Magnetisms in \( p \)-type monolayer gallium chalcogenides (GaSe, GaS)

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Magnetisms in \( p \)-type monolayer GaX (X=S,Se) is investigated by performing density-functional calculations. Due to the large density of states near the valence band edge, these monolayer semiconductors are ferromagnetic within a small range of hole doping. The intrinsic Ga vacancies can promote local magnetic moment while Se vacancies cannot. Magnetic coupling between vacancy-induced local moments is ferromagnetic and surprisingly long-range. The results indicate that magnetization can be induced by hole doping and can be tuned by controlled defect generation.

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I. INTRODUCTION

The researches of two-dimensional (2D) materials have attracted extensive interest recently. A variety of 2D crystals have been discovered which exhibit remarkable properties. These include graphene\(^1–4\), a gapless semiconductor, single-layer boron nitride\(^5,6\), a wide-gap insulator, and monolayer transition metal dichalcogenides, a class of direct band-gap semiconductor with exotic spin and pseudospin physics\(^7–10\). Semiconducting 2D crystals are of interest as the next generation host materials for future electronic applications exploiting internal degrees of freedom of carriers such as spin in addition to the charge\(^11\). An indispensable element of spin-based electronics is magnetism which can play the role of nonvolatile memory. Realizing robust magnetic semiconductor has been a long-term effort in the exploration of semiconductor-based spintronics\(^12\). The conventional approach to introduce magnetism in semiconductors is by doping transition metal elements\(^13–16\). Recently, unexpected high-temperature ferromagnetism have been reported in \( d^0 \) systems\(^17–22\), which do not involve the partially occupied \( d \) or \( f \) orbitals. In carbon structures, first-principles calculations have also shown that magnetism can be induced by nonmagnetic defects\(^23–26\). While the origin of magnetism in these \( d^0 \) systems is not well understood, the large density of states at the band edge is considered to be the key for several materials\(^22\), which implies a new possibility for searching spintronic materials. In 2D crystals like BN, graphene and MoS\(_2\), first-principle calculations have also predicted that local magnetic moment can be induced by nonmagnetic impurities or vacancies\(^27–30\).

GaSe and GaS are stable layered semiconductors, formed by vertically stacked X-Ga-Ga-X sheets held together by van der Waals interactions, as shown in Fig. 1(a). They have attracted considerable interest because of their remarkable nonlinear optical properties\(^31–33\). Very recently, ultrathin GaS and GaSe nanosheets have been synthesized and experimentally studied\(^34,35\). Zolyomi et al. have performed first-principles calculations of GaX monolayers and found a sombrero dispersion near the top of the valence band\(^36\), which gives rise to a large density of states at the valence band edge (VBE).

Therefore, monolayer GaX can be a promising system to explore \( d^0 \) ferromagnetism in the 2D limit.

In this manuscript, we investigate the magnetism in hole-doped GaX monolayers using density functional theory calculations. We find that GaX monolayer becomes ferromagnetic with a small range of hole doping. In this range, the polarization energies first increases then decreases to zero. Under Se-rich condition, a Ga vacancy is more favorable, rendering the GaSe intrinsic \( p \) type. A S vacancy can be spontaneously introduced and makes GaS intrinsic \( n \) type. These are in agreement with the experiment\(^35\). The intrinsic Ga vacancies can promote the formation of local magnetic moments. We also find that the magnetic coupling between these defects is ferromagnetic and surprisingly long-ranged.

