Metallic compounds containing light elements such as H, Li, and B have attracted considerable attention recently due to their potential superconducting properties. Within the weak-coupling BCS theory, high-frequency phonons due to the presence of atoms with light masses ensure a large prefactor in the BCS formula for the superconducting critical temperature $T_c$. Thus, even a moderate electron-phonon coupling can yield a sizable $T_c$. The discovery of superconductivity in MgB$_2$, B-doped diamond, B-doped silicon, and calcium and ytterbium graphite intercalated compounds confirms this picture and extends it by showing that strong covalent bonds between light atoms can provide a sizable contribution to the electronic density of states at the Fermi level, under appropriate "doping" conditions. In MgB$_2$, the Fermi level crosses the covalent $\sigma$ bonds formed by boron atoms. Such states are partially empty as a consequence of the lowering of the $\pi$ bands, caused by the Mg$^{2+}$ attractive potential felt by the B-$\pi$ electrons. In B-doped diamond, substitutional boron atoms provide hole doping to the C-$\pi$ band and the intercalated band.

Nitrogen follows boron and carbon in the first row of the Periodic Table and is characterized, in its elemental form, by a strong triple bond in the low pressure molecular phases and by covalent single bonds in the nonmolecular phase stable at pressures exceeding a megabar. As a consequence, molecular phases are insulating and the nonmolecular phase is semiconducting. In analogy with the boron and carbon-based superconducting compounds described above, search for superconductivity in nitrogen-based systems requires the identification of compounds where covalent bonds between nitrogen atoms persist in a stable form in the presence of doping species and of a resulting metallic state.

To our knowledge only OsN$_2$, a member of the family of late transition-metal nitrides synthesized recently at high pressure and temperature starting from their constituent elements, fulfills the above criteria. The compounds have been obtained by subjecting the parent metal to extreme conditions of pressure and temperature in a nitrogen embedding medium, in a diamond-anvil cell. Interest in these compounds has resided so far in their large bulk modulus, which suggests superhard mechanical properties. Ab initio calculations show that the three compounds synthesized so far (PtN$_2$, IrN$_2$, and OsN$_2$) only OsN$_2$ has a metallic character in agreement with the experimentally observed absence of first-order Raman peaks in this compound. Covalently bonded dinitrogen (N$_2$) units are preserved in the marcasitelike crystal structure of OsN$_2$ (Ref. [16]), which makes this compound an obvious candidate to investigate superconductivity in nitrogen-rich systems.

In this work, we investigate the superconducting properties of OsN$_2$ in the framework of a phonon mediated pairing mechanism. We performed ab initio calculations of the Fermi surface, electronic bands, phonon dispersions, and electron-phonon couplings in OsN$_2$, and demonstrate that the high-frequency modes originating from the covalently bonded N$_2$ units are strongly coupled to the electronic states at the Fermi level and would give rise to a $T_c$ of about 1 K. We also show that the superconducting temperature can be greatly increased by hole doping.

The calculations were performed with the QUANTUM ESPRESSO package employing density functional
theory and the Perdew-Burke-Ernzerhoff exchange-correlation functional. An ultrasoft pseudopotential description of the ion-electron interaction,\textsuperscript{20} with Os 5s and 5p semicore electrons included in the valence, was used together with a plane-wave basis set for the electronic wave functions and the charge density, with energy cutoffs of 40 and 480 Ry, respectively. The dynamical matrices and the electron-phonon coupling constants $\lambda$ were calculated using density functional perturbation theory (DFPT) in the linear response regime.\textsuperscript{18,21} The electronic Brillouin zone (BZ) integration in the phonon calculation was sampled with a $20 \times 16 \times 30$ uniform k-point mesh. The electron-phonon coupling was found to be converged with a finer grid of $26 \times 22 \times 40$ k points and a Gaussian smearing of 0.006 Ry. The dynamical matrix was computed on a $2^3$ mesh of phonon wave vectors $q$. The phonon dispersion was then obtained on a finer $8^3$ $q$ mesh by Fourier interpolation of the real space interatomic force constants. In this way, $\lambda$ is calculated over a $8^3$ $q$-point mesh.

![FIG. 1: (Color online) (a) Crystal structure of OsN$_2$ (isostructural to marcasite). The space group is $Pnma$, with osmium atoms (gray) in the Wyckoff sites 2a and nitrogen atoms (blue) in the 4g sites (Ref. 16). (b) Brillouin zone showing the high-symmetry directions used in Figs. 2 and 3](image)

