Oxidation of 2D electrides: structural transition and the formation of half-metallic channels protected by oxide layers

Pedro H. Souza†, Danilo Kuritza‡, José E. Padilha§ and Roberto H. Miwa†

1 Instituto de Física, Universidade Federal de Uberlândia,
C.P. 393, 38400-902, Uberlândia, MG, Brazil and
2 Campus Avançado Jandaia do Sul,
Universidade Federal do Paraná,
86900-000, Jandaia do Sul, PR, Brazil.
(Dated: February 25, 2022)

ABSTRACT

Based on first-principles calculations we performed a systematic study of the energetic stability, structural characterization, and electronic properties of the fully oxidized $A_2B$ electrenes, with $A =$ Ba, Ca, Sr, Y, and $B =$ As, N, P, C. We have considered one side oxidation of single layer electrenes (O/$A_2B$), and two side oxidation of bilayer electrenes (O/($A_2B$)$_2$/O). We show that the hexagonal lattice of the pristine host is no longer the ground state structure in the (fully) oxidized systems. Our total energy results reveal an exothermic structural transition from hexagonal to tetragonal ($h \rightarrow t$) geometry, resulting in layered tetragonal structures [($AOAB$)$^t$ and ($AO(AB)_2AO$)$^t$]. Phonon spectra calculations and molecular dynamic simulations show that the O/$A_2B$ and O/($A_2B$)$_2$/O systems, with $A =$ Ba, Ca, Sr, and $B =$ N, become dynamically and structurally stable upon such a $h \rightarrow t$ transition. Further structural characterizations were performed based on simulations of the near edge X-ray absorption spectroscopy at the nitrogen K-edge. Finally, the electronic band structure and transport calculations reveal the formation of half-metallic bands spreading out through the AN layers, which in turn are shielded by oxide AO sheets. These findings indicate that ($AOAN$)$^t$ and ($AOAN_3AO$)$^t$ are quite interesting platforms for application in spintronics; since the half-metallic channels along the AN or (AN)$_3$ layers (core) are protected against the environment conditions by the oxidized AO sheets (cover shells).

I. INTRODUCTION

Research works in two-dimensional (2D) materials with different functionalities have been boosted in the last few years. Since the successful synthesis of graphene, many 2D materials have been considered as a new paradigm not only in fundamental studies, like the search of topological phases and tuneable magnetic structures in 2D systems, but also addressing technological applications. For instance, the development of new materials for (nano)electronic and spintronic devices like single layer field effect transistors and half-metals based on transition metal dichalcogenides and dihalides.

By taking advantage of the layered structure of their 3D parents, combined with a suitable balance between strong (weak) intralayer (interlayer) binding interactions, these two dimensional materials can be obtained through exfoliation processes. For instance, in a seminal work, Lee et al. revealed the exfoliable nature, and the two dimensional electronic confinement in Ca$_2$N electrenes.

Electrides are ionic crystals characterized by the presence of electrons not bonded to a particular nucleus. These electrons act as ions (with no nucleus) embedded within the crystal lattice, anionic electrons. Further experimental works revealed that these anionic electrons form nearly free 2D electron gas confined between the stacked layers of the electride. It is worth noting that there are other native inorganic electrides with the same lattice structure of Ca$_2$N, like Sr$_2$N and Y$_2$C, meanwhile other ones have been predicted throughout high-throughput computational simulations.

Currently, few layer systems of electrides (electrenes) have attracted research works in fundamental issues, like the search of topological phases throughout the design of kagome lattices on the electron surface, as well as to the development of electronic devices with high carrier density and electronic mobility. Further, theoretical studies have addressed the functionalization of Ca$_2$N electrenes mediated by atomic adsorption. Functionalization is a quite promising route in order to tailor the electronic and magnetic properties of 2D systems. For instance, the rise of ferromagnetic (FM) phases upon full hydrogenation and oxidation of Ca$_2$N and Sr$_2$N electrenes. On the other hand, it is important to stress that the presence of anionic electrons makes the electrone surface very reactive, which may lead to significant changes on the electronic and structural properties of the functionalized systems, giving rise to a new set of physical properties to be exploited.

In this work, by means of first-principles calculations,
we perform a systematic investigation of the energetic stability, structural, and the electronic/magnetic properties of the oxidized $A_2B$ electrones, with $A =$ Ca, Sr, Ba, Y, and $B =$ As, N, P, C. We have considered the fully oxidation of one surface side of single layer electron ($O/\text{A}_2\text{B}$), and two surface sides in bilayer electrones ($\text{O}/(\text{A}_2\text{B})_2/\text{O}$). Our total energy results revealed a barrierless hexagonal (h) to tetragonal (t) structural transition, giving rise to layered tetragonal systems, namely $(\text{AOA}\text{B})^t$ and $(\text{AO}(\text{A})_2\text{AO})^t$. The dynamical and structural stabilities were examined through a combination of phonon spectra calculations, and molecular dynamic simulations. Based on the simulations of the (N K-edge) X-ray absorption near edge spectroscopy (XANES), and the projection of the electronic orbitals, we present a detailed structural analysis of the oxidized systems, and fingerprints of their tetragonal geometries. Finally, focusing on the electronic/magnetic properties, we find that the oxidized $(\text{AOA}\text{B})^t$, and $(\text{AO}(\text{A})_2\text{AO})^t$ systems are characterized by (i) an energetic preference for the FM phase, and (ii) the emergence of half-metallic channels along AN layers shielded by oxidized AO shells (with $A =$ Ca, Sr, and Ba).

