Theoretical Studies on the Local Structure and Electron Paramagnetic Resonance Parameters for Cu$^{2+}$ Centers in TiO$_2$ with one Oxygen Vacancy Adjacent

Chao-Ying Li, Xue-Mei Zheng, and Jie He
School of Physics and Electronic Information, Shangrao Normal University, Shangrao Jiangxi 334000, P. R. China

Reprint requests to C.-Y. L.; E-mail: cyli1962@gmail.com

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Based on the defect model that the impurity Cu$^{2+}$ in TiO$_2$ on the octahedral Ti$^{4+}$ site is associated with one oxygen vacancy $V_O$ along the $C_2$ axis, the electron paramagnetic resonance (EPR) parameters, i.e., the $g$ factors $g_i$ ($i = x, y, z$) and the hyperfine structure constants $A_i$, of the Cu$^{2+}$-$V_O$ center in TiO$_2$ are calculated by using the perturbation formulas of these parameters for a 3$d^9$ ion in a rhombically elongated octahedra. From this study, the impurity Cu$^{2+}$ is found to be away from $V_O$ by a distance $\Delta z$ ($\approx 0.33$ Å) along the $C_2$ axis, meanwhile the four $O^2-$ ions in the plane perpendicular to the $C_2$ axis may be shifted by $\Delta x$ ($\approx 0.28$ Å) towards $V_O$ due to the electrostatic interaction between these ions and $V_O$. The theoretical results based on the above local structure distortions show good agreement with the experimental data.

**Key words:** Electron Paramagnetic Resonance (EPR); Defect Structures; Cu$^{2+}$; Oxygen Vacancies ($V_O$); TiO$_2$.

1. Introduction

When doped with transition metal ions, TiO$_2$ exhibits interesting photocatalysis [1, 2] and magnetic and electronic structural properties [3–6]. These properties or behaviours are usually related to the electronic and structural properties of the doped ions in this material. Since the electron paramagnetic resonance (EPR) technique is a powerful tool to study defect structures of paramagnetic impurities in crystals, extensive studies have been carried out on the defect structures and interactions between impurity and ligands for some transition-metal ions (i.e., Cu$^{2+}$, Fe$^{3+}$, Mn$^{2+}$, Co$^{2+}$) doped TiO$_2$ by analyzing their EPR data [7–10]. Decades ago, the EPR spectra of Cu$^{2+}$-doped TiO$_2$ crystals were measured [11] and attributed to the impurity Cu$^{2+}$ occupying the 6-fold coordinated octahedral Ti$^{4+}$ site with no charge compensation despite charge mismatch between the host Ti$^{4+}$ and the impurity Cu$^{2+}$. The EPR parameters and the local lattice distortion for this Cu$^{2+}$ center were also investigated [7, 12]. Whereas, recently, Brant et al. proposed a new model for the impurity Cu$^{2+}$ doped in TiO$_2$ crystals, they suggested that the impurity Cu$^{2+}$ is at the 5-fold coordinated octahedral Ti$^{4+}$ site associated with one oxygen vacancy $V_O$ along the $C_2$ axis forming the Cu$^{2+}$-$V_O$ center due to the charge compensation (see Fig. 1). The EPR parameters (the anisotropic $g$ factors $g_i$ ($i = x, y, z$) and the hyperfine structure constants $A_i$) were also measured [13]. However, no theoretical explanations for the above Cu$^{2+}$ centers in TiO$_2$ have been made until now.

In view of that information about local structures and electronic states for the Cu$^{2+}$ centers in TiO$_2$, it would be helpful to understand the microscopic mechanisms of EPR behaviours for these materials containing Cu$^{2+}$ dopants. Further investigations on the EPR parameters and defect structures for these Cu$^{2+}$ centers are of fundamental and practical significance. In this work, the perturbation formulas of the EPR parameters for a Cu$^{2+}$ (3$d^9$) ion under rhombically elongated octahedral are adopted, including the reasonable local lattice distortion (i.e., the impurity displacement $\Delta z$ along the $C_2$ axes and the ligand shift $\Delta \lambda$ towards $V_O$) due to the electrostatic interaction between these ions and $V_O$ (see Fig. 2).

