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# Electronic and Magneto-Optical Properties of the Molybdenum-Vacancy Center in Zirconia and Its Qubit Applications

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cubic zirconia was selected to expand the taxonomy of available defective systems acting as a qubit. To theoretically prove the feasibility of its qubit applications, investigation of the electronic and magneto-optical properties of the neutral  $V_OMo_{Zr}$  center was carried out via firstprinciples calculations. The center possesses a trigonal symmetry  $(C_{3\nu})$ with a spin-triplet ground state (GS). The molecular orbital combinations were qualitatively analyzed by using the group theory. For guiding the qubit-specific manipulation, its GS zero-field splitting was investigated and measured to be 2208.29 MHz, its zero-phonon line was located at 1.03 eV, and the Stoke and anti-Stoke shifts were at 201.8 and 136.5 meV, respectively. This study shows that the neutral  $V_OMo_{Zr}$ 



center is competent for a qubit and paves the way toward the further implementation of qubit applications based on the neutral  $V_0Mo_{Zr}$  center.

# ■ INTRODUCTION

Defect complexes in solid-state materials<sup>1-3</sup> have gained unprecedented attention due to their potential applications in quantum technology, such as quantum information processing (QIP)<sup>4,5</sup> and quantum sensing (QS).<sup>6</sup> The negatively charged nitrogen-vacancy (NV) center in diamond is the most widely studied complex<sup>7,8</sup> and has excellent performance both in QIP<sup>5,9,10</sup> and QS.<sup>11-13</sup> The NV center consists of substituted nitrogen and a proximate carbon vacancy. When the neutral NV center captures an extra electron from the lattice, it becomes the most famous negatively charged NV center. The wide range of applications of NV center in diamond is inseparable from its extraordinary properties, such as favorable spin coherence time,<sup>14</sup> ground state (GS) that can be manipulated with microwaves (MWs),<sup>15</sup> and visible light initialization and detection.<sup>16</sup> Although the NV center has unparalleled advantages as a qubit candidate, its disadvantages are also very difficult to overcome in a short time. From an engineering perspective, it is difficult to grow or fabricate devices on diamonds. Consequently, the exploration of new color centers to expand the taxonomy of available defective systems is of great significance. In some cases, these compounds may present an even higher performance than the NV centers, for instance, the existence of lower excitation energy, and host materials with more mature and convenient device processing technology. For achieving this objective, several candidates, such as titanium-related color centers in diamond,<sup>17</sup> silicon vacancies,<sup>18</sup> divacancy<sup>19</sup> in SiC, and V<sub>B</sub>O<sub>N</sub>

center in cubic boron nitride,<sup>20</sup> have been theoretically and/or experimentally investigated. Overall, what physical features a new color center and host material should exhibit is described in detail in ref 3. The criteria for determining potential qubit candidates are also reported in ref 3. Closely following the criteria, while being inspired by the physical properties of the NV center and other color centers, a suitable and promising qubit candidate was explored herein: the molybdenum-vacancy  $(V_0Mo_{7r})$  center in cubic zirconia (CZ). The  $V_0Mo_{7r}$  center consists of a substitutional molybdenum atom (Mo<sub>Zr</sub>) and an adjacent oxygen-vacancy (V<sub>O</sub>) as shown in Figure 1. For the host, the CZ is an ultrawide-band gap (>6  $eV^{21}$ ) semiconductor, which is an indispensable condition for forming a deep-level color center. Furthermore, the cubic structure of CZ is also more conducive to the formation of a color center with  $C_{3\nu}$  symmetry, like the NV center. The existence of Zr and Mo nuclear spins are also beneficial for the expansion of the application field of the VoMozr center, such as quantum information storage. CZ possesses hardness lower than that of the diamond, which renders it more prone to be used for dry etching. Furthermore, it exhibits a better strain modulation

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Figure 1. Geometry of the  $V_OMo_{Zr}$  center in CZ. Mo, vacancy (V), and Zr are labeled in red, green, and blue, respectively.