**II. COMPUTATIONAL DETAILS**

The calculations were performed by using the density functional theory (DFT)\cite{32} as implemented in the computational codes Quantum-Espresso (QE)\cite{34,35} and Vienna Ab initio Simulation Package (VASP).\cite{36,37} We have considered the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE)\cite{38} for the exchange-correlation functional. The single layer and bilayer $A_2B$ electrones were simulated using slab structures within the supercell approach, with a vacuum region of 18 and 22 Å, respectively, and surface periodicities of (1×1) and (√2×√2) for hexagonal and tetragonal structures. The final atomic geometries, and total energies were obtained using the QE code, where the Kohn-Sham\cite{39} orbitals, and the self-consistent total charge densities were expanded in plane wave basis sets with energy cutoffs of 70 and 353 Ry, respectively. The Brillouin zone sampling was performed by using a 8×8×1 k-point mesh.\cite{32} The atomic positions were relaxed until the residual forces were converged to within 5 meV/Å, and the structural relaxation (variable-cell) was performed within a pressure convergence of 0.05 Kbar. The long-range van der Waals (vdW) interactions were taken into account using the self-consistent vdW-DF approach.\cite{40,41,42}

Further structural characterizations were performed through calculations of the X-ray absorption spectra combining the QE results and Xspectrum\cite{43,44,45} simulations. We have considered the K-edge spectra of nitrogen atoms by using the Gauge-Including Projector Augmented-Wave (GIPAW)\cite{46} method to calculate the dipolar cross section,

$$\sigma(\omega) \propto \sum_n |\langle \psi_n | \mathbf{r} | \psi_{1s} \rangle|^2 \delta(\epsilon_n - \epsilon_{1s} - \hbar \omega),$$

within the dipole approximation; $\psi_n/\epsilon_n$ and $\psi_{1s}/\epsilon_{1s}$ are the final $n$ and initial 1s (single particle) orbitals/energies in the presence of core-hole. The absorbing atom is described with a pseudopotential with a full core-hole in the N-1s orbital.\cite{47} In order eliminate spurious interactions between a core-hole and its periodic images, we have considered a distance of $\sim$7 Å between the core-holes.

The electronic structure calculations and structural/thermal stability simulations were performed using the VASP code. We have considered an energy cut-off of 500 eV for the plane wave basis set, and the Brillouin zone was sampled using a 15×15×1 k-point mesh.\cite{48} The structural stability was verified through the calculation of elastic constants and the phonon dispersion using PHONOPY code.\cite{49} The thermal stability was verified by ab initio molecular dynamics simulations (AIMD) at 300 K, with a time step of 1 fs using Nosé heat bath scheme.\cite{50}

The calculation of the electronic transmission probability $(T)$ was performed based on the non-equilibrium Green’s functions (NEGF) formalism using the DFT Hamiltonian as implemented in the Siesta and Transiesta\cite{51,52} codes. The KS orbitals were expanded in a linear combination of numerical pseudo-atomic orbitals, using split-valence double-zeta basis set including polarization functions.\cite{53,54} The BZ samplings were performed using two different set of k-point meshes, 1 × 10 × 200 1 × 20 × 500 according with the electronic transport directions.

The total transmission probability of electrons with energy $E$ and bias voltage $V$, $T(E, V)$, from the left electrode to reach the right electrode passing through the scattering region is given by,

$$T(E) = Tr \left[ \Gamma_L (E, V) G^R (E, V) \Gamma_L (E, V) G^A (E, V) \right],$$

where $\Gamma_{L,(R)} (E, V)$ is the coupling with the left and right electrodes and $G^{R,(A)}$ is the retarded (advanced) Green function matrix of the scattering region. The current $I$ is evaluated by using Landauer-Büttiker formula,\cite{55,56}

$$I(V) = \frac{2e}{h} \int T(E, V) \left[ f(E - \mu_L) - f(E - \mu_R) \right] dE,$$

where $f(\epsilon)$ is the Fermi-Dirac distribution for energy $\epsilon$ and $\mu_{L,R}$ is the electrochemical potential of left (right) electrode. We have considered the zero-bias approximation, $T(E, V) \approx T(E, 0)$, for the calculation of the electronic current calculated at the limit of low bias voltage ($\leq 0.1$ V).
FIG. 1. Structural model of $A_2B$ electrode bulk (a), and single layer electrene, side view (b) and top view (c). The isosurfaces (of $0.003e/\text{Å}^3$) show the localization of the anionic electrons within the energy interval of $\pm 0.5\text{eV}$ with respect to the Fermi level.

III. RESULTS AND DISCUSSIONS

A. Pristine $A_2B$ electrides

The $A_2B$ electrides with $A = \text{Ca, Sr, Ba, Y, and } B = \text{N, P, As, C}$ share the same structure of Ca$_2$N, Fig. 1(a). Our results of equilibrium geometries of $A_2B$ electrides and 2D single layer electrenes, summarized in Table I, are in good agreement with previous experimental and theoretical findings, viz.: Ba$_2$As, Ba$_2$P, Sr$_2$P, Y$_2$C, Ca$_2$N, Sr$_2$N, and Ba$_2$N. The structural properties of these electrides are anisotropic, characterized by a strong intralayer interactions due to the $A$–$B$ ionic chemical bonds, and comparatively weaker interlayer interaction between the $A_2B$ sheets. The latter is ruled by a superposition of (i) Coulombic attractive forces between the positively charged $A_2B$ layer and the anionic electrons, and (ii) repulsive interaction between the positively charged $A_2B$ layers. In order to provide a quantitative picture of the interlayer binding strength, we calculate the interlayer binding energy ($E^b$) defined as:

$$E^b = \frac{1}{S} (E[A_2B]_{\text{ML}} - E[A_2B]_{\text{Bulk}}),$$

where $E[A_2B]_{\text{ML}}$ and $E[A_2B]_{\text{Bulk}}$ are the total energies of single layer electrene, and $A_2B$ electride, respectively, and $S$ is the surface area normal to the $A_2B$ stacking. Our results of binding energies for Ca$_2$N, Sr$_2$N, Ba$_2$N, and Y$_2$C (Table I) are in good agreement with those presented in the current literature.

TABLE I. Details of the equilibrium geometry of $A_2B$ electrides and single layer electrenes, lattice constant $a$ and $A$–$B$ equilibrium bond length (in Å), and the interlayer binding energy, $E^b$ (in J/m$^2$) without/with the inclusion of vdW interactions.

|        | $A_2B$ | $a$  | $A$–$B$ | $E^b$         | $a$  | $A$–$B$ |
|--------|--------|------|---------|---------------|------|---------|
| bulk   |        |      |         |               |      |         |
| Ba$_2$As | 4.64   | 3.21 | 0.41/0.48 | 4.65          | 3.22 |
| Ba$_2$P | 4.65   | 3.18 | 0.44/0.51 | 4.64          | 3.17 |
| Sr$_2$P | 4.45   | 3.01 | 0.59/0.64 | 4.43          | 3.00 |
| Y$_2$C  | 3.61   | 2.47 | 1.60/1.73 | 3.50          | 2.45 |
| Ca$_2$N | 3.60   | 2.42 | 0.97/1.02 | 3.61          | 2.43 |
| Sr$_2$N | 3.84   | 2.60 | 0.78/0.83 | 3.85          | 2.61 |
| Ba$_2$N | 4.02   | 2.76 | 0.58/0.64 | 4.00          | 2.75 |

Given the large $A_2B$–$A_2B$ interlayer distance (> 3 Å), it is worth to examine the contribution of the van der Waals (vdW) interactions in the binding energies. As shown in Table I, the calculations of $E^b$ without/with the inclusion of the vdW interactions reveal a slight increase of $E^b$, for instance between 5 an 10% for the nitrides.

