First-principles study of Ga-vacancy induced magnetism in β-Ga$_2$O$_3$

Ya Yang, Jihua Zhang, Shunbo Hu, Yabei Wu, Jincang Zhang, Wei Ren* and Shixun Cao*

First principles calculations based on density functional theory were performed to study the electronic structure and magnetic properties of β-Ga$_2$O$_3$ in the presence of cation vacancies.

Please check this proof carefully. **Our staff will not read it in detail after you have returned it.**

**Proof corrections must be returned as a single set of corrections, approved by all co-authors.** No further corrections can be made after you have submitted your proof corrections as we will publish your article online as soon as possible after they are received.

Please ensure that:

- The spelling and format of all author names and affiliations are checked carefully. Names will be indexed and cited as shown on the proof, so these must be correct.
- Any funding bodies have been acknowledged appropriately.
- All of the editor’s queries are answered.
- Any necessary attachments, such as updated images or ESI files, are provided.

Translation errors between word-processor files and typesetting systems can occur so the whole proof needs to be read. Please pay particular attention to: tables; equations; numerical data; figures and graphics; and references.

Please send your corrections preferably as a copy of the proof PDF with electronic notes attached or alternatively as a list of corrections – do not change the text within the PDF file or send a revised manuscript. Corrections at this stage should be minor and not involve extensive changes.

Please return your final corrections, where possible within **48 hours** of receipt, by e-mail to: pccp@rsc.org. If you require more time, please notify us by email.
Funder information

Providing accurate funding information will enable us to help you comply with your funders’ reporting mandates. Clear acknowledgement of funder support is an important consideration in funding evaluation and can increase your chances of securing funding in the future. We work closely with Crossref to make your research discoverable through the Funding Data search tool (http://search.crossref.org/fundref).

Further information on how to acknowledge your funders can be found on our webpage (http://rsc.li/funding-info).

What is Funding Data?

Funding Data (http://www.crossref.org/fundingdata/) provides a reliable way to track the impact of the work that funders support. We collect funding information from our authors and match this information to funders listed in the Open Funder Registry. Once an article has been matched to its funders, it is discoverable through Crossref’s search interface.

PubMed Central

Accurate funder information will also help us identify articles that are mandated to be deposited in PubMed Central (PMC) and deposit these on your behalf.

Providing funder information

We have included the funder information you gave us on submission in the table below. The ‘Funder name’ shown and their associated ‘Funder ID’ number is written as listed in the Open Funder Registry. Please check that the funder names and grant numbers in the table are correct. The funder information should match your acknowledgements. This table will not be included in your final PDF but we will share the data with Crossref so that your article can be found via the Funding Data search tool.

<table>
<thead>
<tr>
<th>Funder name</th>
<th>Funder ID (from the Open Funder Registry)</th>
<th>Award/grant/contract number</th>
</tr>
</thead>
<tbody>
<tr>
<td>National Natural Science Foundation of China</td>
<td>501100001809</td>
<td>11547011, 11574194, 51372149, 51672171</td>
</tr>
<tr>
<td>Shanghai Municipal Education Commission</td>
<td>50110003395</td>
<td>12SG34, Eastern Scholar Program</td>
</tr>
<tr>
<td>Science and Technology Commission of Shanghai Municipality</td>
<td>50110003399</td>
<td>14QA1402000, 16DZ2260600</td>
</tr>
</tbody>
</table>

If a funding organisation you included on submission of your article is not currently listed in the registry it will not appear in the table above. We can only deposit data if funders are already listed in the Open Funder Registry, but we will pass all funding information on to Crossref so that additional funders can be included in future.

Researcher information

If any authors have ORCID or ResearcherID details that are not listed below, please provide these with your proof corrections. Please check that the ORCID and ResearcherID details listed below have been assigned to the correct author. Please use this space to add your own unique ORCID iDs and not another researcher’s, as errors will delay publication.

Please also update your account on our online manuscript submission system to add your ORCID details, which will then be automatically included in all future submissions. See here for step-by-step instructions and more information on author identifiers.

