Computational prediction of a two-dimensional semiconductor SnO₂ with negative Poisson's ratio and tunable magnetism by doping

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Based on first-principles calculations, we predict a stable two-dimensional semiconductor, namely tin dioxide SnO₂. By investigating its dynamical, thermal, and mechanical properties, we find that SnO₂ monolayer is an auxetic material with a large in-plane negative Poisson's ratio. Furthermore, our results show that SnO₂ is an indirect-gap semiconductor with a band gap in the region of 3.7 eV and an extremely high electron mobility, $\sim 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Interestingly, the band structure of SnO₂ presents double Mexican-hat-like band edges in the valence bands near the Fermi level. Due to such a unique band feature, a ferromagnetic phase transition takes place with a half-metallic ground state that can be induced by hole doping within a very wide concentration range. Such a magnetic phase can be well explained by the Stoner mechanism. A peculiar feature of the magnetic state is the presence of large magnetocrystalline anisotropy that can switch from in-plane to out-of-plane upon hole doping. Hence, SnO₂ monolayer can be tuned to be either an *XY* magnet or an Ising one, with a magnetic critical temperature above room temperature at proper hole concentrations. These findings demonstrate that the predicted phase of SnO₂ is a rare example of *p*-type magnetism and a possible candidate for spintronic applications.

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I. INTRODUCTION

Since the successful isolation of graphene, atom-thick twodimensional (2D) compounds have attracted a tremendous amount of interest due to their unique physical and chemical properties. In particular, their quantum confinement made them a novel material platform for applications, different from bulk materials [1–5]. In the past decade, in order to overcome the absence of a band gap in graphene, much effort has been spent and advances have been made in exploring various 2D alternatives [6–8]. Among these, phosphorene and transition metal dichalcogenides (TMDCs) have drawn substantial attention due to their appropriate band gap and outstanding physical properties [9–12]. These are now considered as promising candidates for applications in (opto)electronics, photovoltaics, and spintronics [8,13].

One of the drawbacks of phosphorene and TMDCs for applications is the general high sensitivity to the environment and the tendency toward oxidation, a fact that often leads to changes in their structural, chemical, and physical properties

*xhzheng@theory.issp.ac.cn *sanvitos@tcd.ie [14-16]. In contrast, 2D metal oxides have excellent chemical stability and they are relatively easy to fabricate, thus they appear more promising for large-scale production and use [17-20]. In particular, tin oxides form a class of metal oxides of great interest. Zhang et al. have experimentally reported that tin monoxide, SnO, nanosheet anodes exhibit a high specific capacity and stable cyclability in sodium ion batteries [20]. Seixas et al. have theoretically found that 2D α -SnO presents Mexican-hat-like band edges and that a multiferroic phase can be realized by hole doping [21]. Including the Sn +2 and +4 nominal oxidation states, in addition to SnO, also SnO₂ exists. In its bulk form, SnO₂ is an important *n*-type oxide semiconductor with a large band gap of 3.6 eV. SnO₂ is widely used as a transparent conductor and an optically passive component in optoelectronic devices due to its superior optical transparency [22,23]. Additional strong interest in this material is motivated by the claims of room-temperature ferromagnetism and a giant magnetic moment achievable by doping with 3d orbital transition metal impurities [24-26]. Theoretical and experimental studies of SnO₂ have also demonstrated that ferromagnetism can only be observed in thin films but not in bulk samples, when oxygen vacancies are introduced [27-30].

Despite the evidence discussed above for interesting properties of nanoscaled Sn-O compounds, a systematic study of possible tin oxide phases in two dimensions is still missing. In particular, given the claims of magnetism in SnO₂ thin films, it is worth investigating whether a stable SnO₂ 2D phase can be synthesized and if magnetism can be induced. Hints that this may be the case are provided by recent studies of 2D group-IV oxides. Gao et al., for instance, have predicted several novel and stable 2D silica phases, which hold great promise for nanomechanic and nanoelectronic applications [31]. In particular, δ -SiO₂ has an auxetic behavior with an in-plane negative Poisson's ratio. The crystal structures of δ -SiO₂ monolayers are similar to that of the layers that one can produce by periodically interrupting the basic Si-2O framework along the (001) direction of rutile-type SiO₂. As such there is an expectation that 2D SiO₂ monolayer can be synthesized by chemical vapor deposition. On the strength of this result, it appears natural and interesting to investigate whether the 2D δ -phase of SnO₂ is dynamically stable and what are its potential properties.