potential, which leads to an increase in the performance of the color centers. Its lower refractive index (CZ, 2.15-2.18; diamond, 2.42) aids in the generation of higher light emission. Moreover, the maturity in the CZ synthesis technology<sup>22</sup> and its low cost compared to diamond foster its sophisticated implementation in future device applications. This center is expected to have similar or even better physical properties than the NV center in some aspects, thus the exploration of the properties of the center for qubit applications should be carried out. To this end, in this study a thorough first-principles investigation of the electronic and magneto-optical properties of the V<sub>O</sub>Mo<sub>Zr</sub> center was carried out to prove the feasibility and promising potential of being a qubit. In particular, referring to the criteria reported in ref 3, the defect energy level diagrams, the formation energy, the electronic structure, the spin-dependent properties (zero-field splitting (ZFS) and hyperfine interactions (HFIs)), and the nature of optical transitions were evaluated by density functional theory (DFT) calculations. The formation energy calculations were committed to evaluating the stability of the center in a specific charge state. The study of electronic structure is mainly carried out to find out not only whether the GS of this center is a bound state but also whether the center is paramagnetic. The ZFS calculation is mainly carried out to confirm whether this center can be manipulated by electron spin resonance (ESR) technology, which is one of the key prerequisites to find out whether this center can become a potential qubit. The investigation of the HFIs aims to expand the application of the selected center in QIP such as qubit register. Furthermore, the HFIs act as an important source of decoherence. Finally, the study of the optical transition provides a reference for the experimental identification of the center and provides two key parameters, the wavelength of initializing laser and the detectable fluorescence signal.

#### COMPUTATIONAL DETAILS

The Vienna *ab initio* simulation package (VASP)<sup>23</sup> code was employed with the supercell approach to perform all the calculations in this study. For the geometry optimization and electronic structure demonstration, the Perdew–Burke– Ernzerhof (PBE) exchange-correlation functional belonging to the general gradient approximation (GGA)<sup>24</sup> and accurately describing the structural properties of solid-state systems, was Article

employed. A 2 × 2 × 2 CZ supercell with embedded single  $V_OMo_{Zr}$  center was simulated using a 500 eV cutoff energy and with a Monkhorst–Pack (MP) *k*-point meshes grid of 3 × 3 × 3. In the process of minimizing the structural energy, the break conditions for electronic self-consistency and the ionic relaxation loop were set to be  $10^{-5}$  eV and 0.01 eV·Å<sup>-1</sup>, respectively. The LDA+U approach<sup>25</sup> was applied to improve the description of the strongly correlated Zr 4d states, present in the host material. The effective on-site Coulomb interaction for the Zr 4d states,  $U_{eff} = U - J = 4$  eV, was obtained from ref 26.

The formation energy  $E^{f}$  of the V<sub>O</sub>Mo<sub>Zr</sub>, Mo<sub>Zr</sub>, and V<sub>O</sub> centers in different charge state q are defined as follows<sup>27</sup>

$$\begin{split} E^{t}[V_{O}Mo_{Zr}^{q}] &= E_{tot}[V_{O}Mo_{Zr}^{q}] - E_{tot}[bulk] - \mu_{Mo} + \mu_{ZrO} \\ &+ q(\varepsilon_{F} + E_{VBM}^{bulk} + \Delta V) \end{split}$$
(1)

$$E^{t}[Mo_{Zr}^{q}] = E_{tot}[Mo_{Zr}^{q}] - E_{tot}[bulk] - \mu_{Mo} + \mu_{Zr} + q(\varepsilon_{F} + E_{VBM}^{bulk} + \Delta V)$$
(2)

$$E^{f}[V_{O}^{q}] = E_{tot}[V_{O}^{q}] - E_{tot}[bulk] + \mu_{O} + q(\varepsilon_{F} + E_{VBM}^{bulk} + \Delta V)$$
(3)