<table>
<thead>
<tr>
<th>First (given) name(s)</th>
<th>Last (family) name(s)</th>
<th>ResearcherID</th>
<th>ORCID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ya</td>
<td>Yang</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jihua</td>
<td>Zhang</td>
<td>H-9872-2014</td>
<td></td>
</tr>
<tr>
<td>Shunbo</td>
<td>Hu</td>
<td>F-8981-2014</td>
<td>0000-0003-0472-0999</td>
</tr>
<tr>
<td>Yabei</td>
<td>Wu</td>
<td></td>
<td></td>
</tr>
<tr>
<td>First Name</td>
<td>Last Name</td>
<td>ORCID ID</td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>-------------</td>
<td>---------------</td>
<td></td>
</tr>
<tr>
<td>Jincang</td>
<td>Zhang</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wei</td>
<td>Ren</td>
<td>0000-0001-7317-3867</td>
<td></td>
</tr>
<tr>
<td>Shixun</td>
<td>Cao</td>
<td>0000-0002-3915-2621</td>
<td></td>
</tr>
</tbody>
</table>
Queries for the attention of the authors

Journal: PCCP
Paper: c7cp03675b
Title: First-principles study of Ga-vacancy induced magnetism in β-Ga₂O₃

For your information: You can cite this article before you receive notification of the page numbers by using the following format: (authors), Phys. Chem. Chem. Phys., (year), DOI: 10.1039/c7cp03675b.

Editor’s queries are marked on your proof like this Q1, Q2, etc. and for your convenience line numbers are indicated like this 5, 10, 15, ...

Please ensure that all queries are answered when returning your proof corrections so that publication of your article is not delayed.

<table>
<thead>
<tr>
<th>Query reference</th>
<th>Query</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1</td>
<td>Please carefully check the spelling of all author names. This is important for the correct indexing and future citation of your article. No late corrections can be made.</td>
<td></td>
</tr>
<tr>
<td>Q2</td>
<td>Do you wish to add an e-mail address for the corresponding author? If so, please provide the relevant information.</td>
<td></td>
</tr>
<tr>
<td>Q3</td>
<td>Please check that the inserted Graphical Abstract text is suitable. Please ensure that the text fits between the two horizontal lines.</td>
<td></td>
</tr>
<tr>
<td>Q4</td>
<td>The sentence beginning “In β-Ga₂O₃…” has been altered for clarity. Please check that the meaning is correct.</td>
<td></td>
</tr>
<tr>
<td>Q5</td>
<td>In the sentence beginning “Nevertheless, if the Fermi level…” should “deep of the gap” be changed to “below the gap”?</td>
<td></td>
</tr>
<tr>
<td>Q6</td>
<td>The sentence beginning “A similar…” has been altered for clarity. Please check that the meaning is correct.</td>
<td></td>
</tr>
<tr>
<td>Q7</td>
<td>“Moment” appears to be spelled incorrectly as “Monment” in the Graphical Abstract image and in Fig. 7. Please could you supply a corrected version (preferably as a TIF file at 600 dots per inch) with your proof corrections.</td>
<td></td>
</tr>
</tbody>
</table>
1 Introduction

d⁰ ferromagnetism has attracted great attention, ever since it was reported by Coey in a review on materials with an absence of partially filled d or f shells. For instance, there appeared an unexpected magnetism in a HfO₂ film with a Curie temperature exceeding 500 K and a magnetic moment of about 0.15 bohr magnetons per formula unit. In contrast to dilute ferromagnetic semiconductors, it is amazing that ferromagnetism was shown appearing. Based on the research studies of oxygen-vacancies in CeO₂ cluster model have been successfully employed to investigate the properties of oxygen-vacancies in CoO₂ and MgO₂. Researchers have identified that vacancies should be responsible for the interesting magnetism in nonmagnetic systems due to the oxygen-vacancy induced unpaired spin localization. Weng et al. have shown that hole doping in the oxygen p orbital of HfO₂ can induce ferromagnetism and this may be a general phenomenon in ionic oxides. A similar effect was also already found in CaF₂ for cation vacancies. It is reasonable to believe that the intriguing magnetism originates from intrinsic lattice defect states like vacancies. And such results suggest a new way to change the magnetic states of the semiconductors without doping.

