Two-dimensional Gallium and Indium Oxides from Global Structure Searching: Ferromagnetism and Half Metallicity via Hole Doping

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ABSTRACT

There has been tremendous research effort in hunting for novel two-dimensional (2D) materials with exotic properties, showing great promise for various potential applications. Here, we report findings about a new hexagonal phase of 2D Ga₂O₃ and In₂O₃, with high energetic stability, using a global searching method based on an evolutionary algorithm, combined with density-functional theory calculations. Their structural and thermal stabilities are investigated by the calculations of their phonon spectra and by ab-initio molecular dynamics simulations. They are predicted to be intrinsically non-magnetic stable semiconductors, with a flat band edge around the valence band top, leading to itinerant ferromagnetism and half-metallicity upon hole doping. Bilayer Ga₂O₃ is also studied and found to exhibit ferromagnetism without extra hole doping. The Curie temperature of these materials, estimated using Monte Carlo simulations based on the Heisenberg model, is around 40 to 60 K upon a moderate hole doping density.

I. INTRODUCTION

Computational screening of novel materials with intriguing properties has been attracting enormous research attention recently.¹⁻⁴ Among this research, the prediction of new two-dimensional (2D) materials, especially those with magnetic properties, has also been widely explored.⁵⁻⁸ These investigations have facilitated and accelerated the experimental discovery of materials for a variety of applications. Nevertheless, some of the predicted materials, found from property-oriented materials searching, may turn out to be unstable and very challenging to grow or synthesize.⁹⁻¹³ Therefore, stricter criteria are necessary for materials prediction, to make sure the candidate materials have global minimum of free energy, as well as high structural and thermal stabilities.

Various 2D ferromagnetic materials, for example, CrX_3 ($\text{X}=\text{Cl}, \text{Br}, \text{I}$),¹⁴⁻¹⁶ $\text{Cr}_2\text{Ge}_2\text{Te}_6$,^{16,17} Fe_3GeTe_2 ,^{18,19} monolayers, etc. have been theoretically predicted and experimentally synthesized. Further strategies such as electrostatic doping, electric field or strain effects, van der Waals stacking, have been intensively exploited to tune the magnetic properties of those monolayers.^{15,17,18,20-25} Apart from 2D materials with intrinsic magnetic properties, efforts have also been made to induce ferromagnetism in some nonmagnetic 2D semiconductors by e.g. hole doping.²⁶⁻²⁹ The spontaneous ferromagnetic order in those intrinsically nonmagnetic 2D materials originates from the exchange splitting of the electronic states at the top of the valence band, where a sharp Van Hove singularity exists in the density of states (DOS), leading to the Stoner instability. Therefore, these nonmagnetic 2D materials could also be promising for application in novel spintronic devices.

In this work, we explore all possible 2D phases of gallium oxides and indium oxides by means of the Universal Structure Predictor: Evolutionary Xtallography (USPEX) method, on the basis of first-principles calculations, to find out the most energetically stable atomic configurations, i.e. M_2O_3 ($\text{M} = \text{Ga}, \text{In}$). Their stability is demonstrated by the formation energies, phonon dispersions as well as by molecular dynamics simulations. We find that M_2O_3 monolayers are nonmagnetic semiconductors, while hole doping can turn them into ferromagnetic materials over a wide range of hole

concentrations. Their Curie temperatures (T_c) under different hole doping concentrations are also estimated.

