First-Principles Study of the Effect of Native Defects on Spin Polarization and Exchange Coupling Interaction in Semimetal V₃O₄

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ABSTRACT: We use first-principles calculations to investigate the mechanism of the effect of native defects on the spin polarization and exchange coupling interaction in the V₃O₄ semimetal material. Our results reveal that, in contrast to other neutral defects, V vacancy defects in V₃O₄ at A/B sites are in favor of higher spin polarization degrees and lower defect formation energies. Compared to ideal V₃O₄, the V vacancy defects at A/B sites cause slightly lower spin polarization degrees but much higher exchange coupling interactions. Our results suggest an effective route to mediate the spin polarization and exchange coupling by defect engineering, which promotes the applications of the V₃O₄ semimetal material in spintronics.

1. INTRODUCTION

Because of the large spontaneous spin splitting of bands around Fermi energy, spintronics devices exhibit a variety of unique spin-dependent optical and transport properties.⁴ Among these materials, half-metallic ferromagnets with an ultra-high spin polarization degree (∼100% theoretically) stemming from the existence of only one-spin direction at the Fermi level have excellent prospects for spintronic devices.⁴⁻⁷

Vanadium oxides have attracted extensive attention for their unique electrical properties because of the prolific valence state of vanadium ions.⁸⁻⁹ It is interesting that almost all of the binary vanadium oxides can be expressed using a simple formula: VₙO₂ⁿ⁻¹ (n is an integer ≥ 1) or VₙO₂ⁿ+₁ (n is an integer ≥ 2), while V₃O₄ is an exception, because of the lack of an identified integer to confirm the above simple formula.⁸⁻¹⁰ There are few reports on the magnetic property of V₃O₄ in contrast to other vanadium oxides with VₙO₂ⁿ⁻¹ and VₙO₂ⁿ+₁ formulae, such as VO, V₂O₃, and V₂O₅. As displayed in Figure 1a, cubic V₃O₄ is an isomorphism of Fe₃O₄, which has an inverse spinel structure of AB₂O₄. As shown in Figure 1b, the octahedral six-coordinated B sites in the V₃O₄ structure, twice as abundant as A sites, are equally occupied by V³⁺ (3d² state) and V²⁺ (3d³ state), thereby in favor of high spin configuration via t²₂g↑−t²₂g↓ respectively; whereas the tetrahedral four-coordinated A sites are occupied by the remaining V³⁺ with the 3d² state in favor of smaller spin configuration via t¹₈g↑. Therefore, the different spin configurations of vanadium ions at different sites would result in a half-metallic state in the cubic V₃O₄ structure. As reported by Xiao et al., the first-principles density functional theory (DFT) calculation results indicated...
that V_3O_4 was half-metallic and the ultrasmall V_3O_4 quantum dots with an average size of 4.8 nm obtained via a facile solvothermal method displayed ferromagnetism in the temperature range from 16 to 32 K and exhibited superparamagnetic behavior above 32 K with negligible remnant magnetization and coercivity in hysteresis loops. However, the Curie temperature should be improved in view of the practical applications in spintronic devices and the impact of native defects on magnetic property of the V_3O_4 semimetal material is unclear.

Macroscopic ferromagnetism is determined by spin polarization, which further depends on the difference between the spin-up and spin-down DOS at the Fermi level. Curie temperature is determined by spin exchange coupling, which further depends on the difference in the total energies (ΔE) between antiferromagnetic (AFM) and ferromagnetic (FM) states. In addition, the native defects could mediate carriers and introduce defect energy levels near the Fermi level, which provides an effective method to alter the spin polarization and spin exchange coupling interaction. Furthermore, it has been a long-standing goal to mediate intrinsic ferromagnetism without clustering of the magnetic elements and magnetic second phases introduced by a magnetic transition-metal dopant, which has led to the idea of d⁰ ferromagnetism. Therefore, a complete understanding of the physics of the role of native defects in spin polarization and exchange coupling interaction of the V_3O_4 semimetal material provides an essential and effective method to mediate this d⁰ ferromagnetism and Curie temperature, which is a key element in the application of the V_3O_4 semimetal material in spintronics.

This paper reports on the underlying mechanism of the effect of intrinsic defects on the spin polarization and exchange coupling interaction in the V_3O_4 semimetal material using first-principles calculations. The spin-polarized density of states (DOS) of ideal cubic V_3O_4 and V_3O_4 with different intrinsic neutral defects are extensively studied to clarify the impact of neutral defects on the spin polarization in cubic V_3O_4. In addition, the formation energies of different neutral defects in O-rich and V-rich cubic V_3O_4 are calculated to investigate the most energetically favorable defects. To reveal the role of defects in mediating the exchange coupling interaction of the V_3O_4 semimetal material, we compare ΔE values between the AFM and FM states of defective V_3O_4 to those of the ideal V_3O_4. The crucial mechanism of the role of native defects in mediating the spin polarization and exchange coupling interaction of the V_3O_4 semimetal material would provide an effective route to mediate this d⁰ ferromagnetism and Curie temperature, promoting the applications of semimetal V_3O_4 in spintronics.