As a widely used material in the semiconductor industry, at room temperature the stable state β-Ga₂O₃ has a wide band gap of about 4.4–4.8 eV. Due to this, β-Ga₂O₃ has a unique transparency from the visible into the UV (ultraviolet) region, thus being a good candidate for optoelectronic devices. However, Ga₂O₃ is nonmagnetic due to the 3d¹⁰ configuration of the Ga³⁺ ions which limits its use in spintronics. Recently, bulk ferromagnetism was found experimentally in Ga₂O₃, together with large changes in photoluminescence intensity induced by a magnetic field. The authors claimed that magnetism could be formed locally around the special site of oxygen vacancies and for some vacancy densities the magnetism could correspond to the experimental results. Some previous theoretical reports have studied the vacancies and ion doping effect in β-Ga₂O₃ using different methods. Based on the research studies on other semiconductors, most reports have identified that cation vacancies should be responsible for the d⁰ ferromagnetism. Recently, some effects of the intrinsic Ga- and O-defects were investigated in pure and aluminum-doped β-Ga₂O₃ using the GGA+U (generalized gradient approximation plus Hubbard U) method. It is noteworthy that the GGA method may fail to describe systems with d and f electrons, which results in underestimation of the band gap. In β-Ga₂O₃, the GGA+U method has been proved to reproduce reasonable values of the band gap close to those of experiments.
But until now, a microscopic theoretical investigation of the cation-vacancy-induced magnetism in \(\beta\)-Ga\(_2\)O\(_3\) has been lacking. And considering the tetrahedral and octahedral sites of Ga atoms in \(\beta\)-Ga\(_2\)O\(_3\), the possible local clusters induced by the Ga-vacancies would be polarized by the charges, which may facilitate a stable ferromagnetic order.\(^{37,38}\) We test the possible cation vacancies using spin-polarized density functional theory (DFT) calculations. The GGA+U approach is used to get a reasonable electronic structure and spin alignment. And we adopted molecular orbital theory to understand and predict the magnetic behaviors. Therefore, compared to ferromagnetic metals and other nonmagnetic semiconductors, our calculation aims to reveal the origins of the unexpected magnetism appearing in \(\beta\)-Ga\(_2\)O\(_3\) and open an avenue for the development of the \(\beta\)-Ga\(_2\)O\(_3\) applied in the integration of spintronics and semiconductor-based electronics.

2. Computational method

Spin-polarized DFT calculations were performed by using the Vienna ab initio simulation package (VASP) with the projector augmented wave (PAW) method.\(^{39-42}\) The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) was used as the exchange and correlation functional.\(^{43,44}\) The effective Hubbard energy (\(U_{\text{eff}} = U - J\)) was used to describe the electron correlation effect and produce an energy gap (4.2 eV) near the experimental value (4.9 eV)\(^{10}\) with a \(U_s = 30.0\) eV for Ga-4s and \(U_p = 8.5\) eV for O-2p. The electronic configurations 3d\(^{10}\)4s\(^2\)4p\(^1\) and 2s\(^2\)2p\(^1\) are considered as the valence states for Ga and O, respectively. It is noted that our \(U\) values are different from the ones in ref. 35 although the Hubbard \(U\) applied on the Ga-s orbital was just to open the energy gap (see more details in the ESI\(^+\)).\(^{15,46}\) The plane wave cutoff energy is 500 eV. For the bulk \(\beta\)-Ga\(_2\)O\(_3\) and the vacancy-defect structures we adopted and optimized the experimental structures by keeping the lattice parameters unchanged until the forces on the atoms become less than 0.001 eV Å\(^{-1}\). The following experimental values are used in our calculation of \(\beta\)-Ga\(_2\)O\(_3\), \(a = 12.214\) Å, \(b = 3.037\) Å, \(c = 5.798\) Å and \(\beta = 103.830^\circ\) and the space group is \(C2/m\).\(^{47}\) The \(k\)-points were set with a Monkhorst–Pack mesh of \(6 \times 6 \times 6\). The tetrahedron method with Bloch corrections\(^{48}\) was used. In the electronic structure calculations, we use \(10^{-6}\) eV for the energy convergence criterion. We then calculated the magnetic moment and density of states with the more accurate but computationally demanding HSE06 hybrid functional\(^{39,50}\) (see more details in the ESI\(^+\)).

