

# First-principles investigation of the electron-phonon interaction in OsN<sub>2</sub>: Theoretical prediction of superconductivity mediated by N-N covalent bonds

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A first-principles investigation of the electron-phonon interaction in the recently synthesized osmium dinitride (OsN<sub>2</sub>) compound predicts that the material is a superconductor. Superconductivity in OsN<sub>2</sub> would originate from the stretching of covalently bonded dinitrogen units embedded in the transition-metal matrix, thus adding dinitrides to the class of superconductors containing covalently bonded light elements. The dinitrogen vibrations are strongly coupled to the electronic states at the Fermi level and generate narrow peaks in the Eliashberg spectral function  $\alpha^2F(\omega)$ . The total electron-phonon coupling of OsN<sub>2</sub> is  $\lambda=0.37$  and the estimated superconducting temperature  $T_c \approx 1$  K. We suggest that the superconducting temperature can be substantially increased by hole doping of the pristine compound and show that  $T_c$  increases to 4 K with a doping concentration of 0.25 holes/OsN<sub>2</sub> unit.

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Metallic compounds containing light elements such as H, Li, and B have attracted considerable attention recently due to their potential superconducting properties.<sup>1-3</sup> 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  $T_c$ .<sup>4,5</sup> The discovery of superconductivity in MgB<sub>2</sub>,<sup>6</sup> B-doped diamond,<sup>7</sup> B-doped silicon,<sup>8</sup> and calcium and ytterbium graphite intercalated compounds<sup>9</sup> 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<sub>2</sub>, 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<sup>2+</sup> attractive potential felt by the B- $\pi$  electrons.<sup>5,6</sup> In B-doped diamond,<sup>7</sup> substitutional boron atoms provide hole doping to the C-C  $sp^3$  covalent bonds. The strong C-C bonding allows the structure to remain stable even at high doping. In electron-doped graphite intercalated compounds, the Fermi level crosses the graphitic 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.<sup>10</sup> As a consequence, molecular phases are insulating and the nonmolecular phase is semiconducting.<sup>11</sup> In analogy with the boron and carbon-based superconducting compounds described above, a 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<sub>2</sub>, a member of the family of

late transition-metal nitrides synthesized recently at high pressure and temperature starting from their constituent elements,<sup>12-15</sup> 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 among the three compounds synthesized so far (PtN<sub>2</sub>, IrN<sub>2</sub>, and OsN<sub>2</sub>) only OsN<sub>2</sub> has a metallic character,<sup>16,17</sup> in agreement with the experimentally observed absence of first-order Raman peaks in this compound.<sup>13</sup> Covalently bonded dinitrogen (N<sub>2</sub>) units are preserved in the marcasitelike crystal structure of OsN<sub>2</sub> (Ref. 16) [see Fig. 1(a)], which makes this compound an obvious candidate to investigate superconductivity in nitrogen-rich systems.

In this work, we investigate the superconducting properties of OsN<sub>2</sub> 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<sub>2</sub>, and demonstrate that the high-

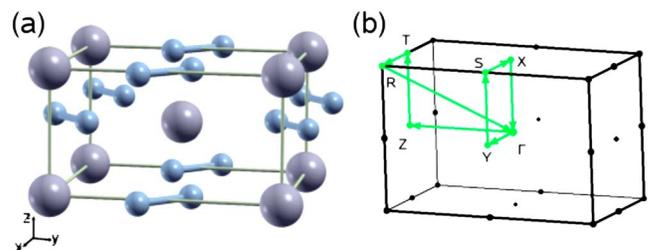


FIG. 1. (Color online) (a) Crystal structure of OsN<sub>2</sub> (isostructural to marcasite). The space group is  $Pn\bar{m}m$ , with osmium atoms (gray) in the Wyckoff sites 2a and nitrogen atoms (blue) in the 4g sites (Ref. 16). (b) Brillouin zone showing the high-symmetry directions used in Figs. 2 and 3.

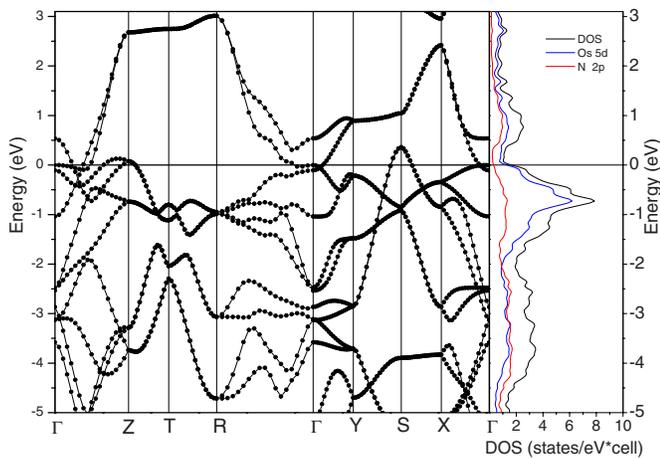


FIG. 2. (Color online) Left panel: electronic bands of marcasite  $\text{OsN}_2$  at ambient pressure along the high-symmetry lines shown in Fig. 1(b). Right panel: electronic density of states and its projection onto the Os  $5d$  (blue) and N  $2p$  (red) orbitals. The Fermi energy is set to zero.