In this paper, first-principles calculations are used to predict a 2D tin dioxide monolayer phase. In particular, we investigate the stability of SnO_2 by computing its phonon dispersion and by performing molecular dynamics (MD) simulations. Furthermore, we calculate its mechanical and electronic properties in its pristine form and the magnetic properties as a function of hole doping. We have found that such a 2D SnO₂ phase is an indirect-gap semiconductor with a double Mexican-hat-like band edge (MHLBE) in the valence band. The compound exhibits an in-plane negative Poisson's ratio and high electron mobility. Moreover, it becomes a half-metal upon hole doping with a ferromagnetic transition temperature estimated to be above room temperature for a hole concentration of about 1.01×10^{15} cm⁻². Interestingly, the magnetic anisotropy compares well with that of standard magnetic transition metals, and it can be tuned from in-plane to out-of-plane upon hole doping. As such, monolayer SnO₂ can be prepared as either an XY or an Ising magnet.

II. COMPUTATIONAL DETAILS

Density functional theory (DFT) calculations are performed with the projector augmented wave method as implemented in the Vienna Ab-initio Simulation Package (VASP) [32,33]. A plane-wave cutoff energy of 600 eV is used for defining the basis-set, while we adopt the Perdew-Burke-Ernzerhof (PBE) parametrization of the exchange and correlation functional in the generalized gradient approximation (GGA) [34]. The GGA is used throughout unless otherwise indicated. A vacuum region of about 16 Å along the out-of-plane direction is applied to eliminate the interaction between adjacent layers due to the periodic boundary conditions. The energy convergence tolerance for the electronic structure calculations is set to 10^{-6} eV, and the atomic positions are fully relaxed until the Hellmann-Feynman forces on each atom are smaller than 1 meV/Å. The k-points in reciprocal space are sampled using a Γ-centered Monkhorst-Pack scheme with a $12 \times 12 \times 1$ grid for structural relaxation and with a $15 \times 15 \times 1$ grid for the electronic structure calculations.

The phonon dispersion is computed with the PHONOPY code [35] based on the density functional perturbation theory method implemented in VASP. In addition, high-temperature

ab initio MD simulations are performed to confirm the SnO₂ thermal stability. The constant-temperature constant-volume (*NVT*) ensemble is considered and the MD simulations are run for 6 ps with a time step of 1 fs. Since the PBE functional fails to describe correctly the energy gap of the system, state-of-the-art hybrid functional calculations based on the Heyd-Scuseria-Ernzerhof (HSE06) functional are carried out to examine the electronic structures of pristine and doped SnO₂. Spin-orbit-coupling (SOC) calculations are also performed to determine the magnetocrystalline anisotropy and examine other magnetic properties in hole-doping conditions.

The carrier mobility, μ_{2D} , is calculated within deformation potential theory [36] by using the following expression [10]:

$$\mu_{2\rm D} = \frac{e\hbar^3 C_{2\rm D}}{k_B T m_e^* m_d \left(E_l^i\right)^2},$$
(1)

where e, \hbar , k_B , and T are the electron charge, Planck constant, Boltzmann constant, and temperature, respectively. In Eq. (1), m_e^* is the effective mass along the transport direction, which can be estimated by $\hbar^2 (\frac{\partial^2 E(k)}{\partial k^2})^{-1}$, while m_d is the average effective mass obtained as $m_d = \sqrt{m_x m_y}$. Finally, C_{2D} is the elastic modulus obtained as $(E - E_0)S_0 = C_{2D}(\Delta l/l_0)^2/2$, where E, E_0 , S_0 , l_0 , and Δl denote the total energy for the deformed structure, the total energy at equilibrium, the lattice area at equilibrium, the equilibrium lattice constant in the transport direction, and the deformation of l_0 , respectively. The term E_l^i denotes the deformation potential constant of the valence-band minimum (VBM) for a hole carrier or the conduction-band maximum (CBM) for an electron carrier along the transport direction, and it is defined as $E_l^i = \Delta V_i(\Delta l/l_0)$. Here ΔV_i is the energy change of the *i*th band under compression or dilatation.