II. COMPUTATIONAL METHODS

Searches for the possible structures of 2D gallium oxides and indium oxides, through an ab-initio evolutionary algorithm, was performed by USPEX,^{30,31} interfaced with the Vienna ab initio simulation package (VASP).^{32,33} The variable-composition searching was considered, with the total number of atoms in the 2D crystals fixed between 2 and 8, and their vacuum spaces restricted to be within 20 Å, respectively. 40 groups of symmetries were used to produce a random symmetric structure generator for the initial population. Then, the full structure relaxations were performed, and the most stable and metastable atomic structures were screened and inherited into the next generation, by comparing their formation enthalpy. The population kept evolving until the most stable configuration stayed unchanged for a further 10 generations, in order to find the globally lowest energy state. All density functional theory (DFT) calculations were performed using VASP, with electron-ion interaction described by projector augmented wave (PAW) pseudopotentials.³² The generalized gradient approximation (GGA), parameterized by the Perdew-Burke-Ernzerhof (PBE) approach³⁴, was used as the exchange correlation functional. The energy cutoff of 550 eV and k-point meshes of $8 \times 8 \times 1$ and $32 \times 32 \times 1$, were used for structural optimizations and self-consistent calculations, respectively. A total energy convergence criterion of 10^{-5} eV and a force convergence criterion of 0.005 eV/Å were chosen for complete relaxations of the lattice constants and the atomic positions. The Heyd-Scuseria-Ernzerhof functional (HSE06),³⁵ which mixes 25% nonlocal exchange with the PBE functional, was used for more accurate electronic band structure and density of states (DOS) calculations. Additionally, the optimized exchange van der Waals functional, optB86-vdW³⁶, was used to take into account the van der Waals interactions in the calculations of the Ga₂O₃ bilayers.

Phonon dispersion curves were calculated by the PHONOPY package³⁷ on the basis

of Density Functional Perturbation Theory (DFPT). The ab-initio molecular dynamics (AIMD) simulations were carried out using 5×5×1 supercells (with 125 atoms) and were equilibrated at 300 K for 10 ps with a time step of 2 fs. The constant-temperature and volume canonical ensemble (NVT) was selected, and the temperature was controlled by means of a Nose thermostat.^{38,39}

The Curie temperatures were estimated using Monte Carlo simulations, as implemented in the VAMPIRE package.⁴⁰ Rectangular supercells of 100×60×3 were used for the simulations, since only orthogonal lattice vectors are supported. The spins were thermalized for 10000 equilibrium steps, followed by 20000 averaging steps for the calculation of the thermal equilibrium magnetization at every temperature.

III. RESULTS AND DISCUSSION

The convex hulls, defined as the enthalpy of formation versus the composition of gallium oxides and indium oxides with all possible stoichiometries, are plotted in the left panel of Fig. 1 (a) and (b), respectively. The formation enthalpy per atom, ΔH , which can be used to determine the relative stability between different compositions and structures, was calculated by

$$\Delta H = (E_{M_xO_y} - xE_M - yE_{O_2}/2)/(x+y) \quad (1)$$

where $E_{M_xO_y}$ is the total energy of M_xO_y , ($M = \text{Ga, In}$), E_M is the energy of the metal atom in its stable bulk structure, E_{O_2} corresponds to the energy of an isolated oxygen molecule in its paramagnetic ground state. Any structure with its formation enthalpy on the convex hull is considered to be thermodynamically stable and experimentally synthesizable. The most stable structures of Ga-O and In-O, highlighted by the red dots in the convex hulls, are Ga_2O_3 and In_2O_3 , respectively. Specifically, their ΔH can respectively reach -1.95 eV/atom and -1.52 eV/atom. In addition, the GaS-like GaO monolayer is also found to be stable, since its formation enthalpy (-1.65 eV/atom) is on the convex hull. In this paper, we only focus on the most stable M_2O_3 monolayers.

Fig. 1. Convex hulls of different stoichiometries searched by USPEX, and the corresponding atomic structures of the most energetically favorable candidates for 2D binary (a) Ga-O and (b) In-O materials. The red dots on the Convex hulls indicate the predicted stable phases. The unit cell is highlighted by yellow ~~solid~~ lines.

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The relaxed crystal structures of single-layer M_2O_3 are given in the right panel of Fig. 1, which consist of five atomic sublayers stacked in the sequence of O-M-O-M-O in the out-of-plane direction. The calculated in-plane lattice constants of Ga_2O_3 and In_2O_3 monolayers are 3.10 Å and 3.04 Å, respectively. The Ga_2O_3 monolayer is non-centrosymmetric (polar), similarly to In_2X_3 ($X = S, Se$) monolayers.^{41,42} On the other hand, the In_2O_3 monolayer is found to be centrosymmetric (non-polar). [The oxygen atoms on the top and bottom layer are bonded to three neighboring metal atoms, while the central oxygen atoms bond to 4 and 6 metal atoms for \$Ga_2O_3\$ and \$In_2O_3\$ monolayers.](#)

respectively. The indium atoms are 6-fold coordinated in In_2O_3 , while in Ga_2O_3 , the gallium atoms in the upper and lower layers are 6 and 4-fold coordinated, respectively.