where  $E^{f}[V_{O}Mo_{2r}^{q}]$ ,  $E^{f}[Mo_{2r}^{q}]$  and  $E^{f}[V_{O}^{q}]$  represent the total energy of the CZ supercell with a  $V_{O}Mo_{Zr}$ ,  $Mo_{Zr}$ , and  $V_{O}$ center in a charge state q, respectively, while  $E_{tot}[bulk]$ indicates the total energy of the perfect CZ supercell.  $\mu_{Mo}$ ,  $\mu_{Zr}$ , and  $\mu_{O}$  are the chemical potentials of the Mo, Zr, O atom, respectively.  $\mu_{ZrO}$  is the energy of a Zr–O pair.  $\varepsilon_{F}$  denotes the Fermi level reference to the valence band maximum (VBM) of the perfect CZ crystal  $E_{VBM}^{bulk}$ . The alignment procedure  $\Delta V$ represents the difference between hosts with and without the  $V_{O}Mo_{Zr}$  center being used to correct the finite-size potential energy for charged-defect supercell calculations.<sup>28</sup>

The ZFS describes electron spin–electron spin interaction in a physical system with a total spin  $S \ge 1$  without an external magnetic field. Hamiltonian of this interaction  $(H_{ss})^{29}$  can be written as follows

$$H_{\rm ss} = -\frac{\mu_0}{4\pi} \frac{g^2 \beta^2}{r^5} [3(\mathbf{s}_1 \cdot \mathbf{r})(\mathbf{s}_2 \cdot \mathbf{r}) - (\mathbf{s}_1 \cdot \mathbf{s}_2)r^2] = \mathbf{S}^{\rm T} \hat{\mathbf{D}} \mathbf{S}$$
(4)

where  $\mu_0$  is the magnetic permeability of vacuum, *g* denotes the Landé factor,  $\beta$  is the Bohr magneton,  $\mathbf{r} = \mathbf{r}_{1,2}$  is the distance of the two-electron spins, and  $\mathbf{s}_i = 1/2[\sigma_{x}, \sigma_{y}, \sigma_z]$  is the spin operator vector of the *i*th particle where  $\sigma_{x}, \sigma_{y}$  and  $\sigma_z$  are Pauli matrices.  $\hat{\mathbf{D}}$  is a second-order traceless tensor also known as the ZFS tensor and can be diagonalized to

$${}^{d}\hat{\mathbf{D}} = \begin{bmatrix} D_{xx} & 0 & 0\\ 0 & D_{yy} & 0\\ 0 & 0 & D_{zz} \end{bmatrix}$$
(5)

where  $D_{xx} + D_{yy} + D_{zz} = T_r({}^d\hat{\mathbf{D}}) = 0$ . Therefore, the Hamiltonian  $H_{ss}$  could be rewritten as follows

$$H_{ss} = D_{xx}S_x^2 + D_{yy}S_y^2 + D_{zz}S_z^2 = D\left(S_z^2 - \frac{2}{3}\right) + E(S_x^2 - S_y^2)$$
(6)

where D and E are axial and transverse ZFS parameters, respectively. By closely following the above-mentioned framework, calculations of  $D_{xx}$ ,  $D_{yy}$ , and  $D_{zz}$  were performed by the projector augmented wave method reported in ref 30. In GS,

the ZFS parameters  $D_{\rm gs}$  and  $E_{\rm gs}$  can be calculated by using the following equations<sup>29</sup>

$$D_{\rm gs} = -\frac{3}{2}D_{zz}, \quad E_{\rm gs} = \frac{D_{yy} - D_{xx}}{2}$$
 (7)

The HFIs characterize the effects of nuclear spin on the  $V_OMo_{Zr}$  center, which plays an important role in the field of QIP.<sup>4,5</sup> In GS, the HFIs can be expressed as follows

$$E_{\rm hyp} = \sum S_i A^{\rm I}_{ij} I_j \tag{8}$$

where  $S_i$  denotes the electronic spins,  $A_{ij}^{I}$  is the hyperfine tensor, and  $I_j$  represents the nuclear spin of the *j*th nucleus. The hyperfine tensor  $A^{I}$  can be expressed as the sum of the isotropic part (the so-called Fermi-contact term)  $(A_{iso}^{I})_{ij}$  and the anisotropic (dipolar contributions) part  $(A_{ani}^{I})_{ij}^{31}$ 