The critical temperature, $T_{\rm C}$, of a 2D Ising magnet ($S \neq 1/2$) can be estimated [37] as

$$T_{\rm C} = T_{\rm C}^{\rm Ising} f\left(\frac{\Delta}{J(2S-1)}\right),\tag{2}$$

where

$$\Delta = A(2S - 1) + BSN_{\rm nn} \tag{3}$$

and

$$f(x) = \tanh^{1/4} \left[\frac{6}{N_{\rm nn}} \log_{10}(1 + \gamma x) \right].$$
 (4)

Here N_{nn} is the number of nearest neighbors ($N_{nn} = 4$ in this case), $\gamma = 0.033$, and the constants A and B are defined as

$$A = \frac{\Delta E_{\rm FM} + \Delta E_{\rm ZAFM}}{2S^2},$$

$$B = \frac{\Delta E_{\rm FM} - \Delta E_{\rm ZAFM}}{N_{\rm nn}S^2},$$
(5)

where $\Delta E_{\rm FM(zAFM)} = E_{\rm FM(zAFM)}^{(100)} - E_{\rm FM(zAFM)}^{(001)}$ are the energy differences between the configurations in which the magnetization is either in-plane (100) or out-of-plane (001) for the ferromagnetic and zigzag antiferromagnetic states studied in this work, respectively. $T_{\rm C}^{\rm Ising}$ is the critical temperature for the corresponding Ising model, which can be written as



FIG. 1. Structural information and dynamical stability of 2D SnO₂. (a) Top and (b), (c) side views of the relaxed atomic structure of a 2D SnO₂ monolayer. (d) Phonon dispersion spectrum of 2D SnO₂ monolayer. The high-symmetry *k* points Γ , *X*, and *M* denote (0,0,0), (0.5,0,0), and (0.5,0.5,0), respectively. (e) Variation of the total energy (in eV/f.u.) with the simulation time in an *ab initio* MD simulation at 800 K. The inset is the top view of the geometrical structure at the end of the simulation.

 $T_{\rm C}^{\rm Ising} = S^2 J \tilde{T}_{\rm C}/k_B$. The constant $\tilde{T}_{\rm C}$ is a dimensionless critical temperature taking the value of 2.27 for the square lattice investigated in this work. The exchange parameter *J* can be extracted as the energy difference between the ferromagnetic and the zigzag antiferromagnetic configurations, $E_{\rm zAFM} - E_{\rm FM} = 8JS^2$; here S = 1.

III. RESULTS AND DISCUSSION

A. Geometrical structure and stability

The optimized crystal structure of 2D SnO₂ monolayer is presented in Figs. 1(a)–1(c). As discussed in the Introduction, it is isostructural to the theoretically predicted 2D δ phase of silicon dioxide, δ -SiO₂, and belongs to the $P\bar{4}m2$ space group (no. 115) [31]. Similar to SiO₂, also SnO₂ has a buckled geometrical configuration and it is composed of regular SnO₄ tetrahedrons, as shown in Figs. 1(a)–1(c). The relaxed lattice constants in the *xy* plane are found to be a = b = 3.38 Å, while the other structural parameters are summarized in Table I.

TABLE I. The PBE-calculated structural parameters of a 2D SnO₂ monolayer. Here *a*, *d*, and $d_{\text{Sn-O}}$ denote the lattice constant, the buckled height, and the Sn-O bond length, respectively. θ_1 , θ_2 , and θ_3 are the bond angles [see Fig. 1(b) for definitions].

Method	a (Å)	d	$d_{\mathrm{Sn-O}}$	θ_1	θ_2	θ_3
PBE	3.38	2.10	1.99	116.3	116.3	106.2



FIG. 2. The cohesive energies of tin oxides SnO_x for various phases presenting different dimensionality.

To evaluate whether the predicted SnO₂ monolayer can be fabricated experimentally, we first calculate its cohesive energy defined as $E_{\rm coh} = (\mu_{\rm Sn} + 2\mu_{\rm O} - E_{\rm SnO_2})/3$. Here $E_{\rm SnO_2}$ is the DFT total energy of SnO₂, while μ_{Sn} and μ_{O} are the chemical potentials taken from the Sn crystal and the O₂ gas phase, respectively. We find that $E_{\rm coh}$ is about 1.57 eV/at, namely it is larger than those of the stable $CrGeTe_3$ (0.57 eV/at) and $GrGaTe_3$ (0.47 eV/at) [38]. In addition, the cohesive energies of other possible competing 2D and 3D tin oxide phases (SnO_x, x = 1, 2) are investigated. Here, the cohesive energy is defined as $E_{\rm coh} = (\mu_{\rm Sn} + x\mu_{\rm O} - E_{\rm SnO_x})/(x+1)$ and the calculated results are shown in Fig. 2. The figure confirms that all the bulk SnO₂ phases are more stable than its 2D monolayer form and that the rutile structure is the most stable of all, in good agreement with previous studies [39]. This demonstrates that the 2D SnO₂ monolayer structure is only metastable. Importantly, the cohesive energy of 2D SnO₂ monolayer is higher than that of its SnO counterpart, which in turn has been already successfully fabricated [40]. This gives us confidence that also 2D SnO₂ can be synthesized with an appropriate out-of-equilibrium strategy.