In the energy range shown in Fig. 2, the total electronic density of states (DOS) is essentially determined by Os 5$d$ and N 2$p$ orbitals (Fig. 2 right panel). At the Fermi level, the N 2$p$ orbitals contribute with about 20% of the total DOS. The projection on the atomic orbitals also shows that 92% of the nitrogen contribution at $E_F$ is due to the N $p_{x,y}$ states and the remaining 8% to N $p_z$ states. The N $p_{x,y}$ orbitals lie in the plane containing the N-N units, and are thus directly involved in the formation of the N-N covalent bond in OsN$_2$. Integrating the DOS in a window of energy close to $E_F$ (between $E_F$ and 1 eV below $E_F$), we find an antibonding character for the electronic states on the N-N units. This is consistent with the considerable weakening of the N-N bond in OsN$_2$ with respect to the molecular triple bond, and is confirmed by the large reduction of the N-N stretching frequency from 2300 cm$^{-1}$ in the molecular state to 500-800 cm$^{-1}$ in the compound. A non-negligible coupling of the electronic states close to $E_F$ with the N-N stretching vibrational modes can thus be anticipated based on simple band-structure considerations. It is interesting to remark that the presence of the Os framework is crucial to the presence of a finite nitrogen component in the DOS at $E_F$. A band-structure calculation for a pure nitrogen system obtained by removing the Os atoms from the crystal structure of OsN$_2$ gives an insulating solid, indicating that the nitrogen component at $E_F$ arises from the coupling of the N-N units with the transition-metal framework, through rehybridization and/or charge transfer.

![FIG. 2: (Color online) Left panel: electronic bands of marcasite OsN$_2$ at ambient pressure along the high-symmetry lines shown in Fig. 1(b). Right panel: electronic density of states and its projection onto the Os 5$d$ (blue) and N 2$p$ (red) orbitals. The Fermi energy is set to zero.](image)

Due to the presence of stiff N-N bonds, the calculated phonons of OsN$_2$, shown in Fig. 3, can be divided into three main groups: a low-frequency group (up to 200 cm$^{-1}$) involving mostly the Os sublattice, an intermediate group corresponding to the librational modes of the N-N units (between 250 and 600 cm$^{-1}$), and a high-frequency manifold corresponding to rotation and stretching of the N-N units (above 600 cm$^{-1}$). The 18 phonon modes of the marcasite structure belong to eight irreducible representations. Four of these representations (B$_{1g}$, B$_{2g}$, B$_{3g}$, and A$_g$) are associated with nitrogen displacements only, with osmium atoms at rest, and are highlighted with symbols in Fig. 4. Representations B$_{2g}$ and B$_{3g}$ have one mode each and involve dinitrogen vibrations along the $\hat{z}$ axis, while representations A$_g$ and B$_{1g}$ have two modes and involve vibrations along the $\hat{x}$ and $\hat{y}$ directions. In B$_{2g}$ and A$_g$ both dinitrogen units oscillate in phase, while in B$_{3g}$ and B$_{1g}$ the N-N units vibrate in counterphase. As we can see from Fig. 4, the nitrogen light mass and the covalent N-N bond ensure a high frequency for these modes, with A$_g$ and B$_{1g}$ modes ranging between 640 and 825 cm$^{-1}$. Raman peaks in this frequency range have been observed experimentally also in PtN$_2$ and IrN$_2$ and have been associated with the stretching of N-N units.\textsuperscript{12,13,14} As a confirmation of the planar ($xy$) nature of bonding in N-N, we note that the $xy$-polarized phonons in the A$_g$ and B$_{1g}$ representations are higher in frequency with respect to $z$-polarized
modes.

Within DFPT, the electron-phonon interaction for a phonon mode \( \nu \) with momentum \( \mathbf{q} \) can be calculated as

\[
\lambda_{\mathbf{q}\nu} = \frac{4}{\omega_{\mathbf{q}\nu} N(E_F) N_k} \sum_{\mathbf{k},n,m} |g^\nu_{\mathbf{k}\mathbf{q}\nu\mathbf{m}}|^2 \delta(\epsilon_{\mathbf{k}}) \delta(\epsilon_{\mathbf{k}+\mathbf{q}\mathbf{m}})
\]

where the sum is over the Brillouin zone. The matrix element is

\[g^\nu_{\mathbf{k}\mathbf{q}\nu\mathbf{m}} = \langle \mathbf{k}\nu|\delta V/\delta \mathbf{u}_{\mathbf{q}\mathbf{m}}|\mathbf{k}+\mathbf{q}\mathbf{m}\rangle/\sqrt{2\omega_{\mathbf{q}\nu}},\]

where \( u_{\mathbf{q}\nu} \) is the amplitude of the displacement of the phonon and \( V \) is the Kohn-Sham potential. The electron-phonon coupling is calculated as a BZ average over the phonon wave vectors \( \lambda = \sum_{\mathbf{q}\nu} \lambda_{\mathbf{q}\nu}/N_q \). The Eliashberg spectral function \( \alpha^2 F(\omega) \) is defined as

\[\alpha^2 F(\omega) = \frac{1}{2N_q} \sum_{\mathbf{q}\nu} \lambda_{\mathbf{q}\nu} \omega_{\mathbf{q}\nu} \delta(\omega - \omega_{\mathbf{q}\nu})\]

and allows to compute \( \lambda(\omega) = 2 \int_0^\omega d\omega' \alpha^2 F(\omega')/\omega' \).