$$(A_{\rm iso}^{\rm I})_{ij} = \frac{2}{3} \frac{\mu_0 \gamma_{\ell}}{\langle S_z \rangle} \delta_{ij} \int \delta_{\rm T}(\mathbf{r}) \rho_{\rm s}(\mathbf{r} + \mathbf{R}_{\rm I}) d\mathbf{r}$$
(9)

$$(A_{\rm ani}^{\rm I})_{ij} = \frac{\mu_0}{4\pi} \frac{\gamma_{\rm I}\gamma_e}{\langle S_z \rangle} \int \frac{\rho_{\rm s}(\mathbf{r} + \mathbf{R}_{\rm I})}{r^3} \frac{3r_i r_j - \delta_{ij} r^2}{r^2} \,\mathrm{d}\mathbf{r}$$
(10)

where  $\gamma_{\rm I}$  and  $\gamma_{\rm e}$  denote the nuclear gyromagnetic ratio of the nucleus I at  $\mathbf{R}_{\rm I}$  and the electron gyromagnetic ratio, respectively.  $\langle S_z \rangle$  corresponds to the expectation value of the *z*-component of the total electronic spin.  $\rho_s$  denotes the electron spin density of electron spin *S*. **r** is taken relative to the position of  $\mathbf{R}_{\rm I}$ .  $\delta_{\rm T}(\mathbf{r})$  is a smeared out  $\delta$  function.<sup>32</sup> The calculated principal values of the hyperfine tensors are often labeled as  $A_{xxy}$   $A_{yyy}$  and  $A_{zz}$ .

Finally, the optical properties were demonstrated to promote the future identification of the center and provide parameters for its optical initialization and signal detection. The V<sub>0</sub>Mo<sub>Zr</sub> center in CZ contributes a zero-phonon line (ZPL), which is the difference in energy between the lowest potential energy surfaces in the GS and excited state (ES). The ZPL value can be calculated via the constraint-DFT (CDFT) method.<sup>33</sup> According to the group theory, we artificially reconfigured the electron occupation of this center in the excited state (ES). Although the PBE functional specializes in accurately describing the material structure, the intrinsic underestimation of the bandgap and effect on energy level positions cannot be ignored. However, the Heyd-Scuseria-Ernzerhof (HSE06)<sup>34</sup> hybrid exchange-correlation functional avoids this problem very well.<sup>35</sup> Hence, the HSE06 functional was employed to carry out the ZPL value with a single gamma point due to the large cell size.

## RESULTS AND DISCUSSION

Initially, the geometry of the V<sub>O</sub>Mo<sub>Zr</sub> center with different charge states (q = +1, 0, -1) was completely relaxed with a fixed lattice parameter. Before geometry optimization, the distance of any Mo—Zr and Zr—Zr adjusting the vacancy was 3.631 Å for all cases. In other words, these four atoms (Mo, Zr<sub>1</sub>, Zr<sub>2</sub>, and Zr<sub>3</sub> shown in Figure 1) form a regular tetrahedron. After optimization, the bond length of Mo—Zr (Zr—Zr) of the V<sub>O</sub>Mo<sub>Zr</sub> center changes to 3.704 Å (3.845 Å), 3.477 Å (3.687 Å), and 3.302 Å (3.600 Å) for q = +1, 0, -1, respectively. Moreover, the space geometry composed of these four atoms changes from a regular tetrahedron to an isosceles tetrahedron in any of the charge states, and the possessed symmetry undergoes a transition from  $T_d$  symmetry to  $C_{3\nu}$  symmetry. The three Zr sites are all equivalent to each other and the Mo–V axis ( $C_{3\nu}$  axis) is shared among these elements.

