Prediction of Interesting Ferromagnetism in Janus Semiconducting Cr$_2$AsP Monolayer

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1. Introduction

Spintronic device using the spin degree freedom of electrons has sparked tremendous interest over the past decades due to its lower power consumption, more incredible data processing speed, and higher integration densities.\(^{[1]}\) 2D magnetic materials provide new opportunities for spintronics and nanoscale spintronic devices. High performance spintronic devices, spintronic devices have superior performance. One of the practical routes to obtain the compatibility of electronic materials is the introduction of highly concentrated magnetic ions to make non-magnetic semiconductors magnetic, or even FM transition. With the development of spintronics materials, new magnetic materials with both magnetic and semiconducting properties have been realized by injecting transition metal ions into a binary semiconductor, contributing to the progress of spintronics. In recent years, Fe-doped semiconductors have received much attention as FM semiconductors because of their high Curie temperatures ($T_C$) and low power consumption, showing the potential use in high-speed spin devices. High $T_C$ ferromagnetism was also observed in Fe-doped InAs, from which n-type and p-type FM semiconductors can be prepared.\(^{[2]}\) Furthermore, it has been found that the doping of small amounts of magnetic elements such as Group II-VI,\(^{[3,4]}\) IV, and III-V into semiconductors.\(^{[5-7]}\) Specifically, the doped magnetic atoms replace cations or anions in the semiconductor unit cell, or the formation of defects in the studied system by defect techniques, which has led to the discovery of many new spintronics materials.\(^{[8,9]}\) Recently, we have identified several half-metallic materials by using transition metal elements to dope group III-V binary semiconductors.\(^{[10-24]}\) Sezã et al.\(^{[25]}\) investigated Mn-doped GaSb using the density functional theory method and found that the doped material has FM half-metallic properties. On the other hand, magnetic half-metallic materials made by doping have better compatibility compared with semiconductors and have shown high research and application value, so the research on this type of half-metallic materials have attracted increasing attention. Doping is a method of...

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/andp.202300163
DOI: 10.1002/andp.202300163
purposefully altering the properties of materials, which can be used to tune the performance of 2D materials and develop functional materials, thus expanding their application prospects. The addition of dopant atoms is an effective way of breaking the inherent symmetry of a crystal, resulting in the formation of a bandgap in the Brillouin zone. Studies have shown that doping of elements of the same period can change the properties of materials. For example, the antiferromagnetic (AFM) semiconductor VCl3 can be prepared as a ferromagnetic (FM) semiconductor by atomic replacement doping (dopant is S).\[26\] The same periodic element has similar chemical properties, and the substitution doping of the element can effectively adjust the carrier type of the system, thus potentially changing the properties of the system. Due to the narrow bandgap of monolayer Cr2AsP, we have selected Se, an element in the same period as As, for doping. This may generate distinct electronic properties compared to those of Cr2AsP, thus further enhancing its exceptional performance.

The modulation and control of spin ordering is a key issue for spintronic device applications. Mechanical strain is commonly considered an effective solution for regulating the electronic structure and magnetic properties of the 2D materials. The excellent mechanical flexibility of 2D magnets further demonstrates the feasibility of strain engineering.\[27,28\] The application of tunable biaxial strain to 2D materials is of great significance for the preparation of spintronic devices. 2D materials are more flexible, and strains can be generated by external manipulations, such as bending and electric fields.\[29–33\] For example, as the strain changes from 10% to -15%, the CrI3 monolayer undergoes a transition from semiconductor to metal.\[34\] Particularly, an AFM to FM transition occurs under a biaxial tensile strain of approximately 13% in MnPSe3.\[35\] Experimentally, applying tunable biaxial strain to 2D materials has also made significant progress.\[36\]