FIG. 2. Structural models of the hexagonal electrene adsorbed by O adatoms, with oxygen coverage of 0.25 (a1), 0.50 (a2), and 0.75 (a3). Hexagonal (b1) and tetragonal (b2) one-sided full oxidized single layer electrene; two-sided full oxidized (c1) hexagonal and (c2) tetragonal bilayer electrene. Oxygen atoms are indicated by red spheres.
Thus, we can infer that the Coulombic attractive forces bring the major contribution to the interlayer interactions.

Our results of $E^b$ indicate that these $A_2B$ electrenes can be classified as “potentially esfoliable” based on the criteria presented, by Mounet et al., in a recent high-throughput computational investigation applied to two dimensional material[13] As shown in Figs.1(b) and (c), at the equilibrium geometry, the single layer electrone exhibits the same $A_2B$ atomic structure of its bulk (electride) parent, with the anionic electrons lying on the electride surface.

**B. Oxidation**

Here we will address the energetic stability, structural characterization, and the electronic properties of the oxidized $A_2B$ electrenes. Firstly, we have considered the one-sided full oxidized single layer electrone [$O/(A_2B)$], and in the sequence the two-sided full oxidized bilayer electrone [$O/(A_2B)_2/O$]. In Figs.2(b) and (c) we present the structural models of $O/A_2B$ and $O/(A_2B)_2/O$.

1. Energetic Stability

The energetic stability of the oxidized electrenes was inferred through the calculation of the formation energy ($E^f$),

$$E^f = E[O_n/A_2B] - E[A_2B] - 2n E[O_2].$$

$E[O_n/A_2B]$ and $E[A_2B]$ are the total energies of the oxidized and pristine $A_2B$ electrenes, where $n$ is the fraction of O adatoms per $2 \times 2$ surface unit cell. The total energy calculations were performed by considering the full relaxation of the atomic positions, and the lattice vectors $a$ and $b$ in Fig.2. $E[O_2]$ is the total energy of an isolated $O_2$ molecule (triplet state).

We found an energetic preference for oxygen adatoms on the hollow site aligned with the (cation) $A$ atom at the opposite side of the $A_2B$ monolayer, as shown in Figs.2(a1)-(a3) and 2(b1) for $n=0.25, 0.50, 0.75,$ and 1, respectively. Our total energy results indicate that the oxidation processes are exothermic, with $E^f$ (in absolute values) proportional to the oxidation rate. In Fig.3(a) we present $E^f$ as a function of the oxygen coverage for $O/A_2B$ with $B=N, O/A_2N$. It is worth pointing out that, although the anionic electrons of $A_2B$ are neutralized for coverage of 50% ($O_{0.5}/A_2B$), the incorporation of oxygen adatoms for $n > 50\%$ is energetically favorable. For instance, $O_{0.5}/Ca_2N$ plus an excess of $O_2$ molecules is less stable than the full oxidized $O/Ca_2N$ system by 0.96 eV/O-atom, $O_{0.5}/Ca_2N + O_2 \rightarrow O/Ca_2N$. Similar results were obtained for the other $O/A_2B$ systems. The formation energies and the equilibrium lattice constant of $O/A_2B$ are summarized in Table II.

However, although the negative values of $E^f$, phonon spectra calculations [Fig.4(a)] revealed imaginary frequencies for all $O/A_2B$ structures, except $O/(Y_2C)$ [Fig.4(b3)], thus indicating that the hexagonal $O/A_2B$ systems $O/(A_2B)^h$, except $O/(Y_2C)^h$, are dynamically unstable. We have also examined structural stability of the hexagonal phases through molecular dynamics (MD) simulations, where found that all $O/(A_2B)^h$ systems, with an exception for $O/(Y_2C)^h$, are structurally unstable [Fig.4 Appendix]

In the sequence, we performed a search for dynamically and structurally stable $O/A_2B$ by changing the in-plane angle ($\gamma$) formed by the lattice vectors $a$ and $b$ [Figs.2(b1)]. Such a structural search was guided by the existence of stochiometrically equivalent $AO$ and $AN$ tetragonal (t) bulk (cubic) parents, namely $CaO$, $SrO$, and $BaO$[22,25] and $CaN$, $SrN$, and $BaN$[25]. Our findings, for $B=N$, show that indeed the full oxidized hexagonal geometry [Fig.2(b)] at $\gamma = 120^\circ$, corresponds to a metastable configuration characterized by a barrierless ($h \rightarrow t$) structural transition [Fig.3(b)] to a tetragonal ($\gamma = 90^\circ$) $AO/AN$ layered phase, $(AOAN)^t$ [Fig.2(b2)].

The energy gain upon such a $h \rightarrow t$ transition is given by the total energy difference between the two structural phases, $\Delta E^{h \rightarrow t} = E^h - E^t$. Our results of $\Delta E^{h \rightarrow t}$, presented in Table II, indicate that the tetragonal phase, $(AOAB)^t$, is energetically more favorable for all $O/A_2B$ systems. On the other hand, phonon spectra calculations revealed that the $(AOAB)^t$ systems are dynamically stable only for $B=N$ [(AOAN)$^t$ and (YOYC)$^t$. As shown in Fig.4(b1), imaginary frequencies present in the hexagonal $O/A_2N$ structures were suppressed in the tetragonal ($CaOCaN)^t$, ($SrOStN)^t$, and ($BaOBaN)^t$ systems, Figs.4(b5)-(b7). In addition, the structural stability of $(AOAN)^t$ and (YOYC)$^t$ was confirmed by MD simulations. We found that the tetragonal structure was preserved at a temperature of 300 K during the 15 ps of MD.