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Centers in TiO$_2$ ≈ 2$\theta$C (Cu is the value for an ideal octahedron). When would be split into three singlets $^2A_{1g}(\theta)$ and $^2A_{1g}(\epsilon)$ with the latter lying lowest. Meanwhile, the higher cubic orbital triplet $^2T_{2g}$ would be split into three singlets $^2B_{1g}(\xi)$, $^2B_{2g}(\eta)$, and $^2B_{3g}(\zeta)$ [13]. For the studied [CuO$_6$]$^{2-}$ octahedral cluster, since the charge-transfer (CT) energy levels are much higher than the crystal-field (CF) energy levels, the contributions of the CT mechanism to the EPR parameters can be neglected. Because the studied TiO$_2$ : Cu$^{2+}$ has insignificant covalency and weak ligand spin–orbit coupling interaction, the formulas based on the conventional CF model are reasonably adopted here for simplicity, considering merely the contributions from the central ion orbitals and spin–orbit coupling interaction. Thus, we have [12, 16]:

$$g_z = g_z + 2k\zeta / E_2 + k\zeta^2 \left[ (2/E_1 - 1/E_3)/E_2 - 4/(E_1E_3) \right] + g_z\zeta^2 \left[ 2/E_1^2 - (1/E_2^2 - 1/E_3^2)/2 \right] - k\zeta^3$$

$$\cdot \left\{ (1/E_2 - 1/E_3)/(1/E_3 + 1/E_2)/(2/E_1) + (2/E_1 - 1/E_2) - (1/E_3 - 1/E_2)/(2E_2E_4) \right\} + (g_z\zeta^3/4) \left[ (1/E_3 - 2/E_1)/E_2^2 + (2/E_3 - 1/E_2)/E_1^2 \right] + 2(1/E_2 - 1/E_3)/E_1^2 + 2 \left( 1/E_3^2 - 1/E_2^2 \right) / E_1 \right\},$$

$$\cdot \left\{ (1/E_2 - 1/E_3)/(1/E_3 + 1/E_2)/(2/E_1) + (2/E_1 - 1/E_2) - (1/E_3 - 1/E_2)/(2E_2E_4) \right\} + (g_z\zeta^3/4) \left[ (1/E_2 - 2/E_1)/E_3^2 + (2/E_2 - 1/E_3)/E_2^2 \right]$$

For a 3$d^9$ (Cu$^{2+}$) ion in rhombically elongated octahedra, its lower orbital doublet $^2E_g$ would be separated into two singlets $^2A_{1g}(\theta)$ and $^2A_{1g}(\epsilon)$ with the latter lying lowest. Meanwhile, the higher cubic orbital triplet $^2T_{2g}$ would be split into three singlets $^2B_{1g}(\xi)$, $^2B_{2g}(\eta)$, and $^2B_{3g}(\zeta)$ [13]. For the studied [CuO$_6$]$^{2-}$ octahedral cluster, since the charge-transfer (CT) energy levels are much higher than the crystal-field (CF) energy levels, the contributions of the CT mechanism to the EPR parameters can be neglected. Because the studied TiO$_2$ : Cu$^{2+}$ has insignificant covalency and weak ligand spin–orbit coupling interaction, the formulas based on the conventional CF model are reasonably adopted here for simplicity, considering merely the contributions from the central ion orbitals and spin–orbit coupling interaction. Thus, we have [12, 16]:

$$g_z = g_z + 2k\zeta / E_2 + k\zeta^2 \left[ (2/E_1 - 1/E_3)/E_2 - 4/(E_1E_3) \right]$$

$$+ g_z\zeta^2 \left[ 2/E_1^2 - (1/E_2^2 - 1/E_3^2)/2 \right] - k\zeta^3$$

$$\cdot \left\{ (1/E_2 - 1/E_3)/(1/E_3 + 1/E_2)/(2/E_1) + (2/E_1 - 1/E_2) - (1/E_3 - 1/E_2)/(2E_2E_4) \right\} + (g_z\zeta^3/4) \left[ (1/E_3 - 2/E_1)/E_2^2 + (2/E_3 - 1/E_2)/E_1^2 \right] + 2(1/E_2 - 1/E_3)/E_1^2 + 2 \left( 1/E_3^2 - 1/E_2^2 \right) / E_1 \right\},$$

$$\cdot \left\{ (1/E_2 - 1/E_3)/(1/E_3 + 1/E_2)/(2/E_1) + (2/E_1 - 1/E_2) - (1/E_3 - 1/E_2)/(2E_2E_4) \right\} + (g_z\zeta^3/4) \left[ (1/E_2 - 2/E_1)/E_3^2 + (2/E_2 - 1/E_3)/E_2^2 \right]$$

Fig. 1 (colour online). TiO$_2$ (rutile) crystal structure showing a Cu$^{2+}$ ion substitutes for a Ti$^{3+}$ ion and has an oxygen vacancy along the $C_2$ axis.