In this work, we investigated the electronic structures and the magnetic properties of the intrinsic, Se-doped and biaxial strain tuning Janus Cr2AsP monolayer by the density functional theory calculations. The results indicated that the Janus Cr2AsP monolayer is an FM semiconductor, which was consistent with previous study. After inducing substituted selenium (Se) dopants, Cr2As1-xSexP (x = 0.25, 0.50, 0.75) with wide bandgaps, show half-metallic ferromagnetism, indicating that Cr2As1-xSexP can be widely used in spintronic devices. Furthermore, we applied a biaxial strain range from -14% to 10% for monolayer Cr2AsP. When an approximately -10.7% compressive strain was applied to the Cr2AsP monolayer, it leads to an FM to AFM transition. Besides, the semiconductor of Cr2AsP becomes half-metal within a certain tensile or compressive strain. These studies first imply that the Janus Cr2AsP monolayer is a potential spintronic material.

2. Results and Discussion

The top and side views of Janus Cr2AsP monolayer are shown in Figure 1a, a sheet of Cr atoms is sandwiched between a sheet of As atoms and a sheet of P atoms. The optimized lattice constant is a = b = 4.24 Å with a Cr–Cr distance of 3.0 Å. 2 × 2 × 1 supercell was used to calculate the magnetic ground state of Cr2AsP monolayer, we selected one FM and three typical AFM configurations as shown in Figure 1a,d–f. We found that the ground state of Janus Cr2AsP monolayer was FM by comparing the energy differences between the FM configuration and the AFM configurations. Furthermore, the magnetic moment of each primitive cell

Figure 1. a) Top and side views of Janus Cr2AsP monolayer. b) Band structure and c) phonon spectra of Janus Cr2AsP. Four magnetic configurations of Cr2AsP: a) FM, d) AFM1, e) AFM2, f) AFM3, the red arrow represents spin-up and the blue arrow represents spin-down.
was about 6 $\mu_B$, and the local magnetic moment of a Cr atom was nearly 3.4 $\mu_B$. The band structure of Janus Cr$_2$AsP monolayer calculated by the PBE+U functional is shown in Figure 1b. And we also tested different U values and found that the selected U value ($U = 3$ eV) asin reference.Thevalencebandmaximum (VBM) is located at the Fermi level showing semiconductivity, which indicates that the Cr$_2$As$_{1-x}$Se$_x$P monolayer has an in-plane magnetization axis, and the exchange splitting bandgap is 0.15 eV, a more accurate value is calculated as 0.46 eV by using Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional. It is important to check the mechanical stability of Cr$_2$AsP by calculating the elastic constants. The calculated $C_{11}$, $C_{12}$, and $C_{44}$ are 35.14, 14.68, and 24.21 Nm$^{-1}$, respectively. The calculated elastic constants satisfy the Born criterion of stability$^{[37]}$: $C_{11}>0$, $C_{12}>0$, and $C_{11}$-$C_{12}$=0. Therefore, Cr$_2$AsP monolayer is mechanically stable. And as shown in Figure 1c, we also calculated the phonon dispersion relation, and the imaginary frequency was found to be absent. These results indicate that the Janus Cr$_2$AsP monolayer is dynamically stable.

In the study of spintronic devices, it is difficult to avoid dopants or defects, but the purposeful induction of dopants or defects can regulate the properties of 2D materials, which plays an important role in facilitating the preparation of spintronic devices. In this article, we investigated the Se-doped Cr$_2$AsP monolayer. We used 2 x 2 x 1 supercell to consider the replacement of As atoms in Cr$_2$AsP monolayer by one, two, and three Se atoms, and the ion-injected Se ratios are 25%, 50%, and 75%. We defined the x as the ion-injected Se ratios.