The dynamic stability of the SnO₂ monolayer is assessed by computing the phonon dispersion, as shown in Fig. 1(d). The spectrum clearly shows no imaginary frequency modes across the entire Brillouin zone, a fact indicating that SnO₂ monolayer is dynamically stable. *Ab initio* MD simulations are performed to further confirm the stability at finite temperature. A $6 \times 6 \times 1$ supercell containing 36 tin and 72 oxygen atoms is used in a simulation 6 ps long at T = 800 K, whose energy is shown in Fig. 1(e). It is found that the system does not display any instability with only small energy fluctuations across the entire duration of the simulation. The inset of Fig. 1(e) displays a snapshot of SnO₂ after 6 ps and shows that neither structural reconstruction nor broken bonds are present. This demonstrate that SnO₂ monolayer is thermally stable at least up to 800 K.

Then, the mechanical properties of SnO_2 are investigated according to elastic solid theory. Following the standard Voigt notation [41,42], the energy per area for a 2D system can be expressed as

$$E_{s} = \frac{1}{2}C_{11}\varepsilon_{x}^{2} + \frac{1}{2}C_{22}\varepsilon_{y}^{2} + C_{12}\varepsilon_{x}\varepsilon_{y} + 2C_{66}\varepsilon_{xy}^{2}, \qquad (6)$$

where ε_x (ε_y) and ε_{xy} denote the uniaxial strain in the x (y) direction and the shear strain, respectively. The coefficients



FIG. 3. Mechanical properties of monolayer SnO₂. (a) The strain in the *x* direction resulting from an applied tensile strain in the *y* direction. (b) The strain in the *y* direction resulting from an applied tensile strain in the *x* direction. The green dashed line denotes a linear relationship between ε_x and ε_y . The in-plane Poisson's ratio is $v_{xy} = -d\varepsilon_y/d\varepsilon_x = v_{yx} = -d\varepsilon_x/d\varepsilon_y = -0.11$. The inset in panel (a) denotes a schematic of the negative Poisson's ratio (see text).

 C_{11} , C_{12} , and C_{66} are the components of the elastic tensor. By fitting the energy-strain curves, the elastic constants are found to be $C_{11} = C_{22} = 81.91$ N/m, $C_{12} = -8.21$ N/m, and $C_{66} = 0.29$ N/m. These values clearly satisfy the criteria for the mechanical stability of a 2D system [42], since we have $C_{11}C_{22} - C_{12}^2 > 0$, $C_{66} > 0$. Moreover, the in-plane Young's modulus obtained as $Y = (C_{11}C_{12} - C_{12}^2)/C_{22}$ is found to be 81.09 N/m, which is significantly larger than those of silicene (61.70 N/m), germanene (44.00 N/m), and stanene (25.20 N/m) [43], demonstrating further the mechanical stability of SnO₂ monolayer.

More interestingly, it is worth noting that the elastic constant C_{12} is negative. This returns us a negative Poisson's ratio (NPR) of $v_{xy} = v_{yx} = C_{12}/C_{22} = -0.10$ due to the structural symmetry. Such a value is quite similar to that computed for δ -SiO₂ ($\nu = -0.11$) [31] and it is larger than those of pentagraphene ($\nu = -0.068$) [42] and borophene ($\nu_x = -0.04$, $\nu_y = -0.02$) [44]. To further confirm the NPR, we calculate the in-plane strain in the y (x) direction when tensile strain is applied along the x (y) direction. As shown in Figs. 3(a) and 3(b), it is found that, as the tensile strain is applied in one direction, the equilibrium lattice constant is increased in the other direction, a unique feature of auxetic materials. Then, the Poisson's ratio in the lateral plane $v_{xy} = v_{yx} = -0.11$ can be obtained by fitting the ε_x - ε_y curves based on the definitions of Poisson's ratio $v_{xy} = -d\varepsilon_y/d\varepsilon_x$ and $v_{yx} = -d\varepsilon_x/d\varepsilon_y$. Note that the in-plane NPR values calculated with this method are in good agreement with those obtained from elastic solid theory. The NPR in our predicted SnO₂ originates from the synergistic interaction of the lattice symmetry and the SnO₄ tetrahedron symmetry [31]. As shown in the inset of Fig. 3(a), a SnO₄ tetrahedron is the basic SnO₂ structural unit. In 2D SnO₂ monolayer the lattice can be stretched along one of two equivalent axes. When tensile strain (denoted by blue arrows) is applied to two O atoms vertically to the twofold axes, the distance of the other two O atoms in the tetrahedron increases (denoted by black arrows), resulting in the NPR.