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Fig. 2. Phonon dispersion spectra, and total energy evolution during molecular dynamics simulations, together with the atomic structures obtained after 10 ps, for (a) Ga_2O_3 and (b) In_2O_3 monolayers at 300 K.

Phonon dispersion calculations, together with AIMD simulations were carried out to evaluate the dynamic stability as well as the room-temperature stability of the two M_2O_3 monolayers; the results are presented in Fig. 2. In the phonon dispersion spectra, merely no imaginary frequency is observed, which suggests that both M_2O_3 monolayers

are dynamically stable. During the AIMD simulations, with the temperature fixed at 300 K, the total energies of M_2O_3 monolayers oscillate within narrow ranges, i.e. ~ 3 eV/cell. In the addition, the atoms only slightly oscillate around their equilibrium positions, and the structural integrity is well retained after 10 ps. Given their low formation enthalpy, dynamical stability, together with their thermal stability, the growth of M_2O_3 monolayers appears highly possible.

Fig. 3. Fat band structures, density of states and partial charge densities of the CBM (blue) and VBM (red) for (a) Ga_2O_3 and (b) In_2O_3 monolayers. The isosurface value is set to $0.2 \text{ e}/\text{\AA}^3$.

From the electronic band structures shown in Fig. 3, one can see that both M_2O_3 monolayers are semiconductors with indirect band gaps. Specifically, the band gap of Ga_2O_3 monolayer is ~ 1.43 eV at PBE level (~ 2.72 eV at HSE06 level, see Fig. S1); the bottom of the conduction band (CB) is contributed by the s and p_z orbital of oxygen

atoms and s orbitals of gallium atoms (denoted as O- s , O- p_z , Ga- s , respectively), whereas the top of the valence band (VB) is mainly contributed by the O- p_y and O- p_z orbitals. In particular, the valence band maximum (VBM) essentially originates from the p_z orbital of the top oxygen atoms, as clearly shown in the partial charge density plot. Concerning the In_2O_3 monolayer, the band gap calculated at PBE level is ~ 1.64 eV (~ 2.93 eV at HSE06 level, see Fig. S1). The bottom CB originates mainly from the hybridization of O- p_z and $\text{In-}s$ orbitals, while the top VB is merely derived from the O- p_z orbital. It is evident that the partial charge density of the VBM is only located on the oxygen atoms of the In_2O_3 monolayer.

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Fig. 4. Magnetic moment and spin polarization energy as a function of hole doping concentration, and spin-polarized partial density of states under different hole doping densities of (a) Ga_2O_3 and (b) In_2O_3 monolayers.

In the DOS of the M_2O_3 monolayers, there is a sharp peak in the edge of valence band. This sharp peak is related to so-called Van Hove singularities. When the Fermi

level approaches the singularity, a transition from a paramagnetic phase to a ferromagnetic phase could occur, as reported in several previous works.²⁶⁻²⁹ Therefore, in the following, we will study hole doping of M_2O_3 monolayers, using spin-polarized DFT simulations, to investigate their possible magnetic properties.

By performing the relaxation of the charged cells, the effect of hole doping on the atomic structures is first investigated. The structural variation of the M_2O_3 monolayers upon hole doping is summarized in Fig. S2. The thickness of the Ga_2O_3 monolayer shrinks when it is hole doped, while for In_2O_3 monolayer, the thickness first decreases when the doping density is lower than $\sim 4 \times 10^{14} \text{ cm}^{-2}$, then it increases and becomes larger than the original thickness before doping for a doping density higher than $\sim 7 \times 10^{14} \text{ cm}^{-2}$. In general, the M_2O_3 monolayers do not suffer pronounced deformation upon hole doping, as the variation of the bond lengths and thicknesses is typically less than 5%, even at a high hole doping concentration of 10^{15} cm^{-2} , except for the In-In distance ($\sim 8\%$ elongation) and a specific O-Ga bond length ($\sim 12\%$ elongation), see Fig. S2. Therefore, we can conclude that hole doping has a limited effect on the atomic structures of the M_2O_3 monolayers.