Table 1 shows the crystal parameters and properties of Cr$_2$As$_{1-x}$Se$_x$P ($x = 0.25$, 0.50, 0.75, 1.00). We can see that the equilibrium lattice constant for Cr$_2$As$_{0.75}$Se$_{0.25}$P, Cr$_2$As$_{0.50}$Se$_{0.50}$P, Cr$_2$As$_{0.25}$Se$_{0.75}$P, and Cr$_2$SeP monolayers are 8.48, 8.56, 8.71, and 8.85 Å, respectively. Then, we calculated the ground state magnetic order of Cr$_2$As$_{1-x}$Se$_x$P ($x = 0.25$, 0.50, 0.75, 1.00) by comparing the energy difference between FM and AFM configurations, and found that the FM energy of the materials after doping is lower, so all of Cr$_2$As$_{1-x}$Se$_x$P exhibit FM ground state. The electronic structures of Cr$_2$As$_{1-x}$Se$_x$P ($x = 0.25$, 0.50, 0.75, 1.00) were calculated in the FM ground state. As shown in Figure 2, Cr$_2$As$_{1-x}$Se$_x$P ($x = 0.25$, 0.50, 0.75, 1.00) show similar energy band structures, the spin-up channel crosses the Fermi level exhibiting metallic, the spin-down channel has band gap at the Fermi level showing semiconductivity, which indicates that they are fully spin-polarized half-metals. After doping, all of Cr$_2$As$_{1-x}$Se$_x$P ($x = 0.25$, 0.5, 0.75, 1.00) exhibit large half-metallic gaps and spin gaps, wide half-metallic gaps and wide spin gaps are the key half-metal parameters in spintronic applications. Herein, the half-metallic gaps of the Cr$_2$As$_{0.75}$Se$_{0.25}$P, Cr$_2$As$_{0.50}$Se$_{0.50}$P, Cr$_2$As$_{0.25}$Se$_{0.75}$P, and Cr$_2$SeP monolayers are 1.01, 1.05, 1.12, and 1.33 eV, respectively, which are larger than the reported in previous research on Mn$_3$PAs (0.68 eV)$^{[38]}$; the spin gaps are 2.09, 2.28, 2.51, and 2.76 eV, respectively. It can be noticed that the half-metallic bandgaps and spin bandgaps increase with the increase of the proportion of injected Se atom.

To further investigate the rationale for the half-metallic nature of this series of half-metallic ferromagnets, we calculated the total density of states (TDOS) and projected density of states (PDOS) of Cr$_2$As$_{1-x}$Se$_x$P ($x = 0.25$, 0.5, 0.75) in Figure S1 (Supporting Information). Since the electronic structure and magnetic properties of most materials are derived from intermetallic orbital $p-d$, $d-d$, and $s-p-d$ orbital hybridization, and the orbitals are also related to the electron configuration of each atom and the distance between the atoms. The valence electron configuration of Cr is 3$d^5$4$s^1$, the Se and As valence electron configurations are 4$s^2$4$p^4$ and 4$s^2$5$p$,$p^4$, the outermost 4$p$ orbit has four electrons and three electrons in Se and As. And the valence electron configuration of P is 4$s^3$5$p^1$, the outermost 3$p$ orbit has three electrons. By comparing the bond lengths and density of states diagrams among the atoms in the crystal, we believe that strong hybridization occurs between the electronic orbitals near the Fermi level and that the electronic hybridization occurs mainly between the transition metal Cr and As, Se, and P atoms. As shown in Figure S1 (Supporting Information), from the density of each atomic fractional wave state, it can be seen that the TDOS for Cr$_2$As$_{1-x}$Se$_x$P is mainly contributed by Cr-$d$ orbital electrons, while other electronic orbitals such as As-$p$, Se-$p$, and P-$p$ contribute less. We find that the spin-down states of Cr-$d$, As-$p$, and P-$p$ have overlapping densities of states around the bandgaps, so that there is $p$-$d$ orbital hybridization in the corresponding energy region, and a small amount of orbital hybridization between Cr-$d$ and Se-$p$ after doping with Se. The $p$-$d$ hybridization from the Cr-3$d$ state with the Se-4$p$ state may lead to a shift in Fermi level, with the spin-down energy band of Cr$_2$As$_{1-x}$Se$_x$P forming a bandgap at the Fermi level. From the band structures that the spin gap values increase with doping concentration, and from this change, it is clear that the $p$-$d$ hybridization between Cr-3$d$ and Se-4$p$ intensifies with increasing doping concentration, which is the main reason for the FM half-metallic properties of Cr$_2$As$_{1-x}$Se$_x$P. The Fermi level of Cr$_2$As$_{0.75}$Se$_{0.25}$P, Cr$_2$As$_{0.50}$Se$_{0.50}$P, and Cr$_2$As$_{0.25}$Se$_{0.75}$P is calculated to have shifted upward by 0.25, 0.22, and 0.20 eV, respectively, when compared to the density of states of the Cr$_2$AsP monolayer. The doped Cr$_2$AsP is thus transformed from a semiconductor to a half-metallic material.