II. ELECTRONIC STRUCTURES AND HOLE-INDUCED MAGNETISM OF MONOLAYER GASE AND GAS

A. Computation method

Our density functional theory (DFT) calculations employ the projector augmented wave (PAW) method encoded in Vienna \textit{ab initio} simulation package (VASP)\(^37–39\), and the generalized-gradient approximation (GGA) for the exchange correlation functional\(^40\) is used. Throughout this work, the cutoff energy of 400 eV is taken for expanding the wave functions into plane-wave basis. The calculated lattice constants for monolayer GaSe and GaS are 3.817 and 3.627 Å, respectively. A \( 12 \times 12 \times 1 \) \( \Gamma \) centered k-point grids are used to sample the Brillouin zone for the primitive cell. In the hole doping calculation, \( 27 \times 27 \times 1 \) k-point grids are adopted. For the vacancy calculation, we adopt \( 4 \times 4 \) supercell to simulate the system with defects, which is large enough to avoid the interaction between the defects. A set of \( 3 \times 3 \times 1 \) \( \Gamma \) centered k-points is used for the defect calculation. A 15 Å vacuum layer is used in our calculation to avoid interaction between slab. The convergence for energy is chosen as \( 10^{-5} \) eV between two steps and the maximum Hellmann-Feynman force acting on each atom is less than 0.02 eV/Å for primitive cell GaX.
The formation energy of neutral vacancies in monolayer GaSe or GaS, $\Delta E_f$, is defined as,

$$\Delta E_f = E_t(nV_Y) - E_t + n\mu_Y$$

(1)

where $E_t(nV_Y)$ is the total energy of monolayer GaSe or GaS with $n$ Y (Y=Ga, Se, S) vacancies. $E_t$ is the energy of pristine monolayer GaSe or GaS and $\mu_Y$ refers to the chemical potential of detached X atom. $\mu_Y$ is obviously environment dependent. We consider two cases: Ga-rich and Se-rich or S-rich. In Ga-rich environment, $\mu_{Ga}$ is calculated from orthorhombic Ga crystal and $\mu_{Se}/S = \mu_{GaSe}/GaS - \mu_{Ga}$, where $\mu_{GaSe}$ ($\mu_{GaS}$) is the chemical potential of a GaSe (GaS) unit in 2H-GaSe (2H-GaS) crystal. In Se-rich or S-rich environment, $\mu_{Se}$ ($\mu_{S}$) is calculated from hexagonal Se (orthorhombic S) crystal and $\mu_{Ga} = \mu_{GaSe}/GaS - \mu_{Se}/S$.

### B. Electronic structures and hole-induced magnetism for Monolayer GaSe and GaS

The band structures of monolayer GaSe and GaS with spin orbit coupling are presented in Fig. 2 and Fig. 3, respectively. Both monolayer GaSe and GaS are semiconductors with indirect bandgaps, which are just slightly lower than the direct bandgaps. The bandgaps of monolayer GaSe and GaS are 2.1 eV and 2.5 eV, respectively. The bottom of the conduction band is mainly attributed to Ga $s$ orbital, hybridized with $p_x$ and $p_y$ orbitals of X (X=Se, S). The top of the valence band is primarily attributed to X $p_z$ orbitals, hybridized strongly with Ga $p_z$. Due to this orbital character, the band near $\Gamma$ point shows rather flat dispersion, which induces a Van Hove singularity near the valence band edge. The density of states (DOS) of GaSe near VBE is twice of that of GaS, indicating that the band of GaSe is flatter. The spin orbital coupling yields the valence band splitting by 10 meV at the maximum point in $\Gamma$-M direction for GaSe while this splitting for GaS is 4 meV.