3. Results and discussion

3.1 The structure optimization and the vacancy formation energy

We first use the DFT-GGA method to optimize the 60-atom supercell Ga\(_2\)O\(_{36}\) and the Ga\(_{23}\)O\(_{36}\) supercell containing a single gallium vacancy (\(V_{Ga}\)) in two different symmetry sites. As shown in Fig. 1, the Ga atoms have two symmetry sites (\(e.g.,\) four-fold and six-fold coordinated sites). For convenience of discussion, we name the four-fold coordinated vacancy as \(V_{tetra}\), and the six-fold one as \(V_{octa}\). In the situations of perfect local symmetry, the four-fold site constructs a tetrahedron with a group of \(T_d\) symmetry and the six-fold site builds an octahedron with a group of \(O_h\) symmetry. However, in the monoclinic crystal structure of the \(\beta\)-Ga\(_2\)O\(_3\) the local geometry of the coordinated anions around the gallium has a distortion of the perfect symmetry. The relaxed structural details are shown in Fig. 1(b) and (c), where the GaO\(_6\) octahedron has two pairs of bonds of equal length in the basal plane and two different bonds along the long axis of the octahedron; whereas the GaO\(_4\) has two equal-length bonds among the four Ga–O bonds. It is also worth noting that the bond angles of the O–Ga–O also have a significant deviation from perfect symmetric values. Hence, the distorted bonds and bond angles are expected to have an impact on the electronic structure of the systems with Ga vacancies.

After identifying the structure including the defect distortion, we calculated the vacancy formation energy \(E_{\text{vd}}\) at the two different sites \(V_{octa, tetra}\) with several possible charge states (neutral, \(-1\), \(-2\) and \(-3\)) as defined in ref. 51:

\[
E_{\text{vd}}[V_{octa, tetra}] = E_{\text{tot}}[V_{octa, tetra}] - E_{\text{tot}}[\text{bulk}] + \sum n_i \mu_i + q(E_F + E_{\text{VBM}})
\]

(1)

Fig. 1 (a) Crystal structure of the pure \(\beta\)-Ga\(_2\)O\(_3\). (b) The local structure of the six-fold coordinated Ga–O octahedron and (c) the four-fold coordinated Ga–O tetrahedron. The green and red balls represent the Ga and O atoms, respectively.
where the $E_{\text{tot}}^{\text{bulk}}$ and $E_{\text{tot}}^{\text{V_{octa},tetra}}$ represent the total energies of the perfect supercell and that containing a vacancy in the charge state $q$. The integer $n_i = 1$ indicates the number of atoms that have been removed from the supercell to form the vacancy defect. The chemical potential $\mu_i(Ga)$ is suggested to be equal to the bulk values for the corresponding metal in a Ga-rich/O-poor environment, and the $E_F$ denotes the Fermi energy and varies between the valence band maximum (VBM) and conduction band minimum (CBM). In a Ga-poor/O-rich environment, $2\mu(Ga) = \mu(Ga_2O_3) - 3\mu(O)$, where $\mu(Ga_2O_3)$ is given by the energy of a formula unit of Ga$_2$O$_3$ and $\mu(O)$ by half of the energy of an O$_2$ molecule. In Fig. 2(a) and (b), we present the Ga-vacancies with $-3$, $-2$, $-1$ and 0 charge states as functions of the Fermi energy $E_F$. The results confirm that the four-fold coordinated $V_{\text{tetra}}$ is more energetically preferable for neutral cation vacancies. As we discuss later for evidence of the magnetism induced by the cation vacancy in $\beta$-Ga$_2$O$_3$, both defects can introduce spin-polarized states with magnetic moments of 0.685 $\mu_B$ for $V_{\text{tetra}}$ and 2.034 $\mu_B$ for $V_{\text{octa}}$. However, the relatively small stability of the $V_{\text{tetra}}$ neutral 0 state is seen in a narrow range of the Fermi energy $E_F$, and upon increasing $E_F$ the $-3$ state of $V_{\text{octa}}$ becomes the most stable one. A similar case occurs in the Ga-poor/O-rich environment but with overall smaller formation energy. Although the $-3$ state of $V_{\text{octa}}$ has a wide-range stability, it would actually suppress the vacancy induced ferromagnetism. Nevertheless, if the Fermi level is set close to the VBM and deep of the gap (e.g., by connecting a metal contact) the neutral $V_{\text{tetra}}$ would be energetically preferred for formation of a large local magnetic moment.