2. Calculations

In the TiO$_2$ (rutile structure) crystal, the Ti$^{4+}$ ion is coordinated to a slightly elongated oxygen octahedron with two longer bond lengths $R_1$ ($\approx 1.988$ Å [14]) parallel to the $C_2$ axis and four coplanar shorter bond lengths $R_{\perp}$ ($\approx 1.944$ Å [14]) perpendicular to the axis with the axial distortion angle $\alpha \approx 88.88^\circ$ [14]. In addition, the planar bond angle $\theta$ ($\approx 90^\circ$) inducing the rhombic distortion (i.e., $\delta \theta = \theta_0 - \theta$ where $\theta_0 = 90^\circ$ is the value for an ideal octahedron). When the impurity Cu$^{2+}$ is doped into the lattice of TiO$_2$, it may replace the host Ti$^{4+}$. However, since Cu$^{2+}$ has less charge as compared with the replaced Ti$^{4+}$, one nearest neighbour oxygen vacancy $V_O$ may occur along the $C_2$ axis as compensator [13]. Accordingly, the Cu$^{2+}$ ion impurity may be displaced away from the center of the octahedron by an amount $\Delta z$ along the $C_2$ axis, meanwhile the four O$^{2-}$ ion ligands in the plane perpendicular to the $C_2$ axis may be shifted by a certain displacement $\Delta x$ towards $V_O$ due to the electrostatic interaction between these ions and $V_O$.

![Fig. 2](colour online). Projective view of the impurity Cu$^{2+}$ center in a TiO$_2$ crystal with one oxygen vacancy adjacent along the $C_2$ axis.
\[
g = g_s + 8k/\zeta + n/\epsilon_1 = \left(1/E_3 + 2/E_1 + 2/E_2 - 4/E_3 + 1/E_2 - 2/E_1 + 2/E_2 - 1/E_3 + 2/E_2 - 1/E_1 + 2/E_3 \right)
\]

(1)

\[
g = g_s + 8k/\zeta + n/\epsilon_1 + 1/\zeta^2\left(1/E_3 + 1/E_1 - 1/E_2 + 1/E_3 - 1/E_1 + 1/E_2 + 1/E_3\right)
\]

(2)

\[
\Delta_z \approx \Delta + \Delta \cos \alpha \approx 1/2, \quad R_2 \approx R_1 + \Delta_z, \quad \cos \beta \approx (\Delta + \Delta \sin \alpha)/R_1.
\]

(3)

For the studied Cu\(^{2+}\) center in the octahedral \([\text{CuO}_6]\)\(^{18-}\) cluster, the five ligands are divided into two parts, i.e., the four planar ones with bond lengths \(R_1\) and one with bond length \(R_2\) due to the impurity displacement \(\Delta z\) along the \(C_2\) axis and the shift \(\Delta \) of the planar ligands towards \(V_0\). The angle between the planar bond length \(R_1\) and the \(C_2\) axis is defined as \(\beta\). Thus, the local bond lengths and bond angle are determined as (see Fig. 1)

\[
\Delta_z \approx \Delta + \Delta \cos \alpha \approx 1/2, \quad R_2 \approx R_1 + \Delta_z, \quad \cos \beta \approx (\Delta + \Delta \sin \alpha)/R_1.
\]

(4)

From the local geometry and the superposition model [18], the related rhombic crystal-field parameters can be expressed as

\[
D_e \approx (2/7)A_{2g}(R_0) + (3 \cos^2 \beta - 1)(R_0/R_1)^2
\]

(5)

\[
 \approx \cos \beta \approx (\Delta + \Delta \sin \alpha)/R_1.
\]

Here \(t_2 \approx 3\) and \(t_4 \approx 5\) are the power-law exponents due to the dominant ionic nature of the bonds [19, 20]. \(A_{2g}(R_0)\) and \(A_{4g}(R_0)\) are the intrinsic parameters with the reference distance \(R_0 \approx 1.959\) \(\text{Å}\), which is the metal–ligand distance related to the octahedral \(\text{Ti}^{4+}\) site in the host \(\text{TiO}_2\) crystal [14]. The ratio \(A_{2g}(RO)/A_{4g}(RO)\) is in the range of 9 ~ 12 [12, 21 - 23]; we take \(A_{2g}(RO) \approx 9 A_{4g}(RO)\) here. For \(\text{Cu}^{2+}\) ions in octahedral clusters, the relationship \(A_{4g}(RO) \approx (3/4)D_e\) [21] is held for many systems, where \(D_e\) is the cubic field parameter of the studied system. Since no optical spectral data

Table 1. g factors \(g_i (i = x, y, z)\) and hyperfine structure constants \(A_i\) (in \(10^{-4}\) cm\(^{-1}\)) for \(\text{Cu}^{2+}\) with one oxygen vacancy adjacent along the \(C_4\) axis.