**FIG. 3.** (a) Formation energy of the oxidized $O/A_2B$ electrone, and (b) the total energy difference as a function of the in-plane angle ($\gamma$) formed by the lattice vectors $a$ and $b$ [Figs.2(b1)] of the fully oxidized electrenes, $O/A_2B$, with $\gamma = 120^\circ$ for the hexagonal (h) phase and $90^\circ$ for the tetragonal (t) phase.
TABLE II. Formation energy ($E_f$ in eV/O-atom), for $n=1$, of the hexagonal and tetragonal oxidized single layer (O/$A_2B$), and bilayer [O/($A_2B$)$_2$/O] electrenes, and the total energy gain upon hexagonal $\rightarrow$ tetragonal structural transition ($\Delta E^{h\rightarrow t}$ in eV/O-atom). The lattice constant (a) and the vertical distances (d and h in Fig. 2) are in Å. The lattice constant of the pristine hexagonal $A_2B$ electrene are within parentheses.

| O/$A_2B$ | hexagonal $\rightarrow$ tetragonal |
|----------|----------------------------------|
| $A_2B$   | $E_f$   | a | $\Delta E^{h\rightarrow t}$ | a | h |
| Ba$_2$As | $-1.79$ | 4.07 (4.65) | $-0.51$ | 3.75 | 2.80 |
| Ba$_2$P  | $-2.08$ | 4.42 (4.64) | $-0.63$ | 4.18 | 2.64 |
| Sr$_2$P  | $-2.21$ | 4.33 (4.43) | $-0.76$ | 3.92 | 2.50 |
| Y$_2$C   | $-5.46$ | 3.64 (3.50) | $-0.20$ | 3.40 | 2.58 |
| Ca$_2$N  | $-2.99$ | 3.85 (3.61) | $-0.90$ | 3.36 | 2.40 |
| Sr$_2$N  | $-3.00$ | 4.11 (3.85) | $-0.80$ | 3.59 | 2.54 |
| Ba$_2$N  | $-3.08$ | 4.35 (4.00) | $-0.57$ | 3.83 | 2.61 |
| O/($A_2B$)$_2$/O | hexagonal $\rightarrow$ tetragonal |
| $A_2B$   | $E_f$   | a | $\Delta E^{h\rightarrow t}$ | a | d |
| Ca$_2$N  | $-3.04$ | 3.92 | $-1.68$ | 3.40 | 2.57 |
| Sr$_2$N  | $-3.07$ | 4.19 | $-1.27$ | 3.63 | 2.85 |
| Ba$_2$N  | $-3.02$ | 4.33 | $-1.10$ | 3.86 | 3.22 |

We next have examined the surface oxidation of bilayer electrenes [(A$_2B$)$_2$] with $B=N$, O/($A_2N$)$_2$/O [Fig. 2(c)]. Similarly to what we have found in the single layer systems, the O/($A_2N$)$_2$/O structures are (i) energetically stable ($E_f < 0$ in Table II), and also (ii) present exothermic h $\rightarrow$ t structural transitions, with $\Delta E^{h\rightarrow t}$ almost twice compared with those of their O/$A_2B$ counterparts. Further phonon spectra calculations, and molecular dynamics simulations of O/($A_2N$)$_2$/O, Figs. 5 and 12 (Appendix), respectively, show that the tetragonal ($AO(AN)_2AO$) systems are dynamically and structurally stable. We found no imaginary frequencies in the tetragonal phases, Fig. 5(b), and the MD simulations reveal that the atomic structures of the ($AO(AN)_2AO$)$_t$ systems have been preserved [Fig. 12(b), Appendix], whereas the ones of the hexagonal phase are no longer maintained after 15 ps of simulation, Fig. 12(a) (Appendix).

At the equilibrium geometry, the tetragonal phase of the oxidized electrenes is characterized by a layered structure indicated as AO and AN in Fig. 2(c2), where the inner AN bilayer structure, with interlayer bond distance $d$ (indicated in Table II), is shielded by oxidized AO sheets, ($AO(AN)_2AO$)$_t$. As expected, such geometries somewhat mimic the ones of their (stoichiometrically equivalent and energetically stable) AO and AN bulk cubic parents, namely CaO, SrO, and BaO [56,57,58].
FIG. 6. XANES spectra of pristine single layer Ca$_2$N electrene for the polarization vector (a1) perpendicular, $\vec{\epsilon}^\perp$, and (b1) parallel, $\vec{\epsilon}^\parallel$, to the electrene surface. XANES spectra of O/Ca$_2$N for $\vec{\epsilon}^\perp$ (e1), $\vec{\epsilon}^\parallel$ (d1), and the density of states of (CaOCaN)$_2^\parallel$ projected on the N-2$p_z$ (e2), Ca-4$p_x$ (e3), N-2$p_{x,y}$ (d2), and Ca-4$p_{x,y}$ (d3) orbitals. XANES spectra of O/(Ca$_2$N)$_2$/O, for $\vec{\epsilon}^\perp$ (e1), $\vec{\epsilon}^\parallel$ (f1), and the density of states of (CaO(CaN)$_2$CaO) projected on the N-2$p_z$ (e2), Ca-4$p_z$ (e3), N-2$p_{x,y}$ (f2), and Ca-4$p_{x,y}$ (f3) orbitals. The XANES spectra of the tetragonal (hexagonal) phase are indicated by solid (dashed) lines. Spin-down and spin-up channels are indicated by purple and black solid lines.

we will present our results for $A = \text{Ca}$, namely Ca$_2$N, O/Ca$_2$N and O/(Ca$_2$N)$_2$/O; the other systems, with $A = \text{Sr}$ and Ba, present quite similar spectra and interpretations.