### 3.2 The electronic structure

Then the electronic structures of the pure and vacancy systems were calculated as shown in Fig. 3(a)–(d). The pure Ga$_2$O$_3$ without vacancies has a nonmagnetic state with a gap of 4.2 eV at the GGA+$U$ level close to the experimental value of 4.9 eV. (We have also tested the gaps with different $U$ values as shown in the ESI.†) In addition, the total density of states (TDOS) of the $V_{\text{tetra},\text{octa}}$ configurations are also shown in Fig. 3(a) exhibiting two different defect-states. In detail, for the $V_{\text{octa}}$ a half-
metal-like state can be found around the Fermi level. In the $V_{\text{tetra}}$ system, defect states are located inside the band gap for both spin up and spin down electrons. In Fig. 3(b) we give the projected density of states (PDOS) of the Ga ions in the pure Ga$_2$O$_3$ onto two coordination sites of tetrahedral and octahedral symmetries. Furthermore, from inspection of the PDOS for the vacancy systems shown in Fig. 3(c) and (d), it can be confirmed that the defect states are formed by the coordinated O-2p orbitals. Therefore, it is necessary to explain the vacancy properties by constructing the molecular orbitals based on the coordinated O-2p states.

Before analysing the molecular orbitals, we look at the spin charge density in Fig. 4. It is clear to see that the dangling bonds of the coordinated O anions create local magnetic moments with the shape of 2p orbits. Simultaneously, some next nearest neighboring O anions also have small moments possibly for the extended tails of the defect wave functions. It is interesting to see that the dangling bonds almost point to the vacancy center for the s–p hybridization. However, we also note that some coordinated O anions contribute very little spin polarization. Further, the spin charge density tends to distribute mostly at the high symmetry sites of O anions bonded by the originally equal Ga–O bonds. A similar phenomenon was also found in HfO$_2$ with Hf-vacancies where the spin charge density will clump to the molecular orbitals. Next, we will explain the distinct properties of the $V_{\text{tetra}}$ and $V_{\text{octa}}$ hiding in the different symmetries.

### 3.3 The molecular orbital theory approach

Let us begin from the neutral Ga vacancy situation. Both the neutral $V_{\text{tetra}}$ and $V_{\text{octa}}$ would introduce electrons into the molecular orbitals formed by the coordinated O anions. The reasonable molecular orbitals will lead to a direct introduction of the behaviors of the defect states. For the perfect $V_{\text{tetra}}$, the nearest four O anions form a local environment with $T_d$ symmetry. Under this $T_d$ symmetry, the linear combination of the p orbitals will result in a lowest energy level which is a single $a_1$ molecular orbital and a high energy level with a triple degenerate $t_2$ molecular orbital. All the possible states originate from the irreducible representations of the tetrahedral group $T_d$, for example:

$$a_1 : v = \frac{1}{\sqrt{6}}(\psi_1 + \psi_2 + \psi_3 + \psi_4)$$

$$t_2 : t_c = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2 - \psi_3 - \psi_4)$$

$$t_r = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2 - \psi_3 + \psi_4)$$

$$t_c = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2 + \psi_3 - \psi_4)$$

where $\psi_i$ is expressed as a function of the atomic orbitals, $\psi_i = (s + p_x + p_y + p_z)$ corresponding to the four dangling bonds pointing towards the vacancy site and the other three orbitals are given as $\psi_j (j = 2, 3, 4)$. Chanier et al. have used this sp$^3$ molecular orbital model to explain the cation vacancies in ZnA ($A = S, Se, Te$).

Analogously, the perfect $V_{\text{octa}}$ coordinated symmetry belongs to the $O_h$ group. According to the irreducible representations of the octahedral group $O_h$, we could also get two molecular orbitals ($a_1$ and $t_1$) similar to the $V_{\text{tetra}}$ as shown in Fig. 5(a) and (e). For example:

$$a_1 : v = \frac{1}{\sqrt{6}}(\psi_1 + \psi_2 + \psi_3 + \psi_4 + \psi_5 + \psi_6)$$

$$t_1 : t_c = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2)$$

$$t_r = \frac{1}{\sqrt{2}}(\psi_3 - \psi_4)$$

$$t_c = \frac{1}{\sqrt{2}}(\psi_5 - \psi_6)$$

the $\psi_j (j = 1, 2, 3, 4, 5, 6)$ are corresponding to the six coordinated O atoms.

But it is very important to point out the difference between $V_{\text{tetra}}$ and $V_{\text{octa}}$. The breaking of the local vacancy structure symmetry results in different Ga–O bonds and a heterogeneous spin charge density distribution. One state of the three t orbitals would be lifted to a higher energy state, such that the t level is divided into lower doubly degenerate e levels and a higher singlet b level. Then, we use the SymApps software to confirm the local symmetry of the relaxed vacancy structure. Based on the distorted local structure and applied group theory, it is convenient to construct the new molecular orbitals. As shown in Fig. 6, by taking off the central Ga$^{3+}$ ions the local structure will be distorted away from the perfect symmetry of the $O_h$ group for the $V_{\text{octa}}$ and reduced to a $D_{4d}$ group; the $T_d$ group of the $V_{\text{tetra}}$ will be reduced to a $S_4$ one. According to the

--

Fig. 4 Spin charge density of the surrounding O$^{2-}$ anions of (a) $V_{\text{octa}}$ and (b) $V_{\text{tetra}}$. The isosurface level is 0.035 e Å$^{-3}$. Larger blue and smaller red balls represent the Ga and O atoms, respectively. The dotted-line circles represent the Ga atoms which have been taken off.
character table of the $S_4$ group, we can deduce the new molecular orbitals:

\[ a_1 : v = \frac{1}{2} (\psi_1 + \psi_2') + \psi_3 + \psi_4 \]  
\[ e : t_x = \frac{1}{2} (\psi_1' - \psi_2' - \psi_3 + \psi_4) \]  
\[ t_y = \frac{1}{2} (\psi_1 + \psi_2' + \psi_3 - \psi_4) \]  
\[ t_z = \frac{1}{2} (\psi_1' + \psi_2' - \psi_3 - \psi_4) \]  

Taking into account the spin charge density in Fig. 4(b), we suggest that two of the four atomic orbitals ($\psi_3$ and $\psi_4$) are similar to the ones for the perfect $T_d$ group in $V_{\text{tetra}}$ with $S_4$ symmetry. The $\psi_1'$ and $\psi_2'$ are located on the O1 and O2 atoms (in Fig. 1c). The results suggest that the $t_x$ and $t_y$ are degenerate with the double e orbitals, and the $t_z$ level is lifted as a high energy single b orbital.