<table>
<thead>
<tr>
<th>(g_i)</th>
<th>(g_x)</th>
<th>(g_y)</th>
<th>(g_z)</th>
<th>(A_{1/2})</th>
<th>(A_{5/2})</th>
<th>(A_{3/2})</th>
<th>(A_{5/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cal.</td>
<td>2.1056</td>
<td>2.0915</td>
<td>2.3471</td>
<td>18.18</td>
<td>25.83</td>
<td>-82.77</td>
<td>19.50</td>
</tr>
</tbody>
</table>
of TiO$_2$:Cu$^{2+}$ were reported, the spectral parameters $D_q \approx 1350$ cm$^{-1}$ and $N \approx 0.83$ can be obtained from the optical spectral studies for Cu$^{2+}$ in KTaO$_3$ and some oxides [21, 24]. Then the spin–orbit coupling coefficient $\zeta$ for TiO$_2$:Cu$^{2+}$ is acquired as the free-ion value $\zeta_0 \approx 829$ cm$^{-1}$ [15, 21]) multiplying $N$.

Thus, in the above formulas for the $g$ factors in (1), there are only two unknown parameters, i.e., the impurity displacement $\Delta z$ and the planar ligand shift $\Delta x$ towards VO for the studied Cu$^{2+}$ center in TiO$_2$. Substituting the related values into (1) and fitting the theoretical results to the experimental data, one gets

$$\Delta z \approx 0.33 \text{ and } \Delta x \approx 0.28 \text{ Å}.$$  \hspace{1cm} (6)

From these values, the local structure parameters can be obtained, i.e., $R_1 \approx 1.828 \text{ Å}$, $R_2 \approx 1.624 \text{ Å}$. The calculated $g$ factors are compared with the experimental values in Table 1.

In the formulas of the hyperfine structure constants, the dipolar hyperfine structure parameters $B_0$ are $388 \cdot 10^{-4}$ cm$^{-1}$ and $416 \cdot 10^{-4}$ cm$^{-1}$ for the free $^{63}$Cu and $^{65}$Cu [25], respectively. The core polarization constant can be determined from the relationship $\kappa \approx -2\zeta/(3\langle r^{-3}\rangle)$, where $\zeta$ is characteristic of the density of unpaired spins at the nucleus of the central ion, and $\langle r^{-3}\rangle$ is the expectation value of the inverse cube of the 3d radial wave function. From the data $\langle r^{-3}\rangle \approx 8.25$ a.u. [15] and $\zeta \approx -3.40$ a.u. [25] for Cu$^{2+}$ in TiO$_2$, one can obtain $\kappa \approx 0.23$. Substituting the above parameters into (1) and fitting the calculated $A$ factors to the observed values, the anisotropic core polarization constant can be obtained, i.e.,

$$\kappa' \approx 0.02.$$  \hspace{1cm} (7)

3. Discussion

According to Table 1, one can find that the calculated $g$ factors $g_i$ and the hyperfine structure constants $A_i$ based on the above local lattice distortion agree reasonably with the experimental data. Thus the observed EPR results are interpreted in this work, and the defect structure (i.e., Cu$^{2+}$–VO) model proposed in [13] of TiO$_2$:Cu$^{2+}$ is also confirmed.

(i) The signs of $\Delta z$ and $\Delta x > 0$ show that the displacement direction of the Cu$^{2+}$ ion impurity and that of the O$^{2-}$ ion ligands in the studied [CuO$_5$]$^{8-}$ cluster are consistent with the expectation based on the electrostatic interaction between these ions and VO$_2$. Moreover, due to the relatively larger distance between VO$_2$ and the four O$^{2-}$ ions in the plane perpendicular to the $C_2$ axis compared to $R_2$ for the impurity Cu$^{2+}$ ion, the obtained $\Delta z \approx 0.33$ Å being slightly larger than $\Delta x \approx 0.28$ Å from the analysis of the EPR parameters is physically reasonable. Interestingly, similar impurity displacements $\Delta z \approx 0.2$ ~ 0.3 Å due to the apical VO$_2$ were also reported for various transition-metal ions (e.g., Co$^{2+}$, Cu$^{2+}$, Fe$^{3+}$, Ni$^{3+}$) on the octahedral Ta$^{5+}$ (or Nb$^{5+}$) site in KTaO$_3$ (or KNbO$_3$) based on the EPR analysis [21, 26–29], shell-model simulations, and embedded-cluster calculations [30].

