1. Introduction

Metal-insulator transitions (MIT) have long been a focal point of condensed matter physics [1] due to the inherent conceptual complexity, which has stimulated the development of many theories [2], and to the possibility to control the (reversible) suppression of electrical conductivity in technological applications [3]. Understanding and describing MIT is a considerable task. In the most simple scenario, metals and insulators can be distinguished within the non-interacting Wilson’s picture based on the filling of the electronic bands [4, 5]. Wilson’s approach correctly predicts the insulating nature of fully-filled/empty $d$-bands transition metal oxides (TMO) such as SrTiO$_3$ ($d^0$) and LaCoO$_3$ ($t_{2g}^6$), but breaks down for partially filled $d$-bands TMOs like NiO and many others [6]. With his pillar works, Mott has resolved this limitation by considering the effect of electron–electron correlation and formulated one of the most influential paradigm in solid state physics, the Mott insulator [2, 7], that is still the subject of intense research nowadays.

Doping-induced insulator-metal transition in the Lifshitz magnetic insulator NaOsO$_3$

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Abstract

By means of first principles schemes based on magnetically constrained density functional theory and on the band unfolding technique we study the effect of doping on the conducting behaviour of the Lifshitz magnetic insulator NaOsO$_3$. Electron doping is treated within a supercell approach by replacing sodium with magnesium at different concentrations (Mg$_x$Na$_{1-x}$OsO$_3$, $x = 0.125, 0.25, 0.375, 0.5$). Undoped NaOsO$_3$ is subjected to a temperature-driven Lifshitz transition involving a continuous closing of the gap due to longitudinal and rotational spin fluctuations (Kim et al 2016 Phys. Rev. B 94 241113). Here we find that Mg doping suppresses the insulating state, gradually drives the system to a metallic state (via an intermediate bad metal phase) and the transition is accompanied by a progressive lowering of the Os magnetic moment. We inspected the role of longitudinal spin fluctuations by constraining the amplitude of the local Os moments and found that a robust metal state can be achieved below a critical moment. In analogy with the undoped case we conjecture that the decrease of the local moment can be controlled by temperature effects, in accordance with the theory of itinerant electron magnetism.

Keywords: DFT, metal to insulator transition, magnetism, Lifshitz, itinerant, oxides, 5$d$

(Some figures may appear in colour only in the online journal)
The recent discovery of novel types of MITs in spin–orbit coupled 5d TMOs, such as the Dirac–Mott regime in Sr$_2$IrO$_2$ [8–12] and the magnetically itinerant phases of 5$d$ osmates NaOsO$_3$ [13–16] and Cd$_2$Os$_2$O$_7$ [17–19] has given additional momentum to the research on correlated materials. The experimental data evidencing the MIT in NaOsO$_3$ and Cd$_2$Os$_2$O$_7$ are difficult to decipher and rationalize. Both compounds show a continuous, second-order temperature($T$)-driven transition accompanied by the onset of a magnetic order [13, 17]. Initially, the BCS (Bardeen–Cooper–Schrieffer) like-gap inferred by infrared spectroscopy studies [20, 21] and the observation that the Néel temperature ($T_N$) coincides with the critical MIT temperature suggested a Slater-type mechanism. In fact, in a Slater insulator the onset of the insulating regime is combined with the simultaneous formation of a long-range antiferromagnetic (AFM) order [13, 17, 22]. However, it was soon realized that a purely Slater scenario is incomplete as a full explanation of the experimental observations in NaOsO$_3$, in particular the evolution of the resistivity as a function of $T$ which involves a sequence of three distinct regimes: insulator, bad-metal and metal [16, 23]. In fact, the high-degree of magnetic fluctuations and electron itinerancy observed in these Osmates are better captured by an alternative (magnetic) Lifshitz-like picture associated with a rigid upward (downward) shift of electron (hole) bands, preserving the overall band topology [16, 19, 24].

The Lifshitz MIT in undoped NaOsO$_3$ is driven by temperature and is associated with substantial modifications of the spin properties. At high temperatures NaOsO$_3$ is a paramagnetic metal, with strongly fluctuating magnetic moments. By decreasing temperature the magnetic fluctuations are gradually frozen, leading to the continuous vanishing of electrons pockets in the Fermi surface, that do not involve any substantial modification of the underlying band topology [16]. More precisely, the measured resistivity curve [23] shows two anomalies at $T_A \approx 30$ K and $T_N \approx 410$ K that mark the onset of two different regimes. At $T < T_A$ NaOsO$_3$ is an insulator and exhibits a long-range AFM ordering. At $T_A$ the indirect electronic gap closes and the system enters a pseudogap phase with low resistivity, assimilable to a poor metal state; this phase is characterized by longitudinal modulations of the spin moment which causes a continuous lowering of the local magnetic moment with increasing temperature [16]. At $T_N$ rotational spin fluctuations destroy the long range AFM state and the system becomes a paramagnetic metal [16].