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A nonzero paramagnetic electronic spin GS is one of the key criteria for its qubit applications.<sup>3</sup> The spin multiplicities were investigated to confirm whether this center possesses a paramagnetic defect bound state. The spin multiplicities of the optimized  $V_OMo_{Zr}$  center are different due to their different charge states. On the basis of our calculations, the values of total spin angular momentum (*S*) of the  $V_OMo_{Zr}$  center are 1/2, 1, 3/2 for q = +1, 0, -1, respectively, and these values are all nonzero. Next, the relative energetic stability of these three states was evaluated by their formation energies. Furthermore, the competing impurities and defects such as  $Mo_{Zr}$  and  $V_O$  were also investigated. The formation energies  $E^{\rm f}$  of the  $V_OMo_{Zr}$ ,  $Mo_{Zr}$ , and  $V_O$  centers in different charge states as a function of the Fermi level  $\varepsilon_{\rm F}$  are shown in Figure 2,



**Figure 2.** Formation energies  $E^{f}$  of the V<sub>O</sub>Mo<sub>Zr</sub>, Mo<sub>Zr</sub>, and V<sub>O</sub> centers in different charge states as a function of the Fermi level  $\varepsilon_{F}$ .  $E_{c}$  and  $E_{v}$ are the relative energy of the conduction band minimum and the VBM, respectively.

revealing that the neutral V<sub>O</sub>Mo<sub>Zr</sub> center is stable for  $\varepsilon_{\rm F} = 1.78-3.64$  eV (shaded area in Figure 2). The V<sub>O</sub>Mo<sub>Zr</sub> center for q = +1 and -1 charge state is unstable as well as that the center for q = +2 and -2 is relatively stable than for q = +1 and -1 at the same Fermi level  $\varepsilon_{\rm F}$  value. Better yet, the total spin angular momentum of neutral V<sub>O</sub>Mo<sub>Zr</sub> center is analogous to the negatively charged NV center (S = 1). Furthermore, compared to other competitive defects or impurities, the relative stability of the neutral V<sub>O</sub>Mo<sub>Zr</sub> center was also investigated. The defect complex V<sub>O</sub>Mo<sub>Zr</sub> center was formed by the agglomeration of Mo<sub>Zr</sub> and V<sub>O</sub> centers. The neutral V<sub>O</sub>Mo<sup>0</sup><sub>Zr</sub> center was formed by the combination of Mo<sup>0</sup><sub>Zr</sub> and V<sup>0</sup><sub>O</sub> centers. The chemical reaction energy  $E_{\rm rea}$  is<sup>27</sup>

$$E_{\rm rea} = E^{\rm f}[{\rm Mo}_{\rm Zr}^0] + E^{\rm f}[{\rm V}_{\rm O}^0] - E^{\rm f}[{\rm V}_{\rm O}{\rm Mo}_{\rm Zr}^0]$$
(11)

where  $E^{t}$  is formation energy defined in eqs 1–3. On the basis of the results shown in Figure 2, the value of  $E_{rea}$  is 3.196 eV, which indicates that the neutral V<sub>O</sub>Mo<sub>Zr</sub> center is a stable, bound complex.

Noteworthy, the group theory provides excellent physical insight into the nature of the electronic structure in GS for the neutral  $V_OMo_{Zr}$  center. A formalism of group theory reveals that a  $V_OMo_{Zr}$  center with  $C_{3\nu}$  symmetry shows two nondegenerate states  $(a_{1(1)} \text{ and } a_{1(2)})$  and two double

degenerate e states ( $e_x$  and  $e_y$ , i.e., the  $e_{xy}$ ), which belong to the irreducible representations (IRs)  $A_1$  and E. The absence of the O-ion (i.e.,  $V_0$ ) in the CZ crystal produces two electrons. The doped Mo element introduces the other two extra electrons. Therefore, four net electrons are localized near the color center. Under the energetic stabilized circumstance, the neutral VoMozr center in GS is spin-triplet and the calculated total spin angular momentum is S = 1. This characteristic is essential for potential spin qubit applications.<sup>3</sup> Furthermore, combining group theory analysis and the first-principles calculations, the  $a_{1(1)}$  molecular orbital (MO) is occupied by two electrons with different spins ( $\uparrow\downarrow$ ), the  $e_x$  and  $e_y$  MOs are each occupied by an electron with the same spins ( $\uparrow$ ,  $\uparrow$ ), and the  $a_{1(2)}$  MO is unoccupied and merges with the conduction band. To explore the nature of the highest occupied nondegenerate MO  $(a_{1(1)})$ and the lowest unoccupied double degenerate MOs  $(e_{xy})$ , the contributions of the MOs were assessed by analyzing the orbital isosurface, as depicted in Figure 3. The 4d orbitals of



**Figure 3.** (a) Side and (b) top view of the isosurface charge density  $(\rho = 0.006 \text{ lel} \cdot \text{Å}^{-3})$  of the  $a_{1(1)}$  MO. (c) Side and (d) top view of the isosurface charge density  $(\rho = 0.006 \text{ lel} \cdot \text{Å}^{-3})$  of the  $e_{xy}$  MOs.