B. Electronic properties and carrier mobility

We now move to discuss the electronic properties, which are presented in Fig. 4. The band structure calculated with the PBE functional shows that SnO₂ is an indirect-gap semiconductor with a gap of 2.02 eV, where the valenceband maximum (VBM) is located at the X point, while the conduction-band minimum (CBM) is at Γ . The optical gap instead is at Γ and it 2.12 eV, due to the little dispersion of the valence band. Interestingly, at the top valence band around the Γ point, the energy dispersion exhibits a MHLBE with the local minimum value located in between the Γ and the M point and the local maximum at X. The local energy dispersion is only about 0.11 eV. It is also interesting to remark that there is a second MHLBE at around 0.88 eV below the Fermi level, $E_{\rm F}$, with a local energy dispersion of 0.05 eV. Figures 4(c) and 4(d) show in more detail the features of such double Mexican-hat bands. It is found that the first Mexican-hat-like band is very flat around the Γ point, while for the second one, there is an isovalue circle with a slight energy difference around Γ as well. These unique band features lead to a sharp density of states (DOS), which will be discussed later.

The existence of a double MHLBE in this system is rather unusual among 2D compounds [21,46]. Since the PBE



FIG. 4. Electronic structure of monolayer SnO_2 . (a) The PBE band structure (red solid line) compared to the HSE06 one (purple dashed line). (b) The PBE total DOS and the projected DOS over the Sn-*d*, Sn-*p*, and O-*p* orbitals (black gray shade, red, yellow, and blue, respectively). The 3D band edges for (c) the first MHLB and for (d) the second MHLB. The result is obtained with the aid of the VASPKIT code [45].

functional generally underestimates the band gap, we have also performed calculations with HSE06, and the result is presented as a purple dashed line in Fig. 4(a). In general, HSE06 opens up both the indirect and the direct gaps, which are now 3.72 and 3.70 eV, respectively, but it changes little the qualitative features of the bands. In particular, the double MHLBE structure of the valence bands is maintained, with the local energy dispersions now at 0.07 and 0.01 eV, respectively. A Mexican-hat-like band dispersion in a 2D material can give rise to a sharp van Hove singularity in the DOS, and this can easily result in an electronic instability [21,46], a feature also confirmed by our first-principles calculations. As shown in the DOS of Fig. 4(b) and similarly to other 2D systems [21], two van Hove singularities can be found at 0.33 and 0.88 eV below $E_{\rm F}$. From the analysis of the total and projected DOS (PDOS), it is found that the O-p orbitals and to some degree the Sn-dcontribute the most to the top of the valence band. Given the d^{10} configuration of tin, this indicates strong O-p/Sn-d hybridization.

Since usually carrier mobility has a great effect on the performance of (opto)electronic devices, we are here computing that of SnO₂ monolayer by using deformation potential theory [10,36] (the calculation details can be found in Sec. II). The calculated effective mass, m^* , deformation-potential constant, E_l , 2D in-plane elastic modulus, C_{2D} , and carrier mobility, μ , are summarized in Table II. It is found that m^* for heavy holes, 13.03 m_e , is 27 times larger than that of electrons, 0.49 m_e , due to the existence of the MHLBE in the valence band. This leads to a giant difference between the hole and electron

TABLE II. The calculated effective mass, m^* , deformationpotential constant, E_l , 2D elastic modulus, C_{2D} , and carrier mobility, μ , in the *x* and *y* directions at 300 K. *e* and *h* denote electron and hole carriers, respectively.