3. RESULTS AND DISCUSSION

The calculated DOS curves (Figure 1c) of the ideal cubic V_3O_4 demonstrate that the spin-down states display a broad band gap being insulating. Whereas the spin-up states being metallic exhibit no gap, and are fully polarized at the Fermi energy mainly originating from the 3d states of V atoms. The calculation results indicate that V_3O_4 exhibits a typical half-metallic character resulting from the difference between the spin-up and spin-down DOS at the Fermi level, resulting in a total magnetic moment of 7.00 μ_B per formula unit. Based on Bader charge analysis, the less electronegative V atoms lose 1.82–1.67 electrons per atom at A/B sites and the more electronegative O atoms obtain 1.29 electrons per atom. Thus, ideal V_3O_4 can be written as V(A)V(B)O_4 in view of the V atoms at B sites twice as abundant as A sites, and further can be written as V(A)+1.82(V(B)+1.67)O_4. Moreover, the larger average valence state of the V atom at the A site than that of the V atom at the B site illustrates that more electrons are transferred from the V atoms at A sites to the nearest neighbor O atoms than from the V atoms at B sites, which mainly results from the smaller V(A)–O bond length of 1.85 Å than the V(B)–O bond length of 2.05 Å to form a stronger chemical bond.

Eight V_3O_4 systems with native neutral defects under O-rich (Figure 2a–d) and V-rich (Figure 2e, f) conditions provide a further insight into the mechanism of the impact of native neutral defects on spin polarization in half-metallic V_3O_4: (a) a V(A) vacancy created by removing one V atom at the A site, denoted as the V(A) vacancy; (b) a V(B) vacancy created by removing one V atom at the B site, denoted as the V(B) vacancy; (c) one V atom at the A site replaced by an O atom denoted as the O_v(a) antisite; (d) one V atom at the B site replaced by an O atom denoted as the O_v(b) antisite; (e) an O vacancy created by removing one O atom, denoted as the O_v antisite; and (f) one O atom replaced by a V atom denoted as the O_v antisite.

For an in-depth understanding of the role of native neutral defects under O-rich conditions in modulating the spin polarization of half-metal V_3O_4, we calculate and compare the spin-polarized DOS of the four V_3O_4 systems with one native neutral V vacancy and O antisite defect at different V(A) and V(B) sites, as shown in Figure 3a–d. Theoretical calculations in Figure 3a demonstrate that one neutral V vacancy at the V(A) site introduces the half-occupied defect states in the spin-down channel in the original forbidden band gap close to the bottom of the conduction band mainly composed of V 3d orbitals, which decreases the difference in spin DOS between spin-up and spin-down near the Fermi level.
V$_3$O$_4$ system with one neutral V vacancy at the V(A) site has a smaller spin polarization degree with a smaller magnetic moment of 6.12 $\mu_B$ per formula unit. In the case of one neutral V vacancy at the V(B) site (Figure 3b), compared to the perfect V$_3$O$_4$ system, two impurity states appear in the original wide band gap below and above the Fermi energy in the spin-down channel, which results in the lower spin polarization degree near Fermi energy. The calculated magnetic moment of 6.11 $\mu_B$ per formula unit is slightly less than that of the neutral V vacancy at the V(A) site because of the more impurity states induced by the neutral V vacancy at the V(B) site in the original wide band gap near Fermi energy.

Next, the impact of the native neutral defects under V-rich conditions on the spin polarization of half-metal V$_3$O$_4$ are investigated. The computed spin-polarized DOS of two V$_3$O$_4$ systems with a neutral O vacancy and VO antisite defects are shown in Figure 4a,b. As observed in Figure 4a, a neutral O vacancy introduces impurity acceptor levels above the valence bands in both the spin-up and spin-down channels, which are mainly contributed by the coupling between V 3d and O 2p orbitals. The impurity acceptor levels in the spin-up channel crossing the Fermi level are found to be partially filled, whereas in the spin-down channel appearing below the Fermi energy are completely filled, resulting in an asymmetric spin-up and spin-down DOS near Fermi energy and inducing a total spin polarization degree, but is higher than that of the neutral O$_v$ antisite at the A site.
magnetic moment of 4.19 $\mu_B$ per formula unit. The smaller spin polarization degree and magnetic moment compared with those of the pure V$_3$O$_4$ system are probably because of the fully occupied impurity levels in the spin-down channel introduced by the neutral O vacancy decreasing the splitting degree between the spin-up and spin-down states near the Fermi level. In the neutral V$_O$ antisite defect case (Figure 4b), one neutral V$_O$ antisite defect only introduces some acceptor levels, which mainly comes from coupling between the V 3d and O 2p orbitals in the spin-down channel leading to a smaller band gap in the vicinity of the Fermi level. The majority state maintains the metallic nature because of the top of the valence band cutting the Fermi level. Therefore, compared with ideal V$_3$O$_4$, the V$_3$O$_4$ system with one neutral V$_O$ antisite defect maintains semimetallic nature with a smaller magnetic moment of 4.35 $\mu_B$ per formula unit. Therefore, all the above neutral defects under O rich and V rich conditions are in favor of lower magnetic moments and spin polarization degrees compared to those of the ideal V$_3$O$_4$, which mainly results from the introduction of impurity energy levels in spin-down decreasing the difference between the spin-up and spin-down DOS near the Fermi level. Among these neutral defects, the V vacancy defects at both A and B sites contribute the highest magnetic moment and spin polarization degree.