Mo and Zr exhibit an absolute advantage over their respective s and p orbitals in both  $a_{1(1)}$  and  $e_{xy}$  MOs. The Mo 4d orbital exhibits more dominant contributions than the Zr 4d orbital in the  $a_{1(1)}$  MO, and the two 4d orbitals of Mo and Zr are slightly hybridized. The  $e_{xy}$  MOs are almost entirely contributed by the Mo 4d orbital. Further, based on group theory the electronic structure of the neutral V<sub>O</sub>Mo<sub>Zr</sub> center was carefully investigated. Previous analysis indicates that the Mo 4d orbitals,  $d_{Mo}$ ,  $\{d_{Mo} = xy, yz, zx, z^2, x^2-y^2\}$ , provide the major contribution to the  $a_{1(1)}$  and  $e_{xy}$  MOs. The  $d_{Mo}$  orbitals were projected onto each IR of the  $C_{3v}$  point group of the defect to obtain the single electron orbitals  $\varphi_r$  { $\varphi_r = a_{1(1)}, e_{xy}$ }. This consists of a specific combination of different  $d_{Mo}$  orbitals. The expression for  $\varphi_r$  can be calculated by using the following expression<sup>8,36</sup>

$$\varphi_{\rm r} = P^{(r)} d_{{\rm Mo-}i} = \frac{l_j}{6} \sum_{e} \chi_e^{(r)} R_e d_{{\rm Mo-}i}$$
(12)

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where  $P^{(r)}$  corresponds to the  $C_{3\nu}$  projection operator ((r) =  $A_1, A_2, E$ ),  $l_j$  denotes the dimension of the *j*th IR, and  $\chi_e^{(r)}$  is the character of the  $C_{3\nu}$  operation  $R_e$ . The  $C_{3\nu}$  axis corresponds to the [111] axis of the CZ supercell. By applying eq 12 to the  $d_{Mo}$  orbital expression, the single electron orbital bases were obtained (see Section A of the Supporting Information (SI)). By excluding the terms with spherical symmetry ( $x^2 + y^2 + z^2$ ) and due to the linear dependence on the other terms, the following final expressions can be obtained

$$a_{1(1)} = xy + yz + zx \tag{13}$$

$$e_x = 2z^2 - x^2 - y^2, \quad e_y = x^2 - y^2$$
 (14)

$$e'_{x} = 2xy - yz - zx, e'_{y} = zx - xy$$
 (15)

Furthermore, to confirm the exact combination of each  $d_{Mo}$  orbital, the spin-polarized density of states (DOS) of the neutral  $V_OMo_{Zr}$  center (Figure 4a) and the projected density



Figure 4. (a) Total DOS of the neutral  $V_OMo_{Zr}$  center. The component of Zr is the sum of the three Zr atoms surrounding the vacancy (Zr<sub>1</sub>, Zr<sub>2</sub>, and Zr<sub>3</sub> depicted in Figure 1). The contributions of the other Zr atoms in the CZ supercells are small enough to be ignored. (b) PDOS (d-orbitals) of Mo atom in the supercell.

of states (PDOS) of Mo (Figure 4b) provided excellent inspiration. By analyzing Figure 4, the following expressions are derived

$$\varphi_{a_1(1)} = xy + yz + zx \tag{16}$$

$$\varphi_{e_{xy}} = z^2 + (x^2 - y^2) \tag{17}$$

The DOS results indicate that the  $a_{1(1)}$  state is composed of the *xy*, *yz*, and *zx* orbitals; in contrast, the  $e_{xy}$  states consist of the  $z^2$  and  $x^2-y^2$  orbitals. Therefore, the single electron orbital basis of the V<sub>0</sub>Mo<sub>Zr</sub> center can be described as follows: { $a_{1(1)} =$ 

xy + yz + zx,  $e_x = z^2 - x^2 - y^2$ ,  $e_y = x^2 - y^2$ }. The rotation invariance of the  $a_{1(1)}$  state generates a  $C_3$  rotation invariance, which is influenced by the three types of Zr elements surrounding the vacancy.