The computed magnetic moments and spin polarization energies of M_2O_3 monolayers are shown in the left panel of Fig. 4, as a function of the hole doping density. The spin polarization energy is defined as the total energy of the non-magnetic state minus the one of the ferromagnetic state. Thus, a positive spin polarization energy indicates that the ferromagnetic state is more stable. The paramagnetic to ferromagnetic transition occurs at a hole concentration as low as $5 \times 10^{12} \text{ cm}^{-2}$. In this case, the magnetic moment is $\sim 1.0 \mu_B/\text{hole}$ (where μ_B is the Bohr magneton), i.e. the injected holes are fully spin polarized. The spin polarization energy increases monotonously with the hole density, up to a hole concentration of $\sim 10^{15} \text{ cm}^{-2}$ for both M_2O_3 monolayers.

The spin-polarized DOS of M_2O_3 monolayers under different doping levels are presented in the right panel of Fig. 4, where the energy splitting between spin up and spin down states can be observed. The Fermi level crosses the spin down states, while the up-spins are fully occupied at the Fermi level, making these two materials half-

metallic upon hole doping. Obviously, the energy splitting increases with the increase of the hole density i.e., from ~ 0.3 eV (~ 0.2 eV) at $2 \times 10^{14} \text{ cm}^{-2}$, to ~ 0.8 eV (0.6 eV) at $6 \times 10^{14} \text{ cm}^{-2}$ for Ga_2O_3 (In_2O_3) monolayer, respectively. In addition, the valence band top still mainly consists of the p orbitals of the oxygen atoms when the hole doping concentration increases. Therefore, the oxygen atoms mostly contribute to the ferromagnetic order in the M_2O_3 monolayers.

Fig. 5. (a) Fat band structures, (b) partial charge densities of the CBM (blue) and VBM (red), (c) charge density difference (Yellow and Cyan represents charge accumulation and depletion, respectively) (d) magnetic moment and spin polarization energy as a function of hole doping concentration, and spin-polarized partial density of states under different hole doping densities of a Ga_2O_3 bilayer. The isovalues of partial charge densities and charge density differences are fixed to $0.005 \text{ e}/\text{\AA}^3$ and $0.2 \text{ e}/\text{\AA}^3$, respectively.

Similar to the situation in In_2X_3 ($\text{X} = \text{S}, \text{Se}$) monolayers, the centrosymmetry of the Ga_2O_3 monolayer is broken, due to the different coordination environment of the Ga atoms, which results from the asymmetric positions of O atoms in the middle layer. This leads to an intrinsic dipole, pointing from the bottom to the top surface along the out of plane direction. It has been reported that the dipole moment will be almost doubled in In_2X_3 ($\text{X} = \text{S}, \text{Se}$) bilayers.⁴² Consequently, we also considered Ga_2O_3 bilayers to investigate the influence of this enhanced polarization on the magnetic properties. We constructed 6 different stacking patterns, as shown in Fig. S3, and the most stable one was studied further. Using the optB86-vdW functional and spin polarized calculations for the atomic relaxation, the interlayer distance is calculated to be 2.29 Å, and the lattice constant is 3.10 Å. Surprisingly, we found that the Ga_2O_3 bilayer exhibits ferromagnetism without hole doping, with a magnetic moment of $\sim 0.03 \mu_B$ per unit cell, which is comparable to a hole doping density of $\sim 4 \times 10^{13} \text{ cm}^{-2}$. To find out the underlying mechanism responsible for the spontaneous ferromagnetism, we computed the partial band structures, partial charge densities, as well as the charge density difference of the Ga_2O_3 bilayer, presented in Fig. 5. Clearly, the bottom CB of the double layer is solely contributed by the bottom layer, while the top VB is originating from the top layer, which gives rise to the typical type-II band alignment. In addition, the CB crosses the Fermi level, making the bilayer a metal. This is also confirmed by the HSE band structure calculations, as shown in Fig. S1 (c). On the other hand, the p orbitals of the topmost oxygen atoms of the top layer (O_t) mostly contribute to the top VB, as shown in the band structure; this is also confirmed by the partial charge density plot shown in Fig. 5 (b). Note that these topmost oxygen atoms mainly contribute to the magnetic moment of the Ga_2O_3 bilayers. The intrinsic dipole present in the bilayer is induced by electrons transferred from the top layer to the bottom layer, resulting in the “hole doping” of the top layer, and the occurrence of a ferromagnetic order in the material; this is also reflected by the charge density difference plot in Fig. 5 (c).