Let us start with the single layer pristine Ca$_2$N electrene. In Figs. 6(a1) and (b1) we present the absorption spectra for polarization vector perpendicular ($\vec{\epsilon}^\perp$) and parallel ($\vec{\epsilon}^\parallel$) to the surface, respectively. Based on the analysis of orbital projected density of states (DOS, not shown), we found that the edge and near-edge absorption features are mostly dictated by the electronic transition from the N-1$s$ core electron to the unoccupied N-2$p_{x,y}$ and N-2$p_z$ orbitals, for $\vec{\epsilon}^\perp$ and $\vec{\epsilon}^\parallel$, respectively. Due to the electronic confinement along the normal direction with respect to the electrene surface, the broadening of the absorption lines from the Fermi energy ($E_F$) up to $\sim E_F + 6$ eV for $\vec{\epsilon}^\perp$ is slightly smaller compared with that for $\vec{\epsilon}^\parallel$. Meanwhile, in the oxidized systems the energy broadenings for $\vec{\epsilon}^\perp$ (Figs. 6(d1) and (f1)) are significantly larger compared with those for $\vec{\epsilon}^\parallel$, Figs. 6(c1)-(e1), indicating a reduction (increase) of the electronic confinement along the parallel (perpendicular) direction with respect to the surface plane; which is, in its essence, a consequence of the formation of planar Ca–N and Ca–O layered structures upon oxidation [Figs. 2 and insets of Figs. 6(c1) and (d1)]. Further identification of the oxidized structures can be done by comparing the energy position of the absorption edges (AEs). For instance, comparing the AEs of the tetragonal phases, indicated by solid lines in Figs. 6(a1) and (c1), we find that the former lies near the Fermi level, while in the latter the AE starts at about $E_F + 4$ eV, thus, indicating an increase of the N-1$s$ binding energy (BE) in the oxidized systems. Indeed, based on the Löwdin charge population analysis, we found that the total charge of the nitrogen atoms in the oxidized O/Ca$_2$N [O/(Ca$_2$N)$_2$/O] electrenes reduces by 0.34 [0.42] e/N-atom when compared with the one of pristine Ca$_2$N. Thus, we can infer that the increase of the N-1$s$ BE is due to the reduction of the electronic screening at the N nucleus in the oxidized Ca$_2$N.

Next, we examine the nitrogen K-edge XANES spectra of the oxidized tetragonal systems in light of the projected density of states. The projections on the N-2$p_z$ and Ca-4$p_z$ orbitals, Figs. 6(c2) and (c3), indicate that the absorption features 2, 3, and 4 in Fig. 6(c1) are ruled by the electronic transitions to the lowest unoccupied N-2$p_z$ (major contribution) hybridized with the nearest neighbor Ca-4$p_z$ orbitals (minor contribution). It is worth noting that the features 2 and 3 (for $\vec{\epsilon}^\perp$) of the tetragonal phase are also present in the absorption spectra of the hexagonal phase [2’ and 3’ (dashed lines) in Fig. 6(c1)]. However they are shifted by $\sim 1$ eV toward lower energies when compared with their counterparts 2 and 3, thus we can infer that the BE of the N-1$s$ core electrons in the tetragonal phase is larger compared with the one of the hexagonal phase. As discussed above, such an increase of the BE is supported by the reduction of the total charge of the nitrogen atoms (by 0.01 e/N-atom) in the tetrago-
nal O/Ca$_2$N in comparison with that of hexagonal one. Similarly for O/(Ca$_2$N)$_2$/O, as shown Figs. 6(d)-(e), (i) the XANES spectra ($\tilde{\varepsilon}^\perp$) of the tetragonal phase is ruled by the unoccupied N-2$p_x$ states (major role) hybridized with the 4$p_z$ orbitals (minor role) of the Ca atoms embedded in the CaO sheets; and (ii) the edge features of the tetragonal and hexagonal phases indicate that the BE of N-1s core electrons of the former is larger by about 1 eV compared with that of the latter, in agreement with the lower total charge (by 0.04 $\varepsilon$/N-atom) of the N atoms in the tetragonal phase.

In Figs. 7(d) and (f) we present the XANES spectra for a polarization vector parallel to the O/Ca$_2$N and O/(Ca$_2$N)$_2$/O layers, $\tilde{\varepsilon}^\parallel$, and the DOS projected on the N-2$p_{x,y}$ and Ca-4$p_{x,y}$ orbitals of the tetragonal phase. Compared with the absorption spectra with the polarization vector normal to the surface, $\tilde{\varepsilon}^\perp$, we found that the pre-edge absorption (feature 1), attributed to the hybridizations of the partially occupied spin-down N-2$p_{x,y}$ and Ca-4$p_{x,y}$ orbitals, becomes more intense for $\tilde{\varepsilon}^\parallel$. In fact, such a pre-edge absorption spectrum can be considered as a signature of the formation of half-metallic channels, along the CaN layers, which will be discussed below. In the sequence, it is noticeable the well defined absorption spectrum 2', present in the hexagonal phase, has been dimmed in the tetragonal structure, thus suggesting that the structural differences between the tetragonal and hexagonal phases are better captured by looking at the in-plane edge absorption features.

3. Electronic and Magnetic Properties

The electronic band structures of $A_2B$ electronegative systems, with $A =$ Ca, Sr, Ba, and $B =$ N are characterized by parabolic metallic bands, giving rise to nearly free electron (NFE) states localized on the electrone's surface and between the stacked layers. On the other hand, upon the formation of AO oxidized layers these NFE states become unoccupied, and we observe the emergence of magnetic moments in the $A$ layers. Here, we will examine the magnetic and electronic properties of (AOAN)$^t$ and (AO(AN)$_2$AO)$^t$.

Based on the nominal oxidation states and the electronegativities of the involved atoms, we can infer the emergence of a magnetic moment in the oxidized systems. There is a net charge transfer of 2 electrons from each (less electronegative) $A$ atoms to the (more electronegative) O and N atoms, resulting in $A^{2+}$, $O^{2-}$ and $N^{2-}$ oxidation states, Fig. 7(a). The ground state configuration is characterized by an OA (oxidized) layer with closed $p$ shells parallel to a $A$ layer with the N-2$p$ orbitals partially occupied, Fig. 7(b). Similarly, in the bilayer system, (AO(AN)$_2$AO)$^t$ [Fig. 7(c)], we find AN layers with partially occupied N-2$p$ orbitals sandwiched by OA (edge) layers with closed $p$ shells. According to the Hund’s rule, each N atom will carry a net magnetic moment of 1 $\mu_B$. Indeed, within the GGA-PBE approach, we found a net magnetic moment of about 0.8 $\mu_B$ mostly localized on the nitrogen atoms. The projected electronic density of states (PDOS) on the N-2$p$ orbitals of (AOAN)$^t$ and (AO(AN)$_2$AO)$^t$, Figs. 8(a) and (b), reveal that the partial occupation of planar N-2$p_{x,y}$ orbitals brings the major contribution to the polarization of the N atoms.