There are two additional peculiar aspects of the MIT in NaOsO$_3$. First, despite being in a nominally $\Gamma_2$ configuration the ordered moment is only 1 $\mu_B$ [13] due to an high degree of $p–d$ hybridization which place the system close to an (electronic and magnetic) itinerant limit [14, 16, 25]; in addition even though the orbital moment is formally quenched ($L_{eff} = 0$, nominally 5$d^1$ configuration [26]), spin–orbit coupling effects are surprisingly important as they cause a renormalization (weakening) of the electron–electron correlation [16] and a large magnetic anisotropy energy [27].

In general, the ground state of a system can be perturbed by different means including temperature [1], doping [28, 29], pressure [30, 31], strain/heterostructuring [32], and dimensionality [12] to name the most effective stimuli. In this study we inspect the possibility to control the MIT in NaOsO$_3$ via chemical doping by means of first principles calculations. Doping effects can be modeled by following a variety of routes which could involve: (i) a rigid shift of the band (rigid doping); (ii) a controlled change of the number of valence electrons (preserving charge neutrality via an homogeneous background charge); (iii) the virtual crystal approximation or (iv) realistic chemical substitution (supercell approach). We follow this latter strategy by replacing Na with Mg at different concentration within a supercell approach (a sketch of the adopted Na$_{1−x}$Mg$_x$OsO$_3$ supercell is shown in figure 1). The results indicate that by injecting a progressively larger amount of excess electrons the systems undergoes a MIT associated with an almost linear decrease of the ordered moment and a sizable volume reduction.

The manuscript is organized as follows. We start from a brief description of the technical setup. Subsequently, we present and discuss the results on the doping-induced MIT in NaOsO$_3$ and draw a general phase diagram showing the intersection between insulator, bad metal and metallic regimes as a function of doping and size of the magnetic moment.

2. Computational details

Our first-principles calculations were performed using the projector augmented wave method (PAW) [33] as implemented in the Vienna *ab initio* simulation package (VASP) [34, 35]. The plane-wave cutoff for the orbitals was set to 400 eV and to sample the Brillouin zone a $3 \times 3 \times 3$ k-point grid was used, generated according to Monkhorst–Pack scheme.

All calculations were performed using a fully relativistic setup with the inclusion of SOC in the framework of the
DFT + $U$ [36, 37] with an effective $U_{\text{eff}} = U - J = 0.68$ eV [16] and using the PBE parametrization of the exchange-correlation functional.

The unit cell of NaOsO$_3$ contains four formula units consisting of 20 atoms. With respect to the ideal cubic perovskite ($1 \times 1 \times 1$) unit cell the magnetic unit cell of undoped NaOsO$_3$ is constructed by a 45° rotation around the $y$ axis and a doubling of the $b$ lattice parameter, i.e. ($\sqrt{2} \times 2 \times \sqrt{2}$), with experimental lattice parameters $a = 5.3842 \text{ Å}$, $b = 7.5804 \text{ Å}$, $c = 5.3282 \text{ Å}$ [23]. The resulting orthorhombic $Pnma$ structure is subjected to small internal geometrical distortions which leads to slightly different Na–O distances.

Figure 2. Variation of the volume (left scale) and of the ordered Os spin moment (right scale) as a function of Mg concentration $x$. Large symbols represent the data averaged over all studied configurations (1 configuration for $x = 0, 1$; 2 configurations for $x = 0.375$; 3 configurations for $x = 0.125, 0.25$).

Table 1. Collection of structural properties (volume ($\text{Å}^3$ per supercell) and lattice constants (Å)) and Os magnetic moment, in $\mu_B$ as a function of Mg doping $x$ for the considered configurations. The structural data refer to the $2 \times 2 \times 2$ supercell adopted in the calculations.

