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Gate modulation of the long-range magnetic order in a vanadium-doped WSe\(_2\) semiconductor

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**ABSTRACT**

Generation of spin-charge coupling by doping semiconductors with magnetic dopants is a promising approach for gate-tunable spintronic devices without applying an external magnetic field. Here, we demonstrate that the magnetic orders in V-doped WSe\(_2\) can be modulated by tuning carrier densities using *ab initio* calculations. We found that at a low V-doping concentration limit, the long-range ferromagnetic order is enhanced by increasing the hole density. In contrast, this long-range ferromagnetic order is suppressed at high electron density by compensating the p-type V dopant, originating from the strong localized antiferromagnetic coupling between V and W atoms and between V and Se atoms. The hole-mediated long-range magnetic exchange is \(\sim 70\) meV, thus strongly suggesting the ferromagnetism in V-doped WSe\(_2\) at room temperature. Our findings on strong coupling between charge and spin order in V-doped WSe\(_2\) provide plenty of room for multifunctional gate-tunable spintronics.

Magnetic semiconductors, which reveal the electrical manipulation of magnetic properties, are expected to be candidates for low-power spintronic devices. Although the antiferromagnetic semiconductors and insulators are promising for high-speed spin transport devices,\(^{17-20}\) the existence of room-temperature ferromagnetic semiconductors remains controversial for either intrinsic or diluted ferromagnetic semiconductors.\(^{10-13}\) Recently, room-temperature ferromagnetic domains in V-doped WSe\(_2\) have been observed.\(^{14}\) The proposed mechanism of the long-range ferromagnetic order is Ruderman–Kittel–Kasuya–Yosida or Zener interaction, where the free holes play a role as a medium to establish the interaction between V atoms.\(^{3,16}\)

One primary feature of carrier-mediated ferromagnetic semiconductors is their capability of manipulating the magnetic properties or spin states through electrons by modulating the carrier density or external electric field.\(^{17-20}\) This allows for multifunctional spintronic devices to be realized.\(^ {12,21}\) The long-range magnetic order has been previously proposed,\(^ {13}\) but there is no study for the carrier-modulated magnetic properties in V-doped WSe\(_2\). Here, we investigate the response of the magnetic properties of V-doped WSe\(_2\) with different electron–hole densities introduced by carrier injection using density functional calculations. We found that the long-range ferromagnetic order can be modulated by changing the carrier density of V-doped WSe\(_2\). Furthermore, fully compensated electron doping can completely suppress the ferromagnetic order, originating from strong localized antiferromagnetic coupling of V–W atoms and V–Se atoms.

The band structure of V-doped WSe\(_2\) with spin–orbit coupling (SOC) was calculated using the Quantum Espresso code.\(^ {22}\) Projector-augmented wave potentials were used with a cut-off...
energy of 30 Ry,
the convergence test for which was confirmed by considering the band order.
To describe the strong correlation of the $d$ electron, the GGA+U method with $U = 3$ was used for the vanadium atom. The initial spin state is induced along the $z$ direction. Validation of the band structure calculation was confirmed in our previous study using scanning tunneling spectroscopy and a field-effect transistor. To investigate the effect of carriers, a number of charges were introduced to the supercell with a compensating jellium background to avoid the divergences. With a $8 \times 8 \times 1$ supercell, the carrier concentration in our study is in the range from $-3.2 \times 10^{13}$ to $3.2 \times 10^{13}$, which corresponds to charges from $-2e$ to $+2e$.

Figure 1(a) depicts the band structure of pure WSe$_2$ including spin–orbit coupling (SOC), which reveals a bandgap of 1.3 eV with the Fermi level located in the middle of the bandgap. The density of states (DOS) corresponding to the magnetic quantum number $m_{j=5/2} = -1/2$ (red) and $m_{j=5/2} = +1/2$ (blue) [the right panel of Fig. 1(a)] manifests an equal number of DOSs between two magnetic quantum states, implying the non-magnetic characteristics of pristine WSe$_2$. We mainly focus on the analysis of the $j = 5/2$ state since the contribution of the $j = 3/2$ state is far below the valence band edge (see the supplementary material, Figs. S1 and S2). By contrast, the V-doped WSe$_2$ band structure [Fig. 1(b)] manifests the Fermi level shifted to inside the valence band, ensuring the p-type doping effect in vanadium. In addition, a discrepancy in the DOS between $m_{j=5/2} = -1/2$ and $m_{j=5/2} = +1/2$ in the W site is clearly observed, thereby indicating the presence of spin-polarized states. Correspondingly, the spin-polarized states are clearly revealed in the DOS of the V site with a high magnitude [right panel of Fig. 1(b)]. The total magnetization of the W atoms far from the V site is $\sim 0.003 \mu_B$, which is lower than $\sim 1.077 \mu_B$ of the V atom.