The ZFS describes the dipole interactions between the two electrons, which is significantly important for MWs' manipulation of a qubit via ESR technology, and for the identification of a new color center. The calculated results of ZFS parameters  $(D_{\rm gs} \text{ and } E_{\rm gs})$  in GS demonstrate that the  $D_{\rm gs}$  component of the neutral  $V_OMo_{Zr}$  center falls in the MWs' range and has a value of 2208.29 MHz, and the value of  $E_{\rm gs}$  measuring zero is attributed to the perfect  $C_{3\nu}$  symmetry in the modeled supercell with the defect complexes. If there is a strain present in the sample, the value of  $E_{\rm es}$  is not zero; instead, it is 2–3 orders of magnitude smaller than the value of  $D_{gs}$ . ZFS releases the triple degeneracy when an external magnetic field is applied along the  $C_{3\nu}$  axis; the manipulation frequency of the reversal of the electronic population between  $m_s = 0$  and  $m_s = +1$ , and between  $m_{\rm s} = 0$  and  $m_{\rm s} = -1$ , is distinguished by 2 $\Delta$ , where  $\Delta$ =  $\gamma_e B$ .  $\gamma_e$  denotes the electron gyromagnetic ratio (with a value of 2.80 MHz/G) and B is the extra magnetic field (see Figure 5). The calculated ZFS parameters then aid in the



**Figure 5.** Fine structure and Zeeman splitting of the neutral  $V_OMo_{Zr}$  center in GS. The three figures in the black boxes on the right exhibit the electron occupancy corresponding to their spin states.

determination of the center frequency of the MWs' manipulation field in defect-related experiments by using the spin states. Consequently, the results of these analyses may provide significant insights to identify and characterize alternative promising systems.

To expand the potential applications of this center in the quantum register and other similar fields, the HFIs between spins of nuclei in lattice sites and of the center's electrons were investigated. In this study, only the isotopes with nonzero nuclear spins were considered: the  $^{91}$ Zr (natural abundance of 11.23%,), the  $^{95}$ Mo (15.72%), and the  $^{97}$ Mo (9.46%) isotopes as well as the calculated results are presented in Table 1. The

Table 1. Calculated	Values	of HFIs	(in MHz)	)
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isotope and site	magnetogyric ratio (MHz/T)	$A_{xx}$	$A_{yy}$	$A_{zz}$	A <sub>tot</sub>
<sup>95</sup> Mo	2.785	73.369	73.369	76.11	74.282
<sup>97</sup> Mo	-2.844	-74.923	-74.923	-77.722	-75.856
$^{91}\mathrm{Zr}_1$	-3.972	7.168	5.845	13.452	8.822
$^{91}{ m Zr_{2}}$	-3.972	7.168	5.845	13.452	8.822
$^{91}\mathrm{Zr}_3$	-3.972	7.168	5.845	13.452	8.822