| $x$  | $V$  | $a$  | $b$  | $c$  | $m$  |
|------|------|------|------|------|------|
| 0    | 426.00 | 7.530 | 7.513 | 7.530 | 1.23  |
| 0.125| 424.27 | 7.513 | 7.516 | 7.514 | 1.18  |
| 0.125| 421.41 | 7.497 | 7.494 | 7.502 | 1.17  |
| 0.125| 421.44 | 7.496 | 7.495 | 7.502 | 1.19  |
| 0.25 | 418.74 | 7.486 | 7.495 | 7.468 | 1.13  |
| 0.25 | 418.94 | 7.492 | 7.495 | 7.493 | 1.11  |
| 0.25 | 420.69 | 7.509 | 7.499 | 7.480 | 1.15  |
| 0.375| 420.10 | 7.509 | 7.507 | 7.454 | 1.02  |
| 0.375| 418.04 | 7.494 | 7.521 | 7.418 | 1.01  |
| 0.5  | 414.66 | 7.469 | 7.504 | 7.400 | 0.95  |

Figure 3. Evolution of the band structure as a function of $x$ unfolded in the primitive cell for $x = 0, 0.125, 0.25$ and 0.5. The data obtained for $x = 0.375$ are omitted since they are very similar to the $x = 0.25$ case. The lateral bar indicates the amount of Bloch character given by equation (1). The arrows defines the indirect electronic gap.
Electron doping was modeled by chemical substitution of Na with Mg in $2 \times 2 \times 2$ supercells containing 8 Na$_{1-x}$Mg$_x$OsO$_3$ formula unit (40 atoms) for different Mg concentrations $x = 0.125, 0.25, 0.375, 0.5$ and considering different configurations of the dopants. All supercells were fully relaxed including both volume (lattice parameters) and internal atomic positions.

To analyze the effects of doping on the energy band structure, we projected the states of the supercell onto the states of the primitive cell by adopting the unfolding method [38–40] recently implemented in VASP [41, 42]. The projection $P_{Km}(\tilde{k})$, also known as Bloch character, is calculated as

$$P_{Km}(\tilde{k}) = \sum_n |\langle \psi_{Km}^{\text{supercell}}|\psi_{Km}^{\text{primitive}}\rangle|^2$$

where $|\psi_{Km}^{\text{supercell}}\rangle$ and $|\psi_{Km}^{\text{primitive}}\rangle$ are the eigenstates of the supercell and primitive cell, respectively, $K$ and $k$ the respective wave vectors and $m$ and $n$ are energy band indexes (more details on the method can be found in [28, 43]).

3. Results and discussions

As a starting point we inspect the evolution of the structural and magnetic properties upon doping. In fact, considering the strong spin-phonon interaction in NaOsO$_3$ [44], it is expected that the effect of doping should not be limited to purely electronic effects, but rather involve a concerted change of volume and local moment. As a consequence of the smaller atomic radius, Mg-substitution causes a gradual decrease of the volume, as shown in figure 2 and tabulated in table 1. Going from the undoped ($x = 0$) to the half-doped ($x = 0.5$) sample the volume is squeezed by about 3%. This structural change is associated with a huge ($\approx 30\%$) lowering of the local spin moment from $1.23\ \mu_B$ ($x = 0$) to $0.95\ \mu_B$ ($x = 0.5$). In NaOsO$_3$, this should reflect an increased degree of electron and magnetic itineracy. Thus, already at this stage, we expect to have a coupled magnetic-electronic transition induced by electron doping, in analogy with the $T$-driven MIT, where the collapse of the gap is associated with a gradual quenching of the local spin moment (see introduction).

This hypothesis is further verified by computing the electronic dispersion relation and associated density of states (DOS) as a function of doping. The effective band structure, unfolded in the primitive cell, is shown in figure 3 for $x = 0, 0.125, 0.25, 0.375$ and 0.5. The sharpness of the electronic bands measures the amount of Bloch character, as defined in equation (1), which accounts for the effect of the chemical disorder in the primitive cell. At $x = 0$ (figure 3(a)), the system exhibits the characteristic indirect gap of few tens of meV, and the effective band structure shows sharp bands, with a one-to-one correspondence between the primitive cell and the supercell. The energy region around the Fermi level is predominantly formed by Os-$d$ and O-$p$ states, as evinced by the orbital projected DOS shown in figure 4. Upon doping (figures 3(b)–(d)), the energy bands exhibit a pronounced broadening and appear with different degrees of intensity, a clear fingerprint of the chemical disorder. With increasing Mg concentration the bottom of conduction bands is progressively filled with the additional charges carries and the overall band topology is modified with respect to the unperturbed case ($x = 0$). As soon as extra electrons are injected in the system the lower laying conduction bands start to cross the Fermi level and the system become metallic. The DOS at the Fermi level $N(E_F)$ increases as a function of doping: $N(E_F, x = 0) = 0, N(E_F, x = 0.125) = 11.12; N(E_F, x = 0.25) = 15.33; N(E_F, x = 0.375) = 16.13; N(E_F, x = 0.5) = 16.24$, indicating that the conductivity, as expected, should increase with increasing doping (see figure 4). The size of the supercell adopted in this study does not allow to inspect lower doping concentrations, but it is reasonable to expect that the transition from the insulating $x = 0$ phase to the metallic one occurs via an intermediate bad-metal phase, which has also been observed in undoped NaOsO$_3$ [23]. At $x = 0.25$ the pseudogap separating the valence and conduction band is
completely closed (see figures 3(c) and 4(c)); at \( x = 0.5 \) the two Os-d/O-p manifolds start to overlap and a robust metallic phase is fully established (figures 3(d) and 4(c)).