To investigate the possibility of the gate-tunable magnetic properties of V-doped WSe$_2$, the charge is injected into the system. Figure 1(c) shows the total DOS of V-doped WSe$_2$ with different injected carrier densities. Because of the p-type doping effect of the V atom, free holes are clearly revealed on the top of the valence band in the V-doped WSe$_2$ monolayer. The Fermi level is shifted deeper inside the valence band with the hole injection. By contrast, the Fermi level is shifted toward the conduction band edge with electron injection. Interestingly, the Fermi level is shifted to the middle of the bandgap in V-doped WSe$_2$ when a single electron per $8 \times 8$ supercell is injected, indicating that the acceptor state of the V atom is completely filled. In addition to the shifting of the Fermi level, the band structure is also significantly modified with electron injection,

![Image](https://example.com/image.png)
whereas it remains nearly unchanged with hole injection. We later discuss the band structure of electron injection.

Since the long-range ordering in V-doped WSe$_2$ is mediated by free holes,\textsuperscript{15,16} investigating the changes in magnetic properties with different carrier densities is intriguing. The spin density in real space is calculated by injecting one hole [Fig. 2(a)] and one electron in the 8 × 8 supercell [Fig. 2(b)]. The isosurface of 0.0001 $\mu$B/Å$^3$ of the spin density (top panels) and projected total magnetic moments along the $z$ direction (bottom panels) are shown, respectively. Large ferromagnetic moments are clearly manifested at the V and W sites near the V atom. The long-range magnetic order is still maintained with hole injection, implying the existence of a ferromagnetic moment on the W atoms far from the V site [blue spots in Fig. 2(a)]. In contrast, the ferromagnetic moment at the W atoms far from the V site is completely suppressed for one electron injection, whereas high magnetic moments are still present on the V and W/Se atoms near the V site. The magnetic state is antiferromagnetic with a zero net magnetic moment of the supercell. The net magnetic moment of the W atoms far from the V site disappears, as shown in Fig. 2(b), indicating a local antiferromagnetic state by the V–Se–W complex without free holes.

Figure 3 shows the exchange energy, which is defined as the energy difference between the magnetic and non-magnetic states, and the corresponding total magnetic moments of V-doped WSe$_2$ with different injected carrier densities. The exchange energy becomes stronger when holes are injected, and the ferromagnetization accumulated near V atoms is enhanced. This implies that the magnetic moment is modulated with carrier density, which is the concrete evidence of the hole-mediated long-range spin interaction induced by the hybridization between the impurity levels of V atoms and valence band edge of WSe$_2$.\textsuperscript{15,16} At a very high hole density, hole carriers are screened, thereby reducing the total ferromagnetic moment. However, the exchange energy becomes weaker with electron injection, and the magnetic moment approaches nearly zero at a higher electron density, which manifests the tendency of an antiferromagnetic state (e.g., a localized spin state). Indeed, localized antiferromagnetic hybridization for V–W atoms and W–Se atoms emerges at the charge compensation point at which the number of injected electrons ($-1e$) is equal to that of intrinsic holes induced by V atoms.

To confirm the presence of the antiferromagnetic coupling, the magnetic moments located at each atom are calculated (Table I). The magnetic moments of W sites near the V atoms have the opposite sign (spin-down) of that at the V site (spin-up) owing to their strong local exchange interaction, which is distinct from all spin-up (ferromagnetism) configurations in the high hole injection state (+2e). At the charge compensation point, the ferromagnetic moment (spin-up) of the W atoms far from V is diminished. Meanwhile, the antiferromagnetic moment (spin-down) of the W atoms near the V sites are enhanced. Furthermore, the spin-up magnetic moment of the V atoms is reduced, thereby facilitating the formation of the antiferromagnetic state. The magnetic moment located at the Se sites is more narrowly localized than that at W sites. There is no magnetic moment located at Se atoms farther than 7 Å from the V site.