Similarly, for the $V_{\text{octa}}$ with the $D_{2d}$ group, the molecular orbitals are changed as:

\[ a_1 : v = \frac{1}{\sqrt{6}} (\psi_1 + \psi_2 + \psi_3 + \psi_4 + \psi_5 + \psi_6') \]  
\[ e : t_x = \frac{1}{\sqrt{2}} (\psi_1 - \psi_2) \]  
\[ t_y = \frac{1}{\sqrt{2}} (\psi_3 - \psi_4) \]  
\[ b_2 : t_z = \frac{1}{\sqrt{2}} (\psi_5 - \psi_6) \]  

According to Fig. 4(a), the $\psi_6'$ on the top O atom is deviated from the $\psi_6$ in the $O_h$ group. So we can get a higher energy level with $b_2$ symmetry. The remaining two levels are degenerate as a double e orbital.
Therefore, going back to the DOS of the Vtetra and Vocta, we can explain that: (1) the s-like a levels are located deeply in the valence band and thus fully filled. The t levels would retain the neutral state if three electrons are introduced there. (2) For the Vocta system, the half-filled t level leads to a half-metal-like state above the Fermi level in one spin channel and achieves a “high spin” state. (3) For the Vtetra system, the symmetry-breaking t level allows the electrons to configure a relatively low spin state resulting in a totally empty b level, corresponding to the defect level in the gap and also a weaker half-metal-like state in the e level. As shown in Fig. 3(c) and (d), the red circle marks the empty b level in the gap for the defect states of the Vtetra system and the blue stars indicate the partially occupied states in the spin down channel responsible for half-metal-like states. In this way, we clearly illustrate the different behaviors of Vtetra and Vocta, and especially why the defect states only appear in the Vtetra system.

To further test our theory, we calculate the magnetic properties involving the two different vacancy systems with different charge states as shown in Fig. 7. In detail, the moment of the Vocta is monotonously reduced with the increase of the charge states from the neutral to the −3 charged state. However, the moments of the Vtetra have some oscillation vs. the charge states. It can be concluded that for the −3 charge state both the two vacancy systems which are introduced by 3 electrons will be completely compensated, giving rise to a nonmagnetic state just like the pure Ga2O3. To explain this, we analyze the molecular orbitals of the Vtetra and Vocta as shown in Fig. 5(a)–(h). For the Vocta, the introduced electrons will occupy the empty states in the down spin channel one by one. In this process, the uncompensated spins vary from 3 (neutral) to 2 (−1 charged), to 1 (−2 charged) and eventually to the 0 (−3 charged) nonmagnetic state. In contrast, for the Vtetra case the first introduced electron would preferentially occupy the lower e level, forming a nearly nonmagnetic state for the −1 charged vacancy. Then, a second electron in the system would fill the highest b level and generate a one spin state for the −2 charge state. Finally, a nonmagnetic state of the completely-filled t2 level is for the −3 charge state. Therefore, we can well connect the magnetic behaviors with the molecular orbitals and get the correct spin configurations for different charged states. Indeed, as shown in Fig. 7, there is a quantitative difference between the values from first-principles calculations (GGA+U and HSE06) and those deduced from molecular orbital theory. The calculation with a bigger supercell containing 120 atoms (119 atoms for the vacancy structure) confirmed that this is an intrinsic phenomenon originating from the half-metal states of the systems as shown in the Fig. 3. In agreement with the literature, the half-metal states are formed for some partially occupied molecular orbitals. For example, in HFO2, the magnetic moment was found to be 3.5 μB per vacancy which is smaller than the 4 μB from molecular orbital theory for the half-metal state in the down spin states. Additionally, in CaO the partially occupied e− state also leads to a smaller spin moment than predicted from theory. The numerically calculated spin moment on the orbital might be more delocalized than the values based on molecular theory. Therefore, for the intrinsic partially occupied states, we obtain the same trend of spin moments using DFT for different charge states compared with the theoretical model. The molecular orbitals with the higher energy levels, namely the b (or b2) orbital, are thus hinted to be the partially occupied ones with about 60% population.