This doping-induced MIT shares similarities with the temperature-driven MIT discussed in [16] and summarized in the introduction, in particular for what concern the important role played by longitudinal spin fluctuations (attenuation of the local magnetic moment). The analogy is not complete, however, since chemical doping does alter not rigidly the topology of the bands in contrast with a pure Lifshitz scenario where the mutual approaching of the valence and conduction band is theorized to occur rigidly [24].

We conclude our study by linking the temperature MIT in the undoped sample [16] with the doping induced MIT, by constructing a generalized phase diagram which rationalizes within a unique picture these two different type of MITs in NaOsO\(_3\). To this end we conducted a series of constrained magnetic moment calculations at each doping level to check how the electronic properties change as a function of the local moment [11, 16]. We found that by decreasing \( m \) from the ground state values (1.23–0.95 \( \mu_B \)) to 0.5 \( \mu_B \) in steps of 0.05 \( \mu_B \) the separation between the valence and conduction band decreases and \( N(E_F) \) increases (not shown). The results are collected in the phase diagram shown in figure 5, where the filled circles represent the ground state solution (i.e. without any magnetic constrained) and the shaded areas are the result of the magnetically constrained analysis. In the metallic phase we distinguish two sub-regimes, depending on whether the valence and conduction band overlaps or not. The boundary between these two metallic phases is controlled by the size of the local moment as determined by the magnetically constrained calculations.

Following the analysis conducted for the undoped case [16] we speculate that the strength of the local moment can be controlled by temperature effects, as suggested by the model of Mohn and Wohlfarth for itinerant magnetism [45] which maps the amplitude of the local moment to temperature (see arrows on the right side of figure 5). The lower limit is \( T = 0 \), representing the magnetically unconstrained DFT ground state solution. The left side of the phase diagram describe the undoped scenario, characterized by the transition for the low-\( T \) AFM state to the high-\( T \) metal state through an intermediate pseudogap bad metal state, consistent with experimental observations [23] When doping is concern, we conjecture that an increase of temperature should lower the local moment and lead to a band-crossing similar to the one found for \( x = 0.5 \) at \( T = 0 \) (see figure 3(d)), thus establishing a robust metallic state. We hope that this analysis will stimulate experimental measurements on electron-doped NaOsO\(_3\) hopefully confirming our predictions.

4. Conclusion

In conclusion, by means of first principles calculations we have inspected the possibility to induce and control an insulator-to-metal transition in NaOsO\(_3\) using chemical doping. By combining magnetically constrained DFT + \( U \) and the band unfolding scheme we have shown that excess electrons destroy the magnetic Lifshitz state and guide the system into a metallic regime. As a minimal synthesis of this study, we propose a general phase diagram of Mg\(_{x}\)Na\(_{1-x}\)OsO\(_3\) in which the boundaries between the insulating, bad-metal and metallic regimes are determined by the amplitude of the local moment. Increasing \( x \) or reducing \( m \) bring together the valence and conduction band favoring the formation of a robust metallic phase.

The predicted doping-induced insulator to MIT has similar traits with the temperature driven MIT reported in the undoped compound. Both develops in an itinerant background and exhibit a coupled electronic and magnetic behaviour characterized by the gradual quenching of the (pseudo)-gap associated with a reduction of the local spin moment. Unlike the temperature-driven MIT, chemical doping induces substantial modifications of the band structure and the MIT cannot be fully described as a Lifshitz process.

This study reveals once more the peculiar nature of NaOsO\(_3\) in which the electronic and magnetic degrees of freedom are tightly connected within an intrinsically itinerant background. Further studies might be envisioned to possibly preserve the insulating nature in NaOsO\(_3\) in the low-doping range by creating trapping centers or point defects which could immobilize the excess charge carriers, thus providing an additional channel to design novel functionalizations or construct novel type of quantum state of matter.

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