The magnetic properties of the Ga_2O_3 bilayer, induced by increasing further the hole

doping density, was also investigated. The computed magnetic moment, shown in Fig. 5 (d), is larger than 1.0 μ_B/hole , when the hole doping density is less than or equal to $1 \times 10^{14} \text{ cm}^{-2}$, then it decreases gradually to $\sim 1.0 \mu_B/\text{hole}$ when the doping density is further increased. Nevertheless, the magnetic moment gradually declines again when the hole doping is larger than $\sim 5 \times 10^{14} \text{ cm}^{-2}$, and eventually reaches zero at $\sim 7 \times 10^{14} \text{ cm}^{-2}$. Thereafter, the magnetic moment oscillates between zero and one when the hole density further increases. By comparing the DOS at hole concentrations of $4 \times 10^{14} \text{ cm}^{-2}$, $7 \times 10^{14} \text{ cm}^{-2}$ and $8 \times 10^{14} \text{ cm}^{-2}$ in the right panel of Fig. 5 (d), it is evident that the upmost oxygen atoms of the bottom layer (O_b) play more and more important roles when the hole concentration is larger than $\sim 4 \times 10^{14} \text{ cm}^{-2}$, as its contribution to the DOS becomes closer to the Fermi level. Thereafter, at $\sim 7 \times 10^{14} \text{ cm}^{-2}$, the DOS contributed by the O_t and O_b is merely the same, but with opposite spin direction, which is especially noticeable around the Fermi level. This leads to an antiferromagnetic state in the system. Finally, at $\sim 8 \times 10^{14} \text{ cm}^{-2}$, the DOS contributed respectively by the O_t and O_b almost overlap. In this case, the ferromagnetic state is more energetically favorable.

The Curie temperatures (T_c) of the M_2O_3 monolayers as well as the Ga_2O_3 bilayer were next computed, using Monte Carlo simulations. Based on the [2D Ising](#) model, their spin Hamiltonian is given by

$$H = - \sum_{\langle ij \rangle} J_1 \mathbf{S}_i \cdot \mathbf{S}_j - \sum_{\langle\langle ij \rangle\rangle} J_2 \mathbf{S}_i \cdot \mathbf{S}_j \quad (2)$$

where $\langle ij \rangle$ and $\langle\langle ij \rangle\rangle$ are the summation over the pairs of nearest and second nearest oxygen atoms, respectively. J_1, J_2 are the nearest-neighbor and second nearest-neighbor exchange interactions, respectively. $\mathbf{S}_i^*$ (or $\mathbf{S}_j$) is a unit vector. For Ga_2O_3 monolayer and bilayer, we only considered the nearest-neighbor exchange parameter, since only the topmost oxygen atoms contribute to the magnetic moment, while for In_2O_3 monolayer, we considered both exchange parameters, which are derived from the two O atoms in the same or different planes. These exchange parameters can be evaluated using the energy difference between ferromagnetic and antiferromagnetic phases, obtained from first-principles calculations. Details about the construction of the ferromagnetic and antiferromagnetic configurations, as well as the calculation of the

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exchange parameters are given in Fig. S4 and Fig. S5. The values of the exchange parameters under different hole doping concentrations are summarized in Table S3. It is clear that a higher hole density gives rise to larger exchange parameters.