### 3.4 The long range magnetic order

The single isolated vacancy indeed induces some local spin moments around its location. For application purposes, it is necessary to verify the possible long range magnetic ordering in the vacancy systems. So we constructed a bigger supercell (120 atoms) consisting of two neutral Ga vacancies (for the Vtetra pair and Vocta pair) which are separated by a distance of 9.111 Å. By using different initial settings of magnetic moments calculated with UGa = 30 eV, we obtain and compare the two magnetic states namely the ferromagnetic (FM) and antiferromagnetic (AFM) cases. As summarized in Table 1, the FM states have a net moment of 1.368 μB for the two Vtetra and 4.068 μB for the two Vocta. Then, the stable state for the two Vtetra is the FM state while for the two Vocta the stable state is the AFM state. The energy differences (ΔE = EAFM − EMFM) are about 55.0 meV (Vtetra) and −16.0 meV (Vocta) respectively, from which we can estimate the corresponding critical transition temperature TC by the Heisenberg model H = −∑ij Jmimj. In the mean field approximation, the TC values are calculated as 2kBTN = 3JT. The nearest-neighbor exchange parameter J0 can be calculated as J0 = ΔE/nS2 (n = 4 for Vtetra and n = 6 for Vocta). As a result, the calculated values of J0 and TC for the two Vtetra system indicate that a long-range FM order may exist at room temperature. However, for the different ground-states of the two Vocta or two Vtetra, the magnetic interaction may be very complex in bulk with many vacancies in reality. Considering this competition between the FM and AFM, it may be challenging to observe the magnetism of β-Ga2O3 in experiments.
Table 1  The more stable magnetic order, net moment, energy differences ($\Delta E = E_{\text{FM}} - E_{\text{AFM}}$), nearest-neighbor exchange parameter $J_0$ and transition temperature $T_C$ (estimated from $2k_B T_C = 3J_0$) for the 120-atom supercells with a vacancy separation of 9.111 Å

<table>
<thead>
<tr>
<th>vacancy</th>
<th>FM</th>
<th>AM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$ (meV)</td>
<td>$J_0$ (meV)</td>
<td>$T_C$ (K)</td>
</tr>
<tr>
<td>$\nu_{\text{Ga}^2+}$</td>
<td>1.371</td>
<td>55.0</td>
</tr>
<tr>
<td>$\nu_{\text{Ga}^3+}$</td>
<td>4.069</td>
<td>93.5</td>
</tr>
</tbody>
</table>

4. Conclusion

In summary, we have investigated the Ga cation vacancy defects states in $\beta$-Ga$_2$O$_3$ and the electronic structures from first principles calculations. At two different Ga sites, namely the four-fold coordinated and the six-fold coordinated ones, we identified that both the cation vacancies could result in a spin polarization originating from the local moments of surrounding O$^2-$ anions. Using molecular orbital theory, we analysed the effects of the local symmetry on the vacancy states and obtained a picture of the magnetic configurations with possible charge states. It is obvious that the magnetic behaviors could be connected with the different electron occupations of the molecular orbitals. In addition, we also investigated the coexistence and interaction between the two cation vacancies. The computational solution of the magnetic orders and nearest-neighbor exchange parameters indicate a room temperature long-range ferromagnetic order.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (No. 51372149, 51672171, 11574194, 11547011), the National Key Basic Research Program of China (Grant No. 2015CB921600), QiMingXing (No. 14QA1402000) and a research grant (No. 16DZ2260600) of the Shanghai Municipal Science and Technology Commission, Eastern Schooand a research grant (No. 16DZ2260600) of the Shanghai Municipal Education Commission. The Special Program for Applied Research on Super Computation from the Shanghai Municipal Education Commission. The supercomputing services from AM-HPC, and the Shanghai Supercomputer Center are also acknowledged.

References

55 SymApps 6.0 for Windows Bio-Rad Laboratories, Sadtler Division, 3316 Spring Garden St., Philadelphia, PA.