Total energy comparisons between the magnetic and non-magnetic phases, $\Delta E^{\text{mag}} = E^{\text{mag}} - E^{\text{non-mag}}$, support the energetic preference for the spin-polarized systems, $\Delta E^{\text{mag}} < 0$ in Table III. The strength of the magnetic interactions between the nitrogen atoms was examined by comparing the total energies of the ferromagnetic (FM) and antiferromagnetic (AFM) phases as shown in Figs. 7(d) and (e) for the intralayer and interlayer magnetic couplings, respectively. We have considered intralayer interactions ($\Delta E^{\text{FM-AFM}}_{\text{ intra}}$) between the N atoms in the same AN layer [Fig. 7(d)], and interlayer interactions ($\Delta E^{\text{FM-AFM}}_{\text{ inter}}$) between the N atoms lying in different layers [Fig. 7(e)] in the case of (AO(AN)$_2$AO)$^t$. Our results, summarized in Table III, reveal the both systems, (AOAN)$^t$ and (AO(AN)$_2$AO)$^t$, present an energetic preference for the intralayer and interlayer FM coupling between the N atoms. It is noticeable that (i) (CaO(CaN)$_2$CaO)$^t$ presents the largest interlayer FM interaction, $\Delta E^{\text{FM-AFM}}_{\text{ inter}} < -36.5$ meV/N-atom, when compared with the other (AO(AN)$_2$AO)$^t$ systems, leading to (ii) a strengthening of the intralayer FM coupling, namely $\Delta E^{\text{FM-AFM}}_{\text{ intra}} < -8.5 < -22.8$ meV/N-atom. In contrast, (i) we found (relatively)
lower values of $\Delta E_{\text{FM-AFM}}$ for (SrO(SrN)$_2$SrO)$_t$ and (BaO(BaN)$_2$BaO)$_t$ which can be due to the larger interlayer distance ($d$) as indicated in Fig. 8(b2) and Table II, and the more localized feature of the spin-polarized states normal to the stacking direction (c). In Fig. 7(f) we present the spin-density distribution in $(AO(AN)_2AO)_t$, with $A=$Ca, Sr, and Ba where we confirm the localization of the net magnetic moment on the nitrogen atoms. It is noticeable that the projection of the DOS on the N-2p orbitals [Fig. 8(b1)] compared with those of the other oxidized bilayer electrones, Figs. 8(b2) and (b3).

The energetic preference for the FM phase can be attributed to super-exchange interactions between the N$^{2-}$ anions mediated by $A^{2+}$ cations. In this sense, the FM coupling will be favored due to the electron delocalization along the $N^2--A^{2+}--N^{2-}$ bonds, thus lowering the kinetic energy of the system, as schematically shown in Figs. 7(b) and (c) for the intralayer and interlayer couplings, respectively. Further support to the FM coupling between the N$^{2-}$ anions, mediated by super-exchange interactions, can be found in the Goodenough-Kanamori rule, since the N$^{2-}--A^{2+}--N^{2-}$ bonds are characterized by bond angles of $90^\circ$.

The electronic band structures of $(AOAN)_t$ and $(AO(AN)_2AO)_t$, Fig. 9, indicate they are half-metals. In Figs. 9(a1)–(c1) and (d1)–(f1), the metallic channels are characterized by spin-down (purple-lines), whereas the spin-up energy bands (black-lines) are semiconductor with the valence band maximum (VBM) lying at about 0.2 eV below the Fermi level ($E_{\text{VBM}} \approx E_F - 0.2$ eV) for $A=$Ca, while for $A=$Sr and Ba we find $E_{\text{VBM}} \approx E_F - 0.5$ eV. The lowest unoccupied states are spin degenerated, lying between 1 and 2 eV above $E_F$, and characterized by NFE parabolic bands localized on the oxidized surface (OA) [insets of Figs. 9(a1)–(c1) and (d1)–(f1)]. Further real space projections of the electronic states near the Fermi level, $E_F \pm 0.1$ eV, reveal that the half-metallic bands are mostly ruled by in-plane N-2p orbitals localized in the AN layers of $(AOAN)_t$, Figs. 9(a2)–(c2). Similarly, in the bilayer systems the half-metallic bands

| $A$ | $\Delta E_{\text{mag}}$ (meV) | $\Delta E_{\text{FM-AMF intra}}$ (meV) | $\Delta E_{\text{FM-AMF inter}}$ (meV) |
|-----|-----------------|-----------------|-----------------|
| Ca  | -67             | -85             |                 |
| Sr  | -135            | -18.7           | -               |
| Ba  | -92             | -1.9            | -               |
| (CaOCaN)$_t$ | -83 | -22.8 | 36.5 |
| (SrOSrN)$_t$ | -127 | -12.9 | 1.0  |
| (BaOBaN)$_t$ | -93  | -4.4  | 0.5   |

Table III. Total energy differences (in meV/N-atom) between non-magnetic and magnetic phases, $\Delta E_{\text{mag}} = E_{\text{mag}} - E_{\text{non-mag}}$, and between the FM and AFM phases for intralayer ($\Delta E_{\text{FM-AMF intra}}$), and interlayer interactions ($\Delta E_{\text{FM-AMF inter}}$).
spread out through the AN layers. It is worth noting that in (AO(AN)$_2$AO)$_t$, these half-metallic channels are sandwiched by the oxidized AO sheets [Figs. 9(d2)–(f2)]. These oxidized sheets may act as a shield, protecting the half-metallic channels against the environment conditions, which is a quite appealing property for development of spintronic devices based on 2D platforms.

In order to provide a quantitative picture of the emergence of spin-polarized electronic current in the oxidized electrenes, we calculate the electronic transmission probability, $T(E)$, and the electronic current $I(V)$ of the (AOAN)$_t$ and (AO(AN)$_2$AO)$_t$ systems. In Fig. 10(a) we present the simulation setup used for the electronic transport calculations along the b direction, namely two (left and right) electrodes composed by semi-infinite oxidized electrenes, both connected to a (central) scattering region. Our results of $T(E)$, summarized in Figs. 10(b) and (c), reveal that near the Fermi level ($|E_F|\leq 0.1$ eV) the transmission probability is mediated by the spin-down channels, in consonance with the electronic band structure results [Fig. 9]. The transmission channels lie on the inner AN layers, mostly ruled by the in-plane hybridizations between the spin-down N-2p orbitals (N-2p$_{x,y}$) with the nearest neighbor A atoms. For $A=Ca$ we found larger values of $T(E)$ [Figs. 10(b1) and (c1)], and net electronic current [Figs. 10(d1) and (e1)] when compared with the other (AOAN)$_t$ and (AO(AN)$_2$AO)$_t$ systems. In contrast, although the more localized character of the in-plane N-2p$_{x,y}$ orbitals for $A=Ba$ [Figs. 9(b2) and (f2)] compared with the ones obtained for $A=Sc$, Figs. 9(b2) and (e2), we found nearly the same values of transmission probability, and electronic current for low bias voltage [Figs. 10(d2)–(e2) and (d3)–(e3)]. We have also calculated the transmission probability and the electronic current along the bisector direction between a and b, where we found practically the same values of $T(E)$ and $I(V)$ near the Fermi level. Thus, suggesting that the electronic transport through the inner AN layers, at low bias limit, does not present significant directional anisotropy as predicted for other 2D systems.