It is intriguing to estimate the strength of the interaction energy mediated by free holes. The gained magnetic interaction energy involves three components: (i) localized spin formation energy produced by strong hybridization in d–p–d orbitals of V–Se–W atoms (e.g., direct, super, or double exchanges) and long-range interaction energy between (ii) localized spins and free holes and (iii) V and V atoms via free holes. The hole-mediated long-range interaction energy can be estimated by the exchange energy difference of the systems with and without holes (as indicated by the arrow in Fig. 3), which is ~70 meV. This value is much larger than 25 meV of the thermal energy at 300 K, thus explaining the existence of the long-range ferromagnetic order in V-doped WSe$_2$ at room temperature.\textsuperscript{14}

![Figure 2](image_url)

**FIG. 2.** Isosurface (top) and projected magnetic moments (bottom) along the c axis in the cases of injecting (a) one hole and (b) one electron. This isosurface value is 0.0001 $\mu$B/Å$^3$. The color map range is from −0.0007 $\mu$B/Å$^3$ to 0.0007 $\mu$B/Å$^3$ for spin-down and spin-up states, respectively.


**Figure 3** Exchange energy and net magnetic moments of V-doped WSe$_2$ with different carrier doping densities and the corresponding schematic models for the magnetic interaction through free holes. The carrier compensation point is indicated by the red circle. The red and blue atoms in the schematics represent the respective doped and host atoms. The yellow and red wave-like functions indicate the respective localized and free-hole spin densities with the corresponding spin magnetic moment (blue and white arrows).

Figure 4 depicts the antiferromagnetic band structure of V-doped WSe$_2$ doped with one electron. The number of bands decreases compared to the ferromagnetic states as an inherent antiferromagnetic state. In addition, the empty doping state near the conduction band edge, which is present in the ferromagnetic state, disappears in the antiferromagnetic band structure. The projected DOS of the d orbital of the V atom is shown in Fig. 4(b). The contribution of the d orbital in the V atom to the strong hybridization states near the valence band is retained, which is confirmed by the large DOS of V at that energy range. The spin polarization in the V atom is conserved with a smaller absolute magnetic moment as compared to when no carrier injection is conducted (see Table I). Interestingly, the DOS of W atoms far from the V site [Fig. 4(d)] is still spin-polarized despite a zero net magnetic moment. This implies the presence of a long-range d–d hybridization between the V and W atoms even without free holes in the system. This long-range interaction is completely different from the carrier-mediated Zener type (kinetic p–d exchange). Instead, it is rather similar to the secondary super-exchange interaction proposed by the Katayama–Yoshida model. However, the method to distinguish between the degrees of long-range order between the d–d and p–d hybridizations remains unresolved and should be addressed in a future study.

We note that the required electron density to fully compensate holes for 8 × 8 V-doped WSe$_2$ (1.6 at. % of V) is $\sim 1.6 \times 10^{13}$ cm$^{-2}$, which can be fully compensated by the normal SiO$_2$ or high-k oxide gates. Furthermore, the V-doping concentration can be reduced to this critical electron density, which is validated by our calculation at a V concentration of 1 at. % (10 × 10 supercell).

**Table I.** Magnetic moments accumulated at the V and W atoms with different carrier densities. W$_n$ and Se$_n$ are the W and Se atoms far from the V site with different distances. Charge $-\cdot$ $+\cdot$ refers to the electron (hole).

| Distance from the V site (Å) | V | Sc$_1$ | Sc$_2$ | Sc$_3$ | Sc$_4$ | W$_1$ | W$_2$ | W$_3$ | W$_4$ |
|-----------------------------|---|--------|--------|--------|--------|-------|-------|-------|-------|
|                             | 0 | 2.47   | 4.13   | 7.02   | 10.14  | 3.28  | 6.55  | 9.83  | 13.11 |
| Magnetic moments ($\mu_B$)   | Charge $-\cdot$ | 0.459  | $-0.020$ | 0.000  | 0.000  | $-0.032$ | 0.000 | 0.000 | 0.000 |
|                             | Charge 0          | 1.077  | $-0.034$ | 0.006  | 0.000  | $-0.017$ | 0.007 | 0.004 | 0.003 |
|                             | Charge $+\cdot$   | 1.175  | $-0.035$ | 0.006  | 0.001  | $-0.002$ | 0.009 | 0.005 | 0.004 |
|                             | Charge $+2$       | 1.189  | $-0.035$ | 0.006  | 0.001  | 0.000  | 0.003 | 0.007 | 0.002 | 0.001 |
In conclusion, the long-range ferromagnetic order in V-doped WSe$_2$ is modulated by carrier injection. Charge injection can modulate both the exchange energy and net magnetic moment. More interestingly, the transition to the antiferromagnetic from the ferromagnetic state is possible when carriers are fully compensated. Our prediction demonstrates the gate-tunable magnetic properties of diluted magnetic 2D semiconductors, thus providing a better understanding of the V-doped WSe$_2$ system.

The supplementary material for the band structure of the primitive cell for pristine WSe$_2$ has been provided.

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DATA AVAILABILITY

The data that support the findings of this study are available within this article (and its supplementary material).

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