To evaluate the thermodynamic stability of these native neutral defects, we calculate their formation energies under V-rich and O-rich conditions, respectively. The chemical potentials $\mu_V$ and $\mu_O$ of V and O must satisfy the following growth conditions:

$$\mu_{V_{O}} = 3\mu_V + 4\mu_O$$

(1)

where $\mu_{V_{O}}$ is the chemical potential of the ideal V$_3$O$_4$. Under O rich conditions, considering thermodynamic corrections, we use the experimental value of 5.23 eV for the binding energy of the O$_2$ molecule. The atomic energy of oxygen is $-1.90$ eV calculated from a spin-polarized calculation. Then, by subtracting the above binding energy from 2X atomic energy of oxygen, we get $-9.03$ eV for the chemical potential $\mu_O$. Therefore, the chemical potential $\mu_V$ is $-4.52$ eV defined as the oxygen-rich limit, and the chemical potential $\mu_B$ is obtained according to eq 1. In the V rich case, the chemical potential $\mu_V$ is $-8.95$ eV calculated from the metal vanadium, and the chemical potential $\mu_O$ is obtained according to eq 1. The neutral defect formation energies are defined as eq 2:

$$E^f = E_{\text{defect}}^{\text{tot}} - E_{\text{tot}}^{\text{host}} + n\mu_V - n\mu_O$$

(2)

where $E_{\text{defect}}^{\text{tot}}$ is the total energy of the supercell containing the neutral defect, $E_{\text{tot}}^{\text{host}}$ is the total energy of the host supercell, $n_-$ and $n_+$ are the number of atoms being removed and added, respectively, and $\mu_-$ and $\mu_+$ are the corresponding chemical potentials.

Under O rich conditions, one V vacancy defect energy at the A/B site in the V$_{23}$O$_{32}$ system in comparison to the ideal V$_{24}$O$_{32}$ system is obtained according to eqs 1 and 2:

$$E^f = E_{V_{O}}^{\text{O}} - E_{V_{O}}^{\text{V}} + \mu_V$$

(3)

Under O rich conditions, one O$_V$ antisite defect energy at the A/B site in the V$_{23}$O$_{32}$ system in comparison to the ideal V$_{24}$O$_{32}$ system is obtained according to eqs 1 and 2:

$$E^f = E_{O_{V}}^{\text{O}} - E_{O_{V}}^{\text{V}} + \mu_V - \mu_O$$

(4)

Under V rich conditions, one O vacancy defect energy in the V$_{23}$O$_{31}$ system in comparison to the ideal V$_{24}$O$_{32}$ system is obtained according to eqs 1 and 2:

$$E^f = E_{V_{O}}^{\text{V}} - E_{V_{O}}^{\text{O}} + \mu_V$$

(5)

Under V rich conditions, one O$_V$ antisite defect energy in the V$_{23}$O$_{31}$ system in comparison to the ideal V$_{24}$O$_{32}$ system is obtained according to eqs 1 and 2:

$$E^f = E_{O_{V}}^{\text{V}} - E_{O_{V}}^{\text{O}} - \mu_V + \mu_O$$

(6)

As listed in Table 1, under V-rich conditions, both formation energies of the O vacancy and V$_O$ antisite defects are ultra-high, suggesting that defects are less energetically favorable under V rich conditions. The oxygen atom bridges the V–O–V bond, and based on Bader charge analysis the strong bonds exist between the V and O atoms, which makes the strong exchange coupling between the V–O atoms observed in the spin polarized DOS (Figures 1–4) leading to the half-metallic ferromagnetism in V$_3$O$_4$. Therefore, the medium oxygen is hard to be removed to form the O vacancy and replaced by V atoms to form the V$_O$ antisite defects, which probably results in the high formation energies of the O vacancy and V$_O$ antisite defects. In addition, this similar case of the high formation.