Carrier type	$m^*(m_e)$	E_l (eV)	$C_{2D} (J m^{-2})$	$\mu (\text{cm}^2 \text{V}^{-1} \text{s}^{-1})$	
e(x)	0.49	2.36	79.97	1.27×10^{3}	
h(x)	13.03	4.16	79.97	0.51	
e (y)	0.49	2.36	79.97	1.27×10^{3}	
<i>h</i> (y)	13.03	4.16	79.97	0.51	

mobility. In fact, as listed in Table II, the electron mobility reaches out values in excess of $10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, while that for holes is only 0.51 cm² V⁻¹ s⁻¹. The high electron mobility demonstrates that the SnO₂ monolayer can be considered as a channel material in 2D field-effect transistors for high-speed information transfer. It is also important to note that the carrier mobility is isotropic in the *x* and *y* directions because of structural symmetry.

C. Hole-induced magnetism

The presence of van Hove singularities in the DOS just below the Fermi level suggests the possibility to induce a magnetic phase transition by hole doping, as we will now show. In Fig. 5(b) we present the spin polarization energy, defined as the energy difference between the nonmagnetic



FIG. 5. (a) Possible magnetic configurations: NM, FM, zAFM, and sAFM, and the corresponding spin densities for hole-doped SnO₂ at $n_p = 4.38 \times 10^{14}$ cm⁻² (0.5 hole/f.u.). The yellow and cyan isosurfaces denote the spin-up and spin-down charge density, respectively. (b) The dependence of the magnetic energy difference (per formula unit) between the FM and NM, zAFM, and sAFM configurations as a function of the hole concentration. The dependence of the total magnetic moment per hole and the total magnetic moment per formula unit as a function of the hole concentration when calculated at the level of (c) PBE, (d) PBE+SOC, and (e) HSE06, respectively.

	HSE06				PBE			
n_p	$\overline{E_{\rm NM} - E_{\rm FM}}$	$E_{\rm zAFM} - E_{\rm FM}$	$E_{\rm sAFM} - E_{\rm FM}$	$T_{\rm BKT}/T_{\rm C}~({\rm K})$	$\overline{E_{\rm NM} - E_{\rm FM}}$	$E_{\rm zAFM} - E_{\rm FM}$	$E_{\rm sAFM} - E_{\rm FM}$	$T_{\rm BKT}/T_{\rm C}~({\rm K})$
0.05 hole/f.u.	1.22	1.17	1.22	3.0	0.18	0.03	0.18	0.1
0.50 hole/f.u.	179.39	25.29	57.03	65.3	59.77	18.99	50.87	49.0
1.00 hole/f.u.	766.37	167.12	176.21	338.6	212.69	91.88	113.73	125.00
1.10 hole/f.u.	766.37	187.04	176.21	475.7	252.49	112.39	121.17	290.2
1.50 hole/f.u.	1260.48	194.82	123.72	503.0	452.08	213.15	143.27	326.2

TABLE III. The magnetic energy difference of hole-doped SnO₂ at several different hole concentrations calculated by HSE06 and PBE functionals and their corresponding T_{BKT} or T_{C} . The energy unit is meV/f.u.

(NM) and the ferromagnetic (FM) ground state $(E_{\rm NM} - E_{\rm FM})$, black dot), as a function of the hole concentration. The figure clearly shows that the nonmagnetic state is unstable and a spin-polarized solution becomes energetically favorable even at the tiny hole concentration of $n_p = 8.76 \times 10^{13}$ cm⁻². We also find that such spin polarization energy increases with n_p .

We established the magnetic instability of hole-doped SnO₂, and we now determine its magnetic phase. This is achieved by looking at the energetics of two different antiferromagnetic (AFM) configurations, namely a striped and a zigzag AFM arrangement (sAFM and zAFM) obtained within a $\sqrt{2a} \times \sqrt{2a}$ supercell [the associated spin densities are shown in Fig. 5(a)]. The magnetic energy differences of Fig. 5(b) clearly demonstrate that the FM order is lower than both of the AFM ones and so it should be taken as the ground state. HSE06 calculations confirm such a result (see Table III). Figure 5(c) further shows that the total magnetic moment is linear with n_p over a broad range of concentrations, and that the hole density equals the magnetization density, i.e., each hole remains fully spin-polarized (each hole contributes a magnetic moment of $1\mu_B$, with μ_B being the Bohr magneton).

Such a dependence of the magnetic moment upon hole doping is confirmed by both PBE+SOC and HSE06 calculations, as shown in Figs. 5(d) and 5(e). Also in these two cases each hole is fully spin-polarized over a broad range of concentrations, in agreement with the PBE-only results. An analysis of the spin-density distribution clearly demonstrates that the magnetism mainly originates from O atoms [see $n_p = 4.38 \times 10^{14}$ cm⁻² as a typical case in Fig. 5(a)] due to the large exchange interaction of O [47,48], and that the local O magnetic moment increases with n_p .