Then, we calculated the magnetic anisotropy energy (MAE) for Cr$_2$AsP and Cr$_2$As$_{1-x}$Se$_x$P ($x = 0.25$, 0.5, 0.75). The MAE is defined as $E_{\text{MAE}} = E_x - E_z$, where $E_x$ and $E_z$ are the energies of the system with the magnetization direction parallel to in-plane direction (x axis) and out-of-plane direction (z axis). The MAE values of Cr$_2$AsP and Cr$_2$As$_{1-x}$Se$_x$P ($x = 0.25$, 0.5, 0.75) are -0.24, 1.02, 0.16, and 0.10 mev/unit cell, respectively. The calculations show that the Cr$_2$AsP monolayer has an in-plane magnetization axis, while the Cr$_2$As$_{1-x}$Se$_x$P ($x = 0.25$, 0.5, 0.75) magnetization axis
becomes out-of-plane after doping. Moreover, we can see that the MAE decreases with increasing doping concentration. Next, as shown in Figure S1 (Supporting Information), we analyze specifically the change in the magnetic axis due to hybridization. We can see that orbital hybridization between Cr-\( d \) and As-\( p \), Se-\( p \), P-\( p \) occurs near the Fermi level, which is responsible for the change of the magnetic axis from in-plane to out-of-plane. As the doping concentration increases, the hybridization of Cr-\( d \) and As-\( p \) gradually changes to that of Cr-\( d \) and P-\( p \). And the hybridization of Cr-\( d \) and Se-\( p \) gradually increases, which makes the MAE of the system decrease with increasing concentration. Finally, the calculated phonon dispersions in Figure S2 (Supporting Information), support their dynamical stability.

The \( T_c \) effectively determines the applicability of the material, which is a very important parameter for practical application. We carried out the Monte Carlo simulation to estimate the \( T_c \) of the Cr\(_2\)AsP and Se-doped Cr\(_2\)As\(_{1-x}\)Se\(_x\)P \( (x = 0.25, 0.5, 0.75) \) by using the Heisenberg model. The Figure 3 shows the behavior of the magnetism with \( T_c \). Our calculations show that the predicted \( T_c \) of Cr\(_2\)AsP is about 857 K, and the \( T_c \) of Se-doped Cr\(_2\)As\(_{1-x}\)Se\(_x\)P \( (x = 0.25, 0.5, 0.75) \) are about 386, 429, and 674 K. It is worth noting that the \( T_c \) decreases with increasing doping concentration, and the \( T_c \) values for the doped systems are all lower than monolayer Cr\(_2\)AsP. This implies that we can regulate the concentration of doping to manipulate the \( T_c \) of monolayer Cr\(_2\)AsP.

Next, we investigated the electronic and magnetic properties of Janus Cr\(_2\)AsP monolayer under the biaxial strain. The strain is defined as \( \varepsilon = \frac{a - a_0}{a_0} \), where \( a_0 \) and \( a \) are the lattice constant for
The transition of monolayer Cr$_2$AsP caused by elastic strain. We believe that the nearly -10.7% compressive strain of the Cr$_2$AsP monolayer can be achieved. Moreover, the distance of the two nearest-neighbor Cr atoms increases from 2.58 to 3.30 Å under biaxial strain from -14% to 10%. The exchange interaction among Cr-As(P)-Cr can be used to explain the FM to AFM transition in the Cr$_2$AsP monolayer. Because the nearest neighbor Cr-Cr distance gets shorter, the direct exchange dominates over superexchange. When a tensile strain is applied to Cr$_2$AsP, the Cr-Cr distance will become larger, and the bond angles of Cr-As(P)-Cr will be more closer to 90°, thus the system still exhibits FM state. As shown in Figure 5, when the compressive strain and tensile strain are added to -2% and 6%, it changes from semiconductor to half-metal. The half-metallic materials are conducting in one spin channel and insulating in another optional channel, which are 100% spin polarized around the Fermi level. The strained Cr$_2$AsP monolayer with half-metallicity has large spin bandgap that can effectively prevent spin leakage, becoming very important candidate materials in nanoscale spintronic devices. Elastic strain engineering can find more materials with better properties to promote the application of spintronics.

