inter-orbital double-occupancy at different $T$.

Coulomb interaction values used for our calculations [20] remain in any case smaller than those assumed in previous DMFT studies [21] of the low-$T$ behavior of LiOsO$_3$.

The temperature dependence of the local spectral function $A_\omega(\omega)$ of the two-compounds in their paramagnetic phases, obtained from analytic continuation [24–26] of the on-site Green’s function, are reported in Fig. 2. We clearly see that the NaOsO$_3$ spectrum displays a sizably renormalized coherent peak up to the highest $T$ considered ($T = 430$ K $> T_N$), while the corresponding quasi-particle peak visible in the low-$T$ regime of LiOsO$_3$ is quickly washed out upon increasing $T$, with a complete loss of coherence at/above room-$T$. The coexistence of two DMFT solutions [29], a typical hallmark [3] of a close proximity to a Mott-MIT, is found for LiOsO$_3$ at the intermediate temperature of 276 K [27]. The insets in Fig. 2 indicate that the loss of spectral weight at high temperatures in LiOsO$_3$ is linked to an increase of the inter-orbital spin alignment ($\uparrow\downarrow\uparrow\downarrow$) and a corresponding suppression of the intra-orbital double occupancy ($\uparrow\uparrow\downarrow\downarrow$) [20].

Hence, our DMFT results reproduce the experimentally observed presence (disappearance) of coherent quasi-particle excitations in the high-temperature infrared spectra of NaOsO$_3$ (LiOsO$_3$), suggesting the validity of the scenario depicted in Fig. 1.

In order to firmly establish that the agreement between our calculation and experimental data is indeed explained by the proximity of both osmates to the Hund’s-Mott insulator, we consider a simplified interaction term which describes in the most direct way the formation of large local magnetic moments associated with the Hund’s interaction.

In practice we assume an interaction of density-density character by neglecting in Eq. 1 the quantum fluctuation ($c_{r\uparrow}^\dagger c_{r\downarrow}^\dagger c_{m\downarrow}^\dagger c_{m\downarrow}$), pair-hopping ($c_{r\uparrow}^\dagger c_{r\downarrow}^\dagger c_{m\uparrow}^\dagger c_{m\uparrow}$) and correlated-hopping ($c_{r\uparrow}^\dagger c_{r\downarrow}^\dagger c_{r\uparrow} c_{r\downarrow}$) terms in the interaction as well as the orbital off-diagonal hopping terms ($c_{r\uparrow}^\dagger c_{r\sigma}^\dagger c_{r\uparrow}$) which are responsible for the small violation of the (local) $t_{2g}$-degeneracy in our DMFT calculations. As a result of these approximations, the Hund’s-driven orbital off-diagonal spin correlations are enhanced, increasing the localization effects.

Our DMFT calculations (Fig. 3) show that this modification pushes LiOsO$_3$ well inside the adjacent insulating regime, while NaOsO$_3$ remains metallic. The corresponding on-site Green’s function $G$ as a function of the Matsubara frequencies $i\omega_n$ is shown in Fig. 3 for $T = 430$ K. It displays an evident metallic behavior for NaOsO$_3$, which qualitatively reproduces the calculation with the full Coulomb interaction. For LiOsO$_3$, instead, we find a vanishing $\text{Im}G(i\omega_n)$ at the Fermi edge ($\omega_n \rightarrow 0$), characteristic of an insulating state. The Hund’s-Mott nature of this insulating state can be immediately inferred from the double occupancy data of LiOsO$_3$ (inset table), which features a large local moment with almost complete inter-orbital spin alignment ($\uparrow\downarrow=0.5$) and a simultaneous suppression of the intraorbital double occupancy. In NaOsO$_3$, instead, significantly smaller values of $\langle\uparrow\downarrow\rangle$ are found, much closer to what is expected in the uncorrelated case ($\langle\uparrow\downarrow\rangle=0.25$).

Finally, to separate the impact of mere correlation effects from all other potentially relevant aspects (e.g. specific features in the bandstructure), we devise a simple (numerical) “Gedankenexperiment”, where we perform a new DMFT (density-density) calculation for each of the two osmates, but with interchanged interaction parameters ($U, J$ [20]). The consequence of this swapping of interaction parameters is an almost perfect mirroring of the imaginary parts of the Green’s functions (Fig. 3, dashed lines). The Green’s function for LiOsO$_3$ with the slightly different interaction parameters of NaOsO$_3$ displays clear metallic features at the Fermi edge, similar to the origi-
nal NaOsO₃ results. For NaOsO₃ on the other hand, the slightly larger interaction parameters of LiOsO₃ suffice to push it through the Hund’s-Mott transition into the insulating regime. The values of the corresponding spin-alignment get also almost perfectly interchanged. This illustrates how the significant differences in the results of our calculations are driven by small but critical changes in the interaction parameters, convincingly confirming that the physics of the two materials is controlled by the proximity to a Hund’s-Mott insulating transition.

In summary, we performed DFT+DMFT calculations for the paramagnetic phases of NaOsO₃ and LiOsO₃, with realistic, material specific values of their on-site Coulomb interaction. Our results compare remarkably well with the experimental findings for both compounds. We are able to reproduce the occurrence of a crossover from a metallic to an incoherent behavior at room temperature, as observed in the optical spectra of LiOsO₃, as well as its absence across the entire (high) temperature range in the experimental spectroscopy data of NaOsO₃. The picture emerging from the DMFT calculations, supported by an additional analysis of our Gedankenexperiment, provides a comprehensive interpretation of the surprisingly different spectral properties of the two osmates presented here in terms of their slightly different proximity to a Hund’s-Mott insulating phase. While the example of LiOsO₃ demonstrates how electronic correlations can become predominant even in a 5d compound, we observe that this scenario might also be triggered in other Os-based TMOs, by artificially engineering half-filled configurations in nearly degenerate osmium orbitals.

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