Figure 4(a) shows the Eliashberg spectral function \( \alpha^2 F(\omega) \) calculated from Eq. 1. Three separate contributions to the electron-phonon interaction can be distinguished and attributed to the low-frequency, intermediate-frequency, and high-frequency phonons, respectively. Two high-frequency peaks are particularly strong and well resolved, and are associated with the contribution of the two \( A_\sigma \) phonons, while the contribution of the \( B_{3g} \) and \( B_{3g} \) phonons accounts for most of the electron-phonon interaction in the intermediate-frequency range from 500 to 600 cm\(^{-1}\). The integral \( \lambda(\omega) \), represented by a dashed line in Fig. 4(a), shows that the low-frequency phonons that involve mostly nitrogen atoms account for a contribution of \( \lambda = 0.17 \). The high-frequency phonons associated with the stretching of the covalently bonded N-N units contribute with an equivalent amount, which brings the total \( \lambda \) for OsN\(_2\) to 0.37. More insight about the nature of the electron-phonon interaction that leads to such a large contribution to \( \lambda \) from N-N bonds can be obtained by analyzing the changes of the Fermi surface (FS) that arise upon distorting the lattice along the relevant phonon modes. In particular, we concentrate on the \( A_\sigma \) modes that show the highest \( \alpha^2 F(\omega) \) values and dominate the high-frequency contributions. In Fig. 4(b), we compare the FS of the undistorted OsN\(_2\) with that of a distorted OsN\(_2\) crystal obtained by changing by 4% the distance between nitrogen atoms in the N-N units along the \( xy \)-polarized \( A_\sigma \) mode. The most relevant change in the FS is the migration of electrons from the bands that contain the hole pockets at \( Z \) to the bands that contain the electron pockets near \( \Gamma \). Interband electron transfer is generally associated with a large electron-phonon coupling, which is consistent with our finding of a large contribution of the \( A_\sigma \) modes to \( \lambda \).

The superconducting critical temperature can be estimated using the McMillan formula

\[T_c = \frac{\langle \omega_n \rangle}{1.2} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right),\]

where \( \mu^* \) is the screened Coulomb pseudopotential and \( \langle \omega_n \rangle = 280 \) K is the logarithmically averaged phonon frequency. We obtain 0.3\(<T_c<1.2\) for 0.13\(<\mu^*>0.08\) (with \( T_c=1 \) K at the widely accepted value \( \mu^*=0.1 \), see Refs. [22,23,24].
A careful examination of the electronic DOS of OsN$_2$ (Fig. 2) suggests that hole doping could further enhance $T_c$. Hole doping in OsN$_2$ would, in fact, lower the Fermi level toward a region of higher electronic DOS and would, at the same time, stiffen the N-N bonds by partially emptying the antibonding states below E$_F$. The reported synthesis of several nitrides from different transition metals (Pt, Ir, Os, Pd) suggests that the synthesis of transition-metal nitride alloys, i.e., of compounds with N-N units inserted in a matrix of mixed metal composition, is not impossible. Alloys with different composition allow a tuning of the electronic DOS, as observed in transition-metal alloys.

FIG. 5: Eliashberg function $\alpha^2 F(\omega)$ of hole-doped OsN$_2$ (continuous line) and undoped OsN$_2$ (dashed line).

In order to explore the consequences of hole doping, we carried out ab initio calculations of OsN$_2$ with a hole doping of 0.5 holes/unit cell, corresponding, e.g., to a hypothetical alloy with Os$_{0.75}$Re$_{0.25}$N$_2$ composition. As expected, the DOS at E$_F$ increases about 2.4 times with respect to the undoped case. The electron-phonon coupling matrix elements remain approximately the same in the doped and undoped cases, but the phonon frequencies associated with the N-N modes increase by about 200 cm$^{-1}$ (see Fig. 5), which confirms the strong coupling of these modes with the electronic states close to the Fermi level. The frequency increase causes an increase of $\omega_{\text{in}}$ to 310 K. The total electron-phonon coupling parameter, $\lambda$, increases to 0.49, leading to a superconducting critical temperature of $\approx$ 4 K for doped OsN$_2$.

In conclusion, we predict that OsN$_2$ is a superconductor, and that its superconducting properties are connected with a strong coupling between the stretching modes of the covalently bonded N$_2$ units with the electronic states at the Fermi level, similar to what has been observed in a number of boron and carbon-based compounds, including MgB$_2$. We predict an enhancement of the superconducting temperature by doping OsN$_2$ with holes, which we believe can be achieved experimentally by synthesizing the nitride starting from a hole-doped Os alloy. We hope this work will stimulate the experimental search for other members of the dinitride family with metallic character and potential superconducting properties.

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