The physical origin of the magnetism in the hole-doped SnO_2 can be attributed to the Stoner mechanism [49,50], namely a magnetic ground state is induced when the following condition (the Stoner criterion) is fulfilled: $ID(E_{\rm F}) > 1$, where *I* is the Stoner exchange parameter and $D(E_{\rm F})$ is the DOS at the Fermi level in the NM state. The Stoner exchange interaction parameter can obtained from the simple relation $\Delta_{ex} =$ IM [51], where Δ_{ex} is the spin-splitting energy between the two spin subbands and M is the total magnetic moment per atom. Despite the fact that the Stoner exchange parameter for oxygen is large [47], long-range p-type magnetism is extremely rare among oxides. This is because in the solid state oxygen is always found in a closed-shell configuration with strong bonding, which results in a large band dispersion and consequently small $D(E_{\rm F})$. The peculiar electronic structure of the valence band of SnO₂ [see Fig. 4(a) and Table II] defines such a feature of 3D oxides. In this case, $D(E_{\rm F}) \propto$ $m^*\sqrt{E_{\rm VBM}-E_{\rm F}}$, so that moderate doping can result in a large $D(E_{\rm F})$ and hence magnetism. To further verify whether SnO₂ meets the Stoner criterion for hole-doping conditions, we calculate *I* and $D(E_{\rm F})$ at the representative hole concentration of $n_p = 4.38 \times 10^{14} \text{ cm}^{-2}$ (0.5 hole/f.u.). We obtain values of 3.12 eV and 26.21 states/eV, respectively, so that clearly $ID(E_{\rm F}) > 1$.

The change in electronic structure upon hole-doping can be appreciated by looking at the PBE band structure for different n_p , displayed in Fig. 7(a) and Figs. 6(a-1)–6(a-10). As holes are introduced in the system, SnO₂ loses its NM semiconducting characteristics and becomes a FM half-metal, even at n_p as low as 4.38×10^{13} cm⁻² (0.05 hole/f.u). In particular, it is noted that the spin splitting of the valence band increases with n_p , thus inducing a sizable minority-spin gap, a desirable feature for spintronic devices. The picture is thus that of a strong magnet, such as Co, with the only difference being that here the d band is replaced by a p-type one and that there is not an unpolarized, extremely broad, s-type band. Finally, we compute again the band structures, this time including SOC, as shown as a black dashed line in Fig. 7(a). It is found that the SOC barely affects the electronic structure and thus it can be ignored. This is expected since the magnetism takes place in the light 2p orbitals of O. Notably, all our PBE results are confirmed by the HSE06 functional [see Figs. 6(b-1)-6(b-10)], which also returns the half-metal ground state. To complete our analysis of the magnetism in hole-doped SnO₂, we now investigate the magnetic anisotropy energy (MAE), a quantity closely related to the thermal stability of a magnet. This is calculated here by using second-order perturbation theory [52]. In particular, the MAE is defined as the energy difference between the configurations in which the magnetization is either out-of-plane (001) or in-plane (100), i.e., $E_{MAE} = E_{001} - E_{100}$. E_{MAE} is then presented in Fig. 7(c) as a function of n_p , where one can clearly observe a peculiar nonmonotonic behavior. For n_p smaller than $5.26 \times 10^{14} \text{ cm}^{-2}$ (0.60 hole/f.u.), the MAE is positive. This means that in such a range the magnetization will be preferentially in-plane, where we did not find any further anisotropy, so that hole-doped SnO₂ can be considered as a 2D XY magnet. When n_p is further increased beyond 5.26×10^{14} cm⁻², but remains smaller than 7.89×10^{14} cm⁻² (0.95 hole/f.u.), the MAE changes sign and becomes negative. In this case, the system acquires an out-of-plane easy axis so that SnO₂ becomes a 2D Ising magnet. Finally, further increases in n_p reverse SnO₂ back to being a 2D XY magnet. Interestingly, this nonmonotonic behavior of the MAE is characterized by doping conditions associated with large