frequency modes originating from the covalently bonded  $\text{N}_2$  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<sup>18</sup> employing density functional theory and the Perdew-Burke-Ernzerhoff exchange-correlation functional.<sup>19</sup> An ultrasoft pseudopotential description of the ion-electron interaction,<sup>20</sup> 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.<sup>18,21</sup> 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.

In the energy range shown in Fig. 2, the total electronic density of states (DOS) is essentially determined by Os  $5d$  and N  $2p$  orbitals (Fig. 2, right panel). At the Fermi level, the N  $2p$  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  $\text{OsN}_2$ . 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

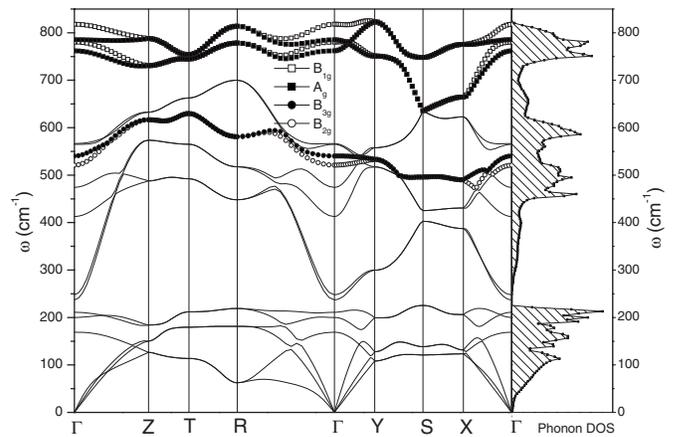


FIG. 3. Phonon dispersions along high-symmetry directions of the Brillouin zone and corresponding phonon density of states (right panel).

$\text{OsN}_2$  with respect to the molecular triple bond, and is confirmed by the large reduction of the N-N stretching frequency from  $2300 \text{ cm}^{-1}$  in the molecular state to  $500\text{--}800 \text{ cm}^{-1}$  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  $\text{OsN}_2$  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.

Due to the presence of stiff N-N bonds, the calculated phonons of  $\text{OsN}_2$ , shown in Fig. 3, can be divided into three main groups: a low-frequency group (up to  $200 \text{ cm}^{-1}$ ) involving mostly the Os sublattice, an intermediate group corresponding to the librational modes of the N-N units (between  $250$  and  $600 \text{ cm}^{-1}$ ), and a high-frequency manifold corresponding to rotation and stretching of the N-N units (above  $600 \text{ cm}^{-1}$ ). 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. 3. 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. 3, 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  $825 \text{ cm}^{-1}$ . Raman peaks in this frequency range have been observed experimentally also in  $\text{PtN}_2$  and  $\text{IrN}_2$  and have been associated with the stretching of N-N units.<sup>12–14</sup> 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.

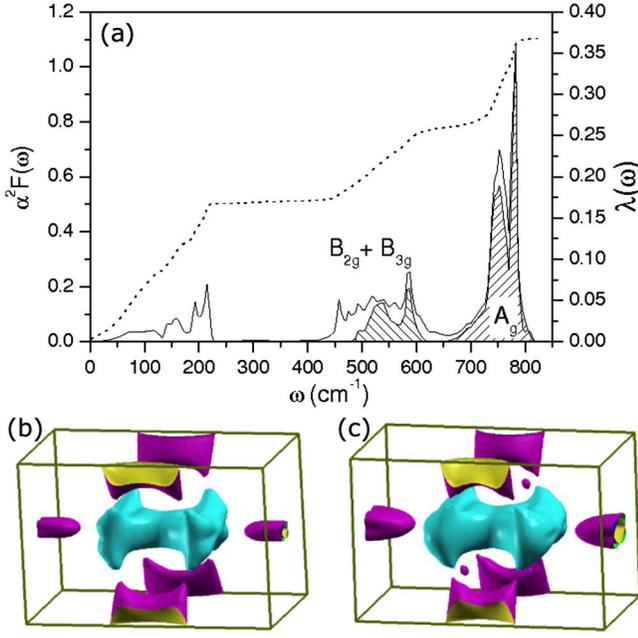


FIG. 4. (Color online) (a) Eliashberg function  $\alpha^2 F(\omega)$  (continuous line) and integrated coupling  $\lambda(\omega)$  (dashed line) of  $\text{OsN}_2$ . The shaded regions are the  $B_{2g}$ ,  $B_{3g}$ , and  $A_g$  contributions to  $\alpha^2 F$ . (b) Calculated Fermi surface of  $\text{OsN}_2$ . The Fermi surface consists of three electron pockets located close to the zone center, only one of which is visible (green pocket), and of four hole pockets, two of them centered at  $Z$  and two at the  $S$  point. (c) Fermi surface upon distortion of the lattice along an  $A_g$  phonon.