### 3. Conclusion

In summary, we have investigated the electronic structures and the magnetic properties of intrinsic, Se-doped, and biaxial strain tuning in the Cr$_2$AsP monolayer by using the first-principles calculations. On the one hand, we found that the Cr$_2$AsP monolayer was an FM semiconductor with an exchange splitting of 0.15 eV. When the Se doping ratio is 25%, 50%, and 75%, the ground states of Cr$_2$As$_{1-x}$Se$_x$P ($x = 0.25, 0.5, 0.75$) were still FM. The Cr$_2$As$_{1-x}$Se$_x$P ($x = 0.25, 0.5, 0.75$) monolayers have the similar energy band structures, all exhibiting half-metallic properties. And Cr$_2$As$_{1-x}$Se$_x$P possess wide half-metallic bandgaps and spin bandgaps, which imply that they are more suitable for practical spintronic applications. Besides, our calculations showed that the predicted $T_c$ of Cr$_2$AsP was about 857 K, and the $T_c$ of Se doped Cr$_2$As$_{1-x}$Se$_x$P ($x = 0.25, 0.5, 0.75$) were about 386, 429, and 674 K. On the other hand, a biaxial strain from -14% to 10% was applied to the Cr$_2$AsP monolayer. The phase transition from FM to AFM occurred at -10.7% compressive strain for Cr$_2$AsP. When compressive strain was added to -2% or a tensile strain was up to 6%, the Janus Cr$_2$AsP monolayer undergoes a transition from semiconductor to half-metallic material. These results will possess potential applications in spintronics and motivate further experimental studies.

### 4. Experimental Section

The present calculations were performed by adopting the Vienna ab initio simulation package (VASP) based on the density functional theory (DFT). The generalized gradient approximation (GGA) functional of Perdew, Burke, and Ernzerhof (PBE) was used to investigate the exchange-correlation function. It used the spin-dependent GGA plus Hubbard U to deal with the strongly correlated interactions of the transition metal Cr element, the Hubbard U term of 3 eV for Cr was used. The plane-wave cutoff energy was chosen to be 500 eV. Monkhorst-Pack special k-point mesh of 9 × 9 × 1 for the Brillouin zone integration. The convergence criteria for energy and force during the relaxation of the structures were
set to $10^{-6}$ eV and 0.01 eVÅ$^{-1}$. The vertical vacuum spacing of 20 Å was used to eliminate interactions between images. Phonon dispersions of the studied materials were obtained using the phonopy code based on the density functional perturbation theory (DFPT).\[51\]

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
This work was supported by the NSFC (No.21873017), the Innovation Capability Improvement Project of Hebei province (22567605H), the Natural Science Foundation of Hebei Province of China (No. B2021203030), the Science and Technology Project of Hebei Education Department (No. QN2023177). The numerical calculations in this paper have been done on the supercomputing system in the High Performance Computing Center of Yanshan University.

Conflict of Interest
The authors declare no conflict of interest.

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

Keywords
2D materials, electromagnetic properties, ferromagnetism, first-principles, Se-doped Cr$_2$AsP, strain

Figure 5. Band structures for Janus Cr$_2$AsP monolayer under the biaxial strain.a) -2%; b) -6%; c) -10%; d) 2%; e) 6%; f) 10%.

Received: April 12, 2023
Revised: June 4, 2023
Published online: September 14, 2023

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