In the band-picture model, spontaneous ferromagnetism appears when the relative exchange interaction is larger than the loss in kinetic energy, that is, when it satisfies the "Stoner Criterion": $D(E_f)J > 1$, where $D(E_f)$ is the DOS at the Fermi energy $E_f$ and $J$ is the strength of the exchange interaction$^{22,44}$. As the DOS near VBE is rather large, we can dope hole into the system to increase $D(E_f)$. We check the stability of magnetization by calculating the polarization energy $E_p$, which is defined as the difference between the nonspin-polarized and spin-polarized states. From Fig. 4, we find that the ground state of the monolayer GaSe is ferromagnetic when the hole concentration is in the range from 0.02 to 0.18 per unit cell. While, the monolayer GaS becomes ferromagnetic in a wider range of hole concentration and the maximum hole concentration is 0.28 per unit cell from Fig 4. When the hole concentration is not in this range, $D(E_f)$ is not large enough and the "Stoner Criterion" is not satisfied, thus the system is nonmagnetic. The critical hole concentration for GaSe (0.18 hole per cell) corresponds to $1.24 \times 10^{14}$ cm$^{-2}$. The low hole concentration in the system can be easily achieved by electric carrier doping, which has been used to induce superconductivity in MoS$_2$.$^{42,43}$ The polarization energies in both cases first increase then decrease to zero with the increasing hole doping. The magnetic moment shows a linear relationship with hole concentration when the system is ferromagnetic. At optimal doping, polarization energies are 0.74 meV and 2.33 meV per cell for Ga$_2$Se$_2$ and Ga$_2$S$_2$, respectively. The corresponding magnetic moments are 0.12 and 0.20 $\mu_B$ per cell.

### III. THE VACANCY IN MONOLAYER GASE AND GAS

According to Ref. 35, the single-sheet GaS and GaSe show typical n-type and p-type conductance, respectively. These may be the consequence of intrinsic vacancies. The calculated formation energies of vacancies in both cases are shown in Table I. In Se rich condition, the formation energy of a Ga vacancy is slightly less than that of a Se vacancy. Thus, a Ga vacancy is more favorable. This may explain the observed p-type conductance in GaSe. However, a Se vacancy is more favorable under Ga-rich condition. In GaS, the formation energies of a S vacancy are always negative under both conditions, indicating that S vacancies can be spontaneously introduced. Therefore, GaS is expected to be an intrinsic n type, which is in agreement with experiment. The formation energy of a Ga vacancy in GaSe is less than that in GaS. In order to get magnetization, we need to dope hole into above systems, thus only Ga vacancies are discussed in the following.
TABLE I: The formation energies of vacancies in monolayer GaSe and GaS under Ga-rich and Se-rich or S-rich conditions. \( V_{2Ga} \) denotes the two bonded Ga vacancy.

| Environment   | \( V_{Ga} \) | \( V_{2Ga} \) | \( V_{Se} \) | \( V_{Ga} \) | \( V_{2Ga} \) | \( V_{S} \) |
|---------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Ga rich       | 2.97         | 5.72         | 1.53         | 4.29         | 7.35         | -3.03        |
| Se or S rich  | 1.81         | 3.40         | 2.69         | 2.93         | 4.64         | -0.32        |

A. one Ga vacancy

After relaxation, Se and S atoms surrounding the neutral Ga vacancy move outward while the Ga under the vacancy moves downward. Thus, the Se-Ga bond lengths in the top and the bottom layer shrink from 2.50 Å to 2.41 Å and 2.37 Å in monolayer GaSe, respectively. In monolayer GaS, the bond lengths of Ga-S in top and the bottom layer shrinks from 2.35 Å to 2.25 Å and 2.22 Å, respectively. Fig. 5(a) shows the spin-resolved density of states (DOS) of the 4×4 supercell containing one Ga vacancy. A local moment of 1.0 \( \mu_B \) is formed due to the spin polarization in both cases. The magnetic moments mainly locate at the three Se or S atoms surrounding the Ga vacancy, shown in Fig. 6.

The formation of the local moment by Ga vacancy can be understood: The point group of monolayer GaX (X=Se, S) with a Ga vacancy is \( C_{3v} \). A Ga vacancy leaves five unpaired electrons on the X and Ga atoms surrounding the vacancy. Under the influence of the crystal field, defect states associated
FIG. 4: (Color online) The top panel and bottom panel show Magnetic moments and polarization energy of hole-doped monolayer GaSe and GaS, respectively.

with Ga vacancy are split into two singlet $a_1$, $a_2$ and a doublet $e$. The fully occupied $a_1$ state lies below the fermi level while $a_2$ is empty. Due to spin polarization, the $e$ state splits into spin-up $e_{\uparrow\uparrow}$ and spin-down $e_{\downarrow}$. Therefore, a Ga vacancy should result in a net local moment of $1 \mu_B$. The polarization energies $E_p$ are about 0.03 eV per defect site in GaSe and GaS.