Fig. 6. Monte Carlo simulations of the normalized magnetization of M_2O_3 monolayers and Ga_2O_3 bilayer (BL) as a function of temperature, for various hole doping densities, as indicated in the figure caption.

The temperature-dependent normalized magnetization curves, computed from Monte Carlo simulations under different hole doping densities, are displayed in Fig. 6. The magnetization remains high in the low temperature range, and then drops to near zero at a certain critical (Curie) temperature. The temperature dependent magnetization is fitted using the Curie-Bloch equation in the classical limit:

$$m(T) = \left(1 - \frac{T}{T_c}\right)^\beta \quad (3)$$

where T is the temperature and β is a critical exponent. Obviously, T_c is proportional to

the exchange interactions and the hole doping concentrations in M_2O_3 monolayers and Ga_2O_3 bilayer. At the same doping level, the In_2O_3 monolayer has the highest T_c , followed by the Ga_2O_3 bilayer, then by the Ga_2O_3 monolayer. At a hole concentration of $\sim 2 \times 10^{14} \text{cm}^{-2}$, the fitted T_c is $\sim 20 \text{ K}/24 \text{ K}/27 \text{ K}$ for Ga_2O_3 monolayer/ Ga_2O_3 bilayer/ In_2O_3 monolayer, respectively, while it increases to $36 \text{ K}/39 \text{ K}/43 \text{ K}$ when the hole doping density reaches $\sim 4 \times 10^{14} \text{cm}^{-2}$. At $\sim 6 \times 10^{14} \text{cm}^{-2}$, T_c is 45 K and 62 K for Ga_2O_3 and In_2O_3 monolayers, respectively, being comparable to the ones of [monolayer](#) CrI_3 (45 K),¹⁶ and [bilayer](#) $Cr_2Ge_2Te_6$ (30 K).⁴³ Although the second nearest-neighbor exchange interaction (J_2) is several times larger in In_2O_3 as compared to Ga_2O_3 , their computed Curie temperatures are comparable. It may be due to the “competition” between J_1 and J_2 , arising from the weaker AFM interaction and stronger FM interaction in the In_2O_3 monolayer, leading to a lower T_c than expected.

IV. CONCLUSIONS

In summary, by combining first-principles calculations with the evolutionary algorithm USPEX, we discovered energetically stable phases of 2D Ga_2O_3 and In_2O_3 . Calculations of their phonon dispersion curves and ab-initio molecular dynamics simulations confirmed their structural and thermal stability. Both Ga_2O_3 and In_2O_3 monolayers are predicted to be intrinsically non-magnetic semiconductors, with flat band edges at the top of their valence bands, resulting in sharp peaks in their electronic density of states. A spontaneous ferromagnetic phase transition occurs upon hole doping of these 2D materials, which turns them into half-metals over a wide range of hole densities.

The bilayer structure of Ga_2O_3 was also investigated and it showed ferromagnetism without external hole doping, resulting from the non-centrosymmetric structure of 2D Ga_2O_3 . In this case, the spontaneous ferromagnetic order is triggered by the charge transfer taking place between the two layers of the Ga_2O_3 bilayer. Using Monte Carlo simulations, based on the Heisenberg model, the estimated Curie temperatures of the Ga_2O_3 and In_2O_3 monolayers and the Ga_2O_3 bilayer are proportional to the hole doping density, and are comparable to the ones of [v](#), CrI_3 [monolayer](#) and 2D $Cr_2Ge_2Te_6$ [bilayer](#).

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at moderate hole doping densities. We hope that our work can inspire the synthesis of these new 2D materials and the experimental study of their predicted magnetic properties upon hole doping.

SUPPLEMENTARY MATERIAL

See the supplementary material for detailed information about the computed hybrid band structures of the M_2O_3 monolayers and Ga_2O_3 bilayer, variation rates of the bond lengths and bond angles of the charged M_2O_3 monolayers after atomic relaxations, schematics of the various magnetic structures, and details about the calculations of the exchange interactions, as well as their computed values.

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AVAILABILITY OF DATA

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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