IV. SUMMARY AND CONCLUSIONS

By means of first-principles DFT calculations, we have performed a theoretical study of the full oxidized 2D single layer, O/A$_2$B, and bilayer, O/(A$_2$B)$_2$/O, electrenes, with $A=Ca$, Ca, Sr, Y, and $B=As$, N, P, C. We found that O/A$_2$B and O/(A$_2$B)$_2$/O systems with $A=Ca$, Sr, Ba, and $B=N$ become stable upon an hexagonal $\rightarrow$ tetragonal structural transition, resulting in layered tetragonal systems, (AOAN)$_t$ and (AO(AN)$_2$AO)$_t$. Further characterizations, through simulations of XANES spectroscopy, allowed us to identify key aspects of the absorption spectra and their correlation with the structural properties the oxidized systems. We found the emergence of a ferromagnetic phase in the oxidized tetragonal structures, with the net magnetic moment mostly ruled by the planar N-2p$_{x,y}$ orbitals. Meanwhile, electronic structure calculations reveal the formation of half-metallic bands spreading out through the AN layers, with nearly negligible contribution from the oxidized AO sheets. The emergence of spin-polarized transmission channels was confirmed through the electronic transport calculations based on the Landauer-Büttiker formalism. These results reveal that the oxidized (AOAN)$_t$ and (AO(AN)$_2$AO)$_t$ systems are quite interesting platforms for spin-polarized transport on 2D
systems, characterized spin-polarized metallic channels shielded by oxide layers. For instance, \((AO(AN)_2AO)\) can be viewed as a core-shell 2D platform with half-metallic channels lying on the \((AN)_2\) layers (core) protected against the environment conditions by the oxidized \(AO\) sheets (shell).

ACKNOWLEDGMENTS

The authors acknowledge financial support from the Brazilian agencies CNPq, CAPES, FAPEMIG, and INCT-Nanomateriais de Carbono, and the CENAPAD-SP and Laboratório Nacional de Computação Científica (LNCC-SCAFMat2) for computer time.

V. APPENDIX

In Figs. [11] and [12] we present our results of MD simulation of oxidized single layer electrone, \(O/(A_2B, \text{ with } A=\text{A}=\text{Ca, Sr, Ba, Y, and } B=\text{N, P, As, C, and bilayer (O/(A_2N)_2/O) electrone, with } A=\text{Ca, Sr and Ba. We have considered a total simulation time of } 15 \text{ ps, and time steps of } 1 \text{ fs. Inset we present the structural model after } 15 \text{ ps of simulation at } 300 \text{ K.}

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, “Electric field effect in atomically thin carbon films,” Science, vol. 306, no. 5696, pp. 666–669, 2004.
[2] C. L. Kane and E. J. Mele, “Z2 topological order and the quantum spin hall effect,” Phys. Rev. Lett., vol. 95, p. 146802, 2005.
[3] C. Weeks, J. Hu, J. Alicea, M. Franz, and R. Wu, “Engineering a robust quantum spin hall state in graphene via adatom deposition,” Physical Review X, vol. 1, no. 2, p. 021001, 2011.
[4] C. M. Acosta, M. P. Lima, R. Miwa, A. J. da Silva, and A. Fazzio, “Topological phases in triangular lattices of ru adsorbed on graphene: ab initio calculations,” Physical Review B, vol. 89, no. 15, p. 155438, 2014.
[5] T. Song, Z. Fei, M. Yankowitz, Z. Lin, Q. Jiang, K. Hwangbo, Q. Zhang, B. Sun, T. Taniguchi, K. Watanabe, et al., “Switching 2d magnetic states via pressure tuning of layer stacking,” Nature materials, vol. 18, no. 12, pp. 1298–1302, 2019.
[6] T. Li, S. Jiang, N. Sivadas, Z. Wang, Y. Xu, D. Weber, J. E. Goldenberger, K. Watanabe, T. Taniguchi, C. J. Fennie, et al., “Pressure-controlled interlayer magnetism in atomically thin cri 3,” Nature materials, vol. 18, no. 12, pp. 1303–1308, 2019.
[7] E. S. Morell, A. León, R. H. Miwa, and P. Vargas, “Control of magnetism in bilayer cri3 by an external electric field,” 2D Materials, vol. 6, no. 2, p. 025020, 2019.
[8] P. d. A. Dominike, I. S. de Oliveira, J. B. Oliveira, W. L. Scopel, and R. H. Miwa, “Magnetic switch and electronic properties in chromium-terminated two-dimensional gpe2,” Physical Review Materials, vol. 5, no. 5, p. 054002, 2021.
[9] B. Radisavljevic, A. Radenovic, J. Brivio, i. v. Giaconetti, and A. Kis, “Single-layer mo2 transistors,” Nature Nanotechnology, vol. 6, no. 3, pp. 147–150, 2011.
[10] Y. Tong, Y. Guo, K. Mu, H. Shan, J. Dai, Y. Liu, Z. Sun, A. Zhao, X. C. Zeng, C. Wu, et al., “Half-metallic behavior in 2d transition metal dichalcogenides nanosheets by dual-native-defects engineering,” Advanced Materials, vol. 29, no. 40, p. 1703132, 2017.
[11] V. V. Kulish and W. Huang, “Single-layer metal halides mx 2 (x=cl, br, i): stability and tunable magnetism from first principles and monte carlo simulations,” Journal of Materials Chemistry C, vol. 5, no. 34, pp. 8734–8741, 2017.
[12] G. Gökoglu and E. Aktürk, “Half metallicity and pressure-induced electronic structure of monolayer fex2 (x= s, so),” Materials Research Express, vol. 4, no. 11, p. 116305, 2017.
[13] Y. Feng, X. Wu, J. Han, and G. Gao, “Robust half-metallicities and perfect spin transport properties in 2d transition metal dichlorides,” Journal of Materials Chemistry C, vol. 6, no. 15, pp. 4087–4094, 2018.
[14] B. Wang, Q. Wu, Y. Zhang, Y. Guo, X. Zhang, Q. Zhou, S. Dong, and J. Wang, “High curie-temperature intrinsic ferromagnetism and hole doping-induced half-metallicity in two-dimensional scandium chloride monolayers,” Nanoscale horizons, vol. 3, no. 5, pp. 551–555, 2018.
[15] N. Mounet, M. Gibertini, P. Schwaller, D. Campi, A. Merkys, A. Marruzzo, T. Sohier, I. E. Castelli, A. Cepellotti, G. Pizzi, et al., “Two-dimensional materials from high-throughput computational exfoliation of experimentally known compounds,” Nature Nanotechnology, vol. 13, no. 3, pp. 246–252, 2018.
[16] K. Lee, S. W. Kim, Y. Toda, S. Matsuishi, and H. Hosono, “Dicalcium nitride as a two-dimensional electrode with an anionic electron layer,” Nature, vol. 494, no. 7437, pp. 336–340, 2013.
[17] D. L. Druffel, A. H. Woomer, K. L. Kuntz, J. T. Pawlik, and S. C. Warren, “Electrons on the surface of 2d materials: from layered electrides to 2d electrone,” Journal of Materials Chemistry C, vol. 5, no. 43, pp. 11196–11213, 2017.
[18] S. Liu, W. Li, S. W. Kim, and J.-H. Choi, “Decisive role of interlayer ionic couplings for the electronic properties of two-dimensional layered electrides,” The Journal of Physical Chemistry C, vol. 124, no. 2, p. 1398, 2020.
[19] J. S. Oh, C.-J. Kang, Y. J. Kim, S. Sinn, M. Han, Y. J. Chang, B.-G. Park, S. W. Kim, B. I. Min, H.-D. Kim, et al., “Evidence for anionic excess electrons in a quasi-two-dimensional ca2n electrode by angle-resolved photoemission spectroscopy,” Journal of the American Chemical Society, vol. 138, no. 8, pp. 2496–2499, 2016.
[20] D. L. Druffel, K. L. Kuntz, A. H. Woomer, F. M. Alcorn, J. Hu, C. L. Donley, and S. C. Warren, “Experimental demonstration of an electrode as a 2d material,” Journal of the American Chemical Society, vol. 138, no. 49, pp. 16089–16094, 2016.
FIG. 11. Total energy fluctuation of hexagonal (a) and tetragonal (b) O/A$_2$B oxidized electrenes, as a function of the time step (1 fs). Insets, strurfical model after 15 ps of molecular dynamics simulation at 300 K.