FIG. 6. The spin-polarized band structures of SnO₂ calculated with (a) the PBE and (b) the HSE06 functional at different hole concentrations n_p : (1) 0.05, (2) 0.1, (3) 0.3, (4) 0.5, (5) 0.7, (6) 0.8, (7) 0.9, (8) 1.1, (9) 1.3, and (10) 1.5 hole/f.u., which correspond to 4.38 × 10¹³, 8.76 × 10¹³, 2.63 × 10¹⁴, 4.38 × 10¹⁴, 6.13 × 10¹⁴, 7.00 × 10¹⁴, 7.88 × 10¹⁴, 9.64 × 10¹⁴, 1.14 × 10¹⁵, and 1.31 × 10¹⁵ cm⁻², respectively. The red and blue solid lines denote the spin-up and spin-down components, respectively.

anisotropy. For instance, at the representative hole density of $n_p = 3.07 \times 10^{14} \text{ cm}^{-2}$ (i.e., close to the first MAE positive peak), the calculated MAE of SnO₂ is 7.82 µeV per O atom, which is comparable to that of bulk nickel (2.7 µeV per Ni atom) and iron (1.4 µeV per Fe atom) [53].

Finally, we look at the critical temperatures associated with the magnetic phase transition. Here the situation is different for the XY and the Ising case. For a 2D XY magnet there

is no macroscopic long-range order at finite temperature, but ferromagnetism can be stabilized by finite-size effects [54], and the Berezinskii-Kosterlitz-Thouless (BKT) transition can be observed at a critical temperature, T_{BKT} . This can be estimated as $T_{BKT} = 0.89J/k_B$ [55–58], where J is the exchange parameter and k_B is the Boltzmann constant. If only the nearest-neighbor interaction is considered, the exchange parameter J can be extracted as the energy difference between



FIG. 7. (a) The band structures of the hole-doped SnO₂ calculated by PBE with and without the spin-orbit coupling (SOC) included, and (b) the spin-polarized DOS at the hole concentration of $n_p = 4.38 \times 10^{14}$ cm⁻² (0.5 hole/f.u.). The red (positive values) and blue (negative values) lines denote the spin-up and spin-down components, respectively. The dashed curve in (a) denotes the PBE+SOC result. (c) The MAE and (d) the T_{BKT} or T_{C} of hole-doped SnO₂ as a function of hole doping concentration n_p . The inset denotes the locally magnified part in (d).

the FM and the zAFM configurations, $E_{zAFM} - E_{FM} = 8JS^2$, where here S = 1. In contrast, the Ising model in two dimensions possesses a phase transition with critical temperature $T_{\rm C}$, which can be estimated with the method proposed by Torelli et al. [37] (more details of the method are found in Sec. II). The dependence of the critical temperature, either $T_{\rm BKT}$ or $T_{\rm C}$, is then presented in Fig. 7(d) as a function of the hole concentration. We find that the maximum value of $T_{\rm C}$ remains modest at only 25 K. However, $T_{\rm BKT}$ can be significantly higher and increases monotonically with n_p , reaching a value of 318.7 K for $n_p = 1.01 \times 10^{15}$ cm⁻². When the same calculation is repeated with the HSE06 functional we find a very similar trend, although in general $T_{\rm BKT}$ seems to be higher than that predicted by PBE. For instance, the value of 338.6 K was obtained already for $n_p = 8.76 \times 10^{14} \text{ cm}^{-2}$ (see Table III). This is perhaps not surprising, since typically the exchange interaction computed by HSE06 exceeds that obtained by PBE.

IV. CONCLUSION

In summary, based on first-principles calculations, we have predicted a stable 2D semiconductor, SnO_2 , with auxetic properties. This is characterized by a negative Poisson's ratio and high electron mobility. In addition, we find that the valence-band structure of SnO_2 presents a Mexican-hat-like band edge near the Fermi level, which results in a high density of states and can be used to easily induce Stoner magnetism when hole-doping is introduced. Our firstprinciples calculations also confirm that a magnetic phase transition occurs and that a hole-doped SnO_2 monolayer behaves like a 2D half-metal. Such a state can be maintained over a wide range of hole doping concentrations. Interestingly, the magnetic anisotropy changes sign twice as the hole concentration is increased, so that SnO_2 behaves like an *XY* magnet for small and large concentrations, but like an Ising magnet at intermediate doping. In the large hole-concentration limit, the Berezinskii-Kosterlitz-Thouless phase-transition temperature can exceed room temperature, and the magnetic anisotropy is comparable with that of ordinary transition metal magnets. These results not only show the great potential of SnO_2 for making nanoelectronic devices, but they also open the door for inducing itinerant ferromagnetism in 2D materials with MHLBE by hole hoping.

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