| Table 1. Calculated Neutral Defect Formation Energies ($E^f$) of Intrinsic Defects of V$_3$O$_4$ |
|---|---|---|---|---|---|
| | V vacancy | O$_V$ antisite | V rich |
| defect type | A site | B site | A site | B site | O vacancy | V$_O$ antisite |
| $E^f$ (eV) | 2.22 | -0.04 | 15.21 | 3.98 | 18.54 | 22.43 |

https://dx.doi.org/10.1021/acsomega.0c00607
ACS Omega 2020, 5, 9442–9447
energy of the O vacancy has been reported by the previous studies.\textsuperscript{29,30} Moreover, under O rich conditions, the defect formation energies of the neutral V vacancy and O\textsubscript{V} antisite defects at B sites are both much lower than those at the A site because of the larger V(B)−O bond length (2.05 Å) than the V(A)−O bond length (1.85 Å) to form a weaker chemical bond, manifesting that the neutral V vacancy and the O\textsubscript{V} antisite defects are more likely to occur at B sites. In addition, the neutral V vacancy defect should be the main defect form because of the lowest defect formation energies among the various types of defects being studied.

Of particular importance is an understanding of the impact of native neutral defects on magnetic exchange coupling, which provides an effective route for mediating the curie temperature of semimetal V\textsubscript{3}O\textsubscript{4}. Owing to the lowest defect formation energies, the highest magnetic moments and spin polarization degrees of neutral V vacancy defects at A and B sites in contrast to other defects, we mainly study the role of the neutral V vacancy defect at different sites in influencing the magnetic coupling exchange of the V\textsubscript{3}O\textsubscript{4} material. Curie temperature is determined by exchange coupling strength, which further depends on the difference in the total energies (\(\Delta E\)) between the AFM and FM states.\textsuperscript{31−33} As illustrated in Figure 5, the FM state is obtained from the collinear spin-polarized optimization of identical spin directions of the V atoms, and the AFM state is just reversing the inter-plane V spin directions in the lattice.

![Figure 5](image_url)

**Figure 5.** (a,b),(c,d), and (e,f) Are the FM and AFM magnetic configurations of the ideal cubic V\textsubscript{3}O\textsubscript{4} unit cell, V\textsubscript{3}O\textsubscript{4} unit cell with two neutral V vacancies at A sites, and V\textsubscript{3}O\textsubscript{4} unit cell with two V vacancies at B sites, respectively. Yellow up and green down arrows indicate the spin up and spin down states at V atoms, separately.

Moreover, under O rich conditions, the defect formation energies of the neutral V vacancy and O\textsubscript{V} antisite defects at B sites are both much lower than those at the A site because of the larger V(B)−O bond length (2.05 Å) than the V(A)−O bond length (1.85 Å) to form a weaker chemical bond, manifesting that the neutral V vacancy and the O\textsubscript{V} antisite defects are more likely to occur at B sites. In addition, the neutral V vacancy defect should be the main defect form because of the lowest defect formation energies among the various types of defects being studied.

Table 2. Calculated Total Energies of FM and AFM States for the Ideal V\textsubscript{3}O\textsubscript{4} System and the Defective V\textsubscript{3}O\textsubscript{4} System with Two Neutral V Vacancies at Two A/B Sites

| energy | ideal V\textsubscript{3}O\textsubscript{4} | V\textsubscript{3}O\textsubscript{4} with two neutral V vacancies |
|--------|-------------------------------|--------------------------------------------------|
| A site | B site                        |                                                  |
| FM (eV) | 420.24990                      | −390.24036 −393.22177                          |
| AFM (eV) | 420.01781                      | −388.46047 −392.05486                          |
| \(\Delta E\) (meV) | 232.09                        | 1779.89 −1166.91                               |

4. CONCLUSIONS

In summary, the crucial mechanism of spin polarization and exchange coupling interaction mediated by native defects is investigated in semimetal V\textsubscript{3}O\textsubscript{4} using first-principles calculations. As revealed using the theoretical calculation results, in contrast to other neutral defects, the V vacancy defects at A and B sites are both in favor of higher spin polarization degrees and lower defect formation energies. In comparison to the ideal V\textsubscript{3}O\textsubscript{4} the V vacancy defects in V\textsubscript{3}O\textsubscript{4} at A and B sites both cause slightly lower spin polarization degrees, but much higher magnetic exchange coupling interactions.

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https://dx.doi.org/10.1021/acsomega.0c00607

ACS Omega 2020, 5, 9442−9447

9446
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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS
This work was funded by the National Natural Science Foundation of China, no. 11947114. We also acknowledge the support from the National Natural Science Foundation of China, no. 51802183.

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