symbols "<sup>m</sup>X<sub>n</sub>" in column 1 represents the isotopic species and atomic sites. The label "m" corresponds to the atomic mass, whereas "n" is the atom label depicted in Figure 1. There is only one Mo atom in the supercell; therefore, there is no "n" corresponding to Mo in the first two rows of the first column. Columns 3-5 represent the principal values of the hyperfine tensors. Column 6 represents the isotropic total Fermi contact term defined in eq 9. The anisotropic dipole-dipole contributions to the hyperfine tensors were very small, thus they are not shown in the main text, but placed in Section B of SI. Moreover, the calculation results of the hyperfine tensors of the nuclei around the center (except the four atoms shown in Figure 1) are also included in the SI. The values of hyperfine tensors presented in Table 1 indicate that the <sup>95</sup>Mo (<sup>97</sup>Mo) isotope is dominant due to its large value of Fermi contact term, which is proportional to the projected size of the charge density at the nucleus site.<sup>31</sup> Figure 3 demonstrates that the electron charge density is nearly entirely localized at the Mo site, which is in excellent agreement with its Fermi contact term. At the same time, the smaller hyperfine tensors and Fermi contact terms of the remaining three Zr nuclei correspond to the weaker localization of electron charge density at the remaining three Zr sites. Furthermore, data summarized in Table 1 provide the following relationship:  $A_{tot}$ =  $(A_{xx} + A_{yy} + A_{zz})/3$ . The study of HFIs paves the way toward the identification of nuclear spins via method techniques such as nuclear magnetic resonance spectroscopy and electronnuclear double-resonance ENDOR techniques. Further, the investigation on the distinguishability of different nuclear spins expands the range of applications in the quantum register and other similar fields.

Finally, the optical transition properties were systematically investigated. The main objective is to complete the characteristics of this center and to guide the optically detected magnetic resonance (ODMR) applications on this center, which is an extremely important approach to realize qubit-specific measurements. Noteworthy, the optical transition was investigated in the form of the configuration coordinates diagram. Figure 6 presents the calculated configuration coordinates diagram of the neutral  $V_OMo_{Zr}$  center. The energy values of the vertical absorption (A  $\rightarrow$  B), vertical emission (C  $\rightarrow$  D), and ZPL (A  $\rightarrow$  C) measure 1.23, 0.89, and 1.03 eV, respectively, and these values fall in the infrared regions. This result indicates that the electrons can be excited from the GS



**Figure 6.** One-dimensional configuration of the coordinate diagram in the Franck–Condon approximation for the neutral  $V_O Mo_{Zr}$  center. The vertical illustration on the right side presents the schematic illustration of a continuous stimulated emission spectrum.

to the ES by providing rather a low photon energy than in the case of the NV center. The values of Stokes ( $\Delta S$ ) and anti-Stoke ( $\Delta AS$ ) shifts were measured to be 201.8 and 136.5 meV, respectively. Importantly, the  $\Delta AS$  value is a vital parameter to determine the emission spectrum, which corresponds to the maximum probability of generating a phonon-assisted emission. This value indicates that the emitting phonons have a maximum energy of 0.89 eV. Moreover, it falls within the peak of the Poisson energy distribution, as depicted in the illustration on the right side of Figure 6. Motivated by the ODMR applications<sup>37,38</sup> in the NV center, the calculated results on the optical and properties may foster future research on the neutral  $V_OMo_{Zr}$  center.

# CONCLUSION

In this study, the neutral VOMoZr center on CZ with potential qubit applications was proposed. For the further development of this center, the electronic and magneto-optical properties of this center were theoretically investigated via first-principles calculations. The spin-triplet neutral  $V_O Mo_{Zr}$  center in GS possesses a  $C_{3\nu}$  symmetry and its MOs were analyzed via the group theory. The vital ZFS parameters,  $D_{gs}$  and  $E_{gs}$  measured 2208.29 and 0 MHz, respectively. The hyperfine tensors were also investigated to extend the application range of the  $V_{\rm O} Mo_{\rm Zr}$ center in QIP. Compared to the NV center, the VoMozr center needs lower initialization energy to prepare a spin coherent state. This study provides an important basis for the physical understanding of the electronic and magneto-optical properties of this center and proves that this center is a prominent candidate for qubit application. Moreover, benefiting from the available mature semiconductor technology and the competitive cost advantage of such host material, the manufacturing process of CZ-based quantum sensors and/or information processors is scalable. Finally, this study provides an excellent example to identify and explore alternative defect complexes, which can act as a qubit for advanced quantum technology applications.

## ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c05387.

Additional information about the group theory analysis of the molecular orbital combinations and the hyperfine interaction tensors (PDF)

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#### Notes

The authors declare no competing financial interest.

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