(ii) From (1), the hyperfine structure constants $A_i$ ($i = x, y, z$) originate mainly from the isotropic contributions proportional to the core polarization constant $\kappa$, characteristic of the Fermi contact between the ground 3s$^2$3d$^9$ configuration and the excited s-orbitals (e.g., 3s$^3$3d$^9$4s$^1$) for the central ion in crystals. The anisotropy parts of the $A$ factors are mainly related to the covalency factor $N$ and the $g$ shifts ($\approx g_{i} - g_{e}$, $i = x, y, z$), which are somewhat relevant to the local structure (rhombic distortion) of the impurity center. However, the small optimal anisotropic core polarization constants $\kappa'$ ($\approx 0.02$), which are much smaller than the isotropic $\kappa \approx 0.23$ and the g anisotropies $\delta g$ ($= g_{e} - g_{i}$) attribute some anisotropic contributions $\delta A$ ($= A_{e} - A_{i}$) for the A factors.

(iii) Unlike the studied Cu$^{2+}$ center on Ti$^{4+}$ site in [7, 12] without charge compensation, the studied impurity center in this work is Cu$^{2+}$ at the 5-fold coordinated octahedral Ti$^{4+}$ site associated with one oxygen vacancy $V_O$ along the $C_2$ axis. The above different local structures for Cu$^{2+}$ in TiO$_2$ may be attributed to the different experimental preparation conditions. This point is also supported by the cubic field parameter $D_q \approx 1350$ cm$^{-1}$ obtained for the Cu$^{2+}$–VO center (i.e., [CuO$_5$]$^{18-}$ cluster) from the optical spectral analysis in [21], which is about 12% smaller than that ($\approx 1540$ cm$^{-1}$ [12]) for Cu$^{2+}$ in TiO$_2$ with no charge compensation (i.e., [CuO$_6$]$^{10-}$ clusters). Interestingly, one and two oxygen vacancies $V_O$ were reported for the [CuO$_5$]$^{18-}$ and [CuO$_4$]$^{16-}$ clusters at the Ta$^{5+}$ site in Cu$^{2+}$ doped KTaO$_3$ due to charge compensation [21].

(iv) There are some errors in the above calculations. First, the approximation of the theoretical model and the formulas can induce some errors for the resultant EPR parameters and the local structural parameters $\Delta z$ and $\Delta x$. Second, it should be pointed out that the above calculations are based on the crystal-field theory, the
contributions of the spin–orbit coupling coefficient of the ligands as well as the ligand p and s orbitals are ignored. Fortunately, for the studied $\text{[CuO}_2\text{]}^{3-}$ cluster, the above contributions can be regarded as negligible because of the much smaller spin–orbit coupling coefficient ($\approx 151 \text{ cm}^{-1}$) of the ligand oxygen than that ($\approx 829 \text{ cm}^{-1}$) of the central Cu$^{2+}$. The ratio $\bar{R}$ is estimated to be not more than 1% when the off-center displacement $\Delta C$ is off-center along the $C_2$ axis. Additionally, the four O$^{2-}$ ions in the plane perpendicular to the $C_2$ axis may shift by an amount $\Delta x$ ($\approx 0.28 \text{ Å}$) towards $V_{\text{O}}$ due to the electrostatic interaction between these ions and $V_{\text{O}}$.

4. Conclusions

The EPR parameters and the local structure for the Cu$^{2+}$ centre in TiO$_2$ with one oxygen vacancy along the $C_2$ axis are theoretically investigated from the perturbation formulas for a 3d$^9$ ion in rhombically elongated octahedra. The impurity Cu$^{2+}$ experiences an off-center displacement $\Delta C$ ($\approx 0.33 \text{ Å}$) away from $V_{\text{O}}$ along the $C_2$ axis. The EPR parameters and the local structural parameters are estimated to be not more than 1% when the ratio $\bar{A}_2(R_0)/\bar{A}_2(\bar{R})$ varies by 10%.

References