B. Two Ga vacancies

With the vacancy of two bonded Ga, the mirror symmetry is restored in the system. The total magnetic moment, mainly localized at the Se atoms surrounding the vacancy, is $3.95 \mu_B$ without relaxation. However, the magnetic moment vanishes after relaxation due to the movement of Se atoms surrounding the Ga vacancy. The length of Ga-Se bonds in both layers shrinks to 2.38 Å. The spin-resolved density of DOS of the $4 \times 4$ supercell containing two Ga vacancies shown in Fig. 5(b). A local moment of $1.0 \mu_B$ is formed due to the spin polarization in both cases.

Two Ga vacancies leave eight unpaired electrons on the surrounding Se atoms. Before relaxation, under the crystal field defect states are split into four singlets $a_1$, $a_1'$, $a_2$, $a_2'$ and two doublets $e_1$, $e_2$, $a_1$ and $a_1'$ are fully occupied while $a_2$ and $a_2'$ are empty. The remaining four electrons occupied $e_{\uparrow\uparrow}$ and $e_{\downarrow\downarrow}$ due to large spin splitting. Thus, a net moment of $4 \mu_B$ is formed. However, the energy of the $e_2$ states increases after relaxation. The energy of $e_{\uparrow\uparrow}$ is higher than that $e_{\downarrow\downarrow}$. Therefore, the $e_1$ states are fully occupied, which results in a nonmagnetic state after relaxation.

IV. THE EXCHANGE COUPLING BETWEEN VACANCIES

To investigate the magnetic coupling between these hole-induced magnetic moments, we employ the $8 \times 4$ supercell with two vacancies in each subsupercell of $4 \times 4$. Two stable magnetic configurations (ferromagnetic and antiferromagnetic) can be obtained depending on the initial moments in...
TABLE II: The energy difference between the FM and AFM state $\Delta E=E_{AFM}-E_{FM}$ for four vacancy configurations. $d$ is the distance between the two vacancies.

| System | $E_M$ (meV) | $J$ (meV) | $T_C$ (K) |
|--------|-------------|-----------|-----------|
| GaSe   | 26.1        | 6.5       | 50        |
| GaS    | 13.4        | 3.4       | 26        |

the calculation. The Heisenberg type of spin coupling is: $H = -\sum_{<ij>} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$. Considering nearest-neighbor interactions, the magnetic energy of the FM state is: $E_{FM} = -6JS^2$. For the case of AFM states, four nearest-neighbors have spins parallel and two have spins antiparallel. Thus, the magnetic energy is: $E_{AFM} = 2JS^2$. The energy difference of AFM and FM states is $E_M = E_{AFM} - E_{FM} = 4JS^2$. Table II shows the energy difference $E_M$ and exchange coupling parameter $J$ for monolayer GaSe and GaS. In FM states, the total magnetic moment is always 2 $\mu_B$ for both cases. From Table II, we find that FM states has a lower energy than the AFM states.

The observed FM state can be explained by kinetic exchange mechanism\(^{21}\). For the isolated Ga vacancy, the majority spin ($e^{-}$) is fully occupied, where the minority spin ($e^{+}$) is partially occupied. Therefore, the parallel spin alignment allows for the virtual hopping between the two defects states, which can lower the kinetic energy of the system. This hopping, however, is not allowed if the spin alignment is antiparallel.