Within DFPT,<sup>21</sup> the electron-phonon interaction for a phonon mode  $\nu$  with momentum  $\mathbf{q}$  can be calculated as

$$\lambda_{\mathbf{q}\nu} = \frac{4}{\omega_{\mathbf{q}\nu} N(E_F) N_{\mathbf{k},\mathbf{k}+\mathbf{q},m}} \sum |g_{\mathbf{k}n,\mathbf{k}+\mathbf{q}m}^\nu|^2 \delta(\epsilon_{\mathbf{k}n}) \delta(\epsilon_{\mathbf{k}+\mathbf{q}m}),$$

where the sum is over the Brillouin zone. The matrix element is  $g_{\mathbf{k}n,\mathbf{k}+\mathbf{q}m}^\nu = \langle \mathbf{k}n | \delta V / \delta u_{\mathbf{q}\nu} | \mathbf{k}+\mathbf{q}m \rangle / \sqrt{2\omega_{\mathbf{q}\nu}}$ , 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

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

and allows one 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  $A_g$  phonons, while the contribution of the  $B_{2g}$  and  $B_{3g}$  phonons accounts for most of the electron-phonon interaction in the intermediate-frequency range from 500 to 600  $\text{cm}^{-1}$ . The integral  $\lambda(\omega)$ , represented by a dashed line in Fig. 4(a), shows that the

low-frequency phonons that involve mostly osmium 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  $\text{OsN}_2$  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  $A_g$  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  $\text{OsN}_2$  with that of a distorted  $\text{OsN}_2$  crystal obtained by changing by 4% the distance between nitrogen atoms in the N-N units along the  $xy$ -polarized  $A_g$  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  $A_g$  modes to  $\lambda$ .

The superconducting critical temperature can be estimated using the McMillan formula:<sup>22</sup>

$$T_c = \frac{\langle \omega_{\text{ln}} \rangle}{1.2} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right), \quad (2)$$

where  $\mu^*$  is the screened Coulomb pseudopotential and  $\langle \omega_{\text{ln}} \rangle = 280$  K is the logarithmically averaged phonon frequency. We obtain  $0.3 < T_c < 1.2$  for  $0.13 > \mu^* > 0.08$  (with  $T_c \approx 1$  K at the widely accepted value  $\mu^* = 0.1$ , see Refs. 22–24).

A careful examination of the electronic DOS of  $\text{OsN}_2$  (Fig. 2) suggests that hole doping could further enhance  $T_c$ . Hole doping in  $\text{OsN}_2$  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.<sup>27</sup>

In order to explore the consequences of hole doping, we carried out *ab initio* calculations of  $\text{OsN}_2$  with a hole doping of 0.5 holes/unit cell, corresponding, e.g., to a hypothetical alloy with  $\text{Os}_{0.75}\text{Re}_{0.25}\text{N}_2$  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  $\text{cm}^{-1}$  (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  $\langle \omega_{\text{ln}} \rangle$  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  $\text{OsN}_2$ .

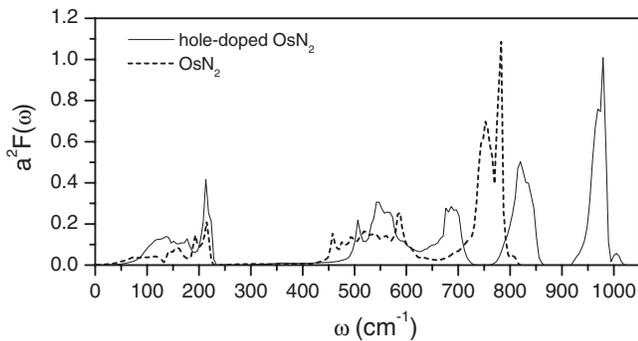


FIG. 5. Eliashberg function  $\alpha^2 F(\omega)$  of hole-doped  $\text{OsN}_2$  (continuous line) and undoped  $\text{OsN}_2$  (dashed line).

In conclusion, we predict that  $\text{OsN}_2$  is a superconductor, and that its superconducting properties are connected with a strong coupling between the stretching modes of the co-

valently bonded  $\text{N}_2$  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  $\text{MgB}_2$ . We predict an enhancement of the superconducting temperature by doping  $\text{OsN}_2$  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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