FIG. 12. Total energy fluctuation of hexagonal (a) and tetragonal (b) O/(A$_2$N)$_2$/O oxidized electrenes, as a function of the time step (1 fs). Insets, strurfical model after 15 ps of molecular dynamics simulation at 300 K.

[21] N. E. Brese and M. O’Keefe, “Synthesis, crystal structure, and physical properties of sr2n,” Journal of Solid State Chemistry, vol. 87, no. 1, pp. 134–140, 1990.
[22] X. Zhang, Z. Xiao, H. Lei, Y. Toda, S. Matsuishi, T. Kamiya, S. Ueda, and H. Hosono, “Two-dimensional transition-metal electride y2c,” Chemistry of Materials, vol. 26, no. 22, pp. 6638–6643, 2014.
[23] T. Tada, S. Takemoto, S. Matsuishi, and H. Hosono, “High-throughput ab initio screening for two-dimensional electride materials,” Inorganic chemistry, vol. 53, no. 19, pp. 10347–10358, 2014.

[24] T. Inoshita, S. Jeong, N. Hamada, and H. Hosono, “Exploration for two-dimensional electrides via database screening and ab initio calculation,” Physical Review X, vol. 4, no. 3, p. 031023, 2014.
[25] S. Zhang, M. Kang, H. Huang, W. Jiang, X. Ni, L. Kang, S. Zhang, H. Xu, Z. Liu, and F. Liu, “Kagome bands disguised in a coloring-triangle lattice,” Physical Review B, vol. 99, no. 10, p. 100404, 2019.
[26] S. Zhao, Z. Li, and J. Yang, “Obtaining two-dimensional electron gas in free space without resorting to electron doping: an electride based design,” Journal of the American Chemical Society, vol. 136, no. 38, pp. 13313–13318, 2014.
[27] X. Zeng, S. Zhao, Z. Li, and J. Yang, “Electron-phonon interaction in a ca 2 n monolayer: Intrinsic mobility of electrene,” Physical Review B, vol. 98, no. 15, p. 155443, 2018.
[28] L. Liu and H. L. Zhuang, “High-throughput functionalization of single-layer electride ca2n,” Mater. Res. Express, vol. 5, p. 076306, 2018.
[29] X.-L. Qiu, J.-F. Zhang, Z.-Y. Lu, and K. Liu, “Manipulating the electronic and magnetic properties of monolayer electride ca2n by hydrogenation,” The Journal of Physical Chemistry C, vol. 123, no. 40, pp. 24698–24704, 2019.
[30] C.-W. Wu and D.-X. Yao, “Intriguing p-orbital magnetic semiconductors and carrier induced half-metallicity in surface oxygen-functionalized two-dimensional x2n (x= ca, sr) crystals,” Journal of Magnetism and Magnetic Materials, vol. 493, p. 165727, 2020.
[31] P. Hohenberg and W. Kohn, “Inhomogeneous electron gas,” Physical review, vol. 136, no. 3B, p. B864, 1964.
2013.

[66] J. B. Goodenough, “Theory of the role of covalence in the perovskite-type manganites [la, m (ii)] mn o 3,” Physical Review, vol. 100, no. 2, p. 564, 1955.

[67] J. Kanamori, “Crystal distortion in magnetic compounds,” Journal of Applied Physics, vol. 31, no. 5, pp. S14–S23, 1960.

[68] J. E. Padiha, R. H. Miwa, and A. Fazzio, “Directional dependence of the electronic and transport properties of 2d borophene and borophane,” Physical Chemistry Chemical Physics, vol. 18, no. 36, pp. 25491–25496, 2016.