We estimate the Curie temperature ($T_C$) based on the mean-field theory and Heisenberg model using the equation,

$$k_B T_C = \frac{2}{3} J_0,$$

where $J_0$ is the onsite exchange parameter reflecting the exchange field created by all the neighboring magnetic moments. The estimated $T_C$ for monolayer GaSe and GaS are 50 and 26 K, respectively. The exchange coupling between local moment in GaSe is almost twice of that in GaS. It indicates the impurity state in GaS is more localized than that in GaSe.

V. CONCLUSION

In summary, we perform DFT calculations to investigate the electronic structure of monolayer GaX. We find that monolayer GaSe(GaS) is a semiconductor with an indirect bandgap of 2.1(2.5) eV and there is a Van Hove singularity near the valence band edge. The monolayer GaX becomes ferromagnetic with small hole doping, which may be achieved by electric carrier doping in experiment. Under Se-rich condition, GaSe is intrinsic $p$ type induced by Ga vacancies. For GaS, a $S$ vacancy can be spontaneously introduced, rendering GaS $n$ type. Ga vacancies can induce local moment around this defect. The coupling between the states of two Ga vacancies is ferromagnetic and extremely long-range.

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(2007).

21 P. Dev, Y. Xue and P. H. Zhang, Phys. Rev. Lett. 100, 117204 (2008).

22 H. W. Peng, H. J. Xiang, S. H. Wei, S. S. Li J. B. Xia and J. B. Li, Phys. Rev. Lett. 102, 017201 (2009).

23 K. Kusakabe and M. Maruyama, Phys. Rev. B 67, 092406 (2003).

24 Y.-H. Kim, J. Choi, K. J. Chang, and D. Tomanek, Phys. Rev. B 68, 125420 (2003).

25 J. A. Chan et al., Phys. Rev. B 70, 041403 (2004).

26 A. N. Andriotis, R. M. Sheetz, E. Richter, and M. Menon Europhys. Lett. 72, 658 (2005).

27 R. F. Liu and C. Cheng, Phys. Rev. B 76, 014405 (2007).

28 O. V. Yazyev and L. Helm, Phys. Rev. B 75, 125408 (2007).

29 Y. Zhang, S. Talapatra, S. Kar, R. Vajtai, S. K. Nayak, and P. M. Ajayan, Phys. Rev. Lett. 99, 107201 (2007).

30 Y. G. Zhou, P. Yang, H. Y. Zu, F. Gao and X. T. Zu, Phys. Chem. Chem. Phys., 15, 10385 (2013).

31 A. Segura, J. Bouvier, M.V. Andres, F. J. Manjon, and V. Munoz. Phys. Rev. B, 56, 4075 (1997).

32 S. Nusse, P.H. Bolivar, H. Kurz, V. Klimov and F. Levy, Phys. Rev. B, 56, 4578 (1997).

33 K. Kato, N. Umemura, Optics Letters, 36, 746 (2011).

34 P.A. Hu, Z.Z. Wen, L.F. Wang, P.H. Tan, K. Xiao, ACS Nano, 6, 5988 (2012).

35 D. J. Late, B. Liu, J.J. Luo, A.M. Yan, H.S.S.R. Matte, M. Grayson, C.N.R. Rao, V.P. Dravid, Advanced Materials, 24 3549 (2012).

36 V. Zolyomi, N. D. Drummond and V. I. Falko, Phys. Rev. B 87, 195403.

37 G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).

38 G. Kresse and J. Furthmuller, Comput. Mater. Sci. 6, 15 (1996).

39 G. Kresse and J. Furthmuller, Phys. Rev. B 54, 11169 (1996).

40 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

41 E. C. Stoner, Proc. R. Soc. A 165, 372 (1938); 169, 339 (1939).

42 K. Taniguchi, A. Matsumoto, H. Shimotani and H. Takagi, Appl. Phys. Lett. 101, 042603 (2012).

43 J. T. Ye, Y. J. Zhang, R. Akashi, M. S. Bahramy, R. Arita and Y. Iwasa, Science 338, 1193(2012).

44 T. Cao, Z. L. Li, S. G. Louie, arxiv:1409.4112.