Local defect structures and EPR studies on \((\text{FeO}_6)^{9-}\) and \((\text{FeO}_4)^{5-}\) clusters in YGG: \text{Fe}^{3+} system

Hui-Li Li \(^a\), Xiao-Yu Kuang \(^a\)\(^b\), Ying Li \(^a\) & Mei-Ling Duan \(^a\)

\(^a\) Institute of Atomic and Molecular Physics, Sichuan University, Chengdu, China; 
\(^b\) International Centre for Materials Physics, Academia Sinica, Shenyang, China

Available online: 04 Dec 2010
RESEARCH ARTICLE

Local defect structures and EPR studies on (FeO$_6$)$_9^{9-}$ and (FeO$_4$)$_5^{5-}$ clusters in YGG: Fe$^{3+}$ system

Hui-Li Li$^a$, Xiao-Yu Kuang$^{abc}$, Ying Li$^a$ and Mei-Ling Duan$^a$

$^a$Institute of Atomic and Molecular Physics, Sichuan University, Chengdu, China; $^b$International Centre for Materials Physics, Academia Sinica, Shenyang, China

(Received 3 September 2008; final version received 15 November 2008)

The octahedral (FeO$_6$)$_9^{9-}$ and tetrahedral (FeO$_4$)$_5^{5-}$ clusters in yttrium gallium garnet (YGG): Fe$^{3+}$ system are investigated based on the 252 complete energy matrices for d$^5$ configuration ions in trigonal and tetragonal ligand fields, moreover, the EPR and optical spectra are made unified calculation. The results indicate that the defect structures around Fe$^{3+}$ centres display expansion effects at different temperatures 4.2 and 295 K, and which are close to those in YIG garnet, respectively. Simultaneously, the defect structure parameters for Fe$^{3+}$ centres in YGG are determined, and the relationship between the defect structure and the temperature has been discussed.

Keywords: EPR; local defect structure; Fe$^{3+}$ centres

1. Introduction

As we all know that garnet crystals are schematically formulated as A$_3$B$_2$C$_3$O$_{12}$ where 'A', 'B' and 'C' denote trivalent cation sites, dodecahedrally, octahedrally and tetrahedrally coordinated, respectively, the three cation sites (A, B and C) with their range of size and coordination numbers allow for an extensive variety of chemical substitutions. In particular, Nd$^{3+}$, Er$^{3+}$, Cr$^{3+}$ and Fe$^{3+}$ as impurity ions doped in garnet crystals have been the subject of intensive investigations [1–6] and found many applications in areas such as solid state laser [7], optical communications, scintillation [8–10], medical procedures, imaging, displays, flow cytometry, holography and remote sensing [11–13]. As one of the large class A$_3$B$_2$C$_3$O$_{12}$ yttrium gallium garnet (YGG) doped with Fe$^{3+}$ ion has been paid much attention by many workers [6,14–17], but among the works, few work about the defect structure has been reported. In order to understand the microstructure and the local environment of Fe$^{3+}$ centre in YGG, EPR may be regarded as a powerful technique [18–20] to help us to study the local defect structure and impurity ion site.

In the present work, the complete energy matrices (252 × 252) for trigonal and tetragonal ligand-field are constructed on the basis of the complete set $\{J, M_J\}$ of d$^5$ configuration ions. Subsequently, by simulating the EPR parameter $b_0^2$, $b_0^4$, the distortion parameters $R$ and $\theta$ of (FeO$_6$)$_9^{9-}$ and (FeO$_4$)$_5^{5-}$ clusters in YGG: Fe$^{3+}$ system will be determined at 4.2 and 295 K, respectively and the independence of defect structure on temperature will be discussed. Moreover, the zero-field energies $\Delta E_1$, $\Delta E_2$ as functions of the structure parameter $\theta$ for octahedral and tetrahedral Fe$^{3+}$ centres in YGG will be described at 4.2 and 295 K, respectively.

2. Theory model

With the Slater’s method, the 252 × 252 complete energy matrices for d$^5$ configuration ions are constructed in a trigonal or tetragonal ligand field. First, by the Clebsch–Gordon coefficients associated with the coupling of two angular moments, the $\{J, M_J\}$ basic functions are expanded into $|L, S, M_L, M_S\rangle$ functions,

$$\langle J, M_J | = \sum_i C_i |L, S, M_L, M_S\rangle = \sum_j C_j \Phi_j, \quad (1)$$

where $C_i$, $C_j$ are the Clebsch–Gordon coefficients, $\Phi_j$ is one of the 252 basic Slater determinants.

Then, according to the $|L, S, M_L, M_S\rangle_j$ functions of the d$^5$ configuration ions in a trigonal or tetragonal

*Corresponding author. Email: scu_kuang@163.com

ISSN 0026–8976 print/ISSN 1362–3028 online
© 2008 Taylor & Francis
DOI: 10.1080/00268970802629486
http://www.informaworld.com
ligand field, we have constructed the complete energy matrices of the Hamiltonian [21]

\[
\hat{H} = \hat{H}_{\text{ee}} + \hat{H}_{\text{ao}} + \hat{H}_{\text{ef}} = \sum_{i<j} \epsilon_{ij} \gamma_{ij} + \xi \sum_i \gamma_i \cdot s_i + \sum_i V_i,
\]

(2)

where the first term denotes the electron–electron interactions, the second term denotes the spin–orbit coupling interactions and the third term denotes the ligand-field potentials. The matrix elements are functions of the Racah parameters \(B, C\), Tress correction \(\alpha\), Racah correction \(\beta\), spin–orbit coupling coefficient \(\xi\) and ligand-field parameters \(B_{20}, B_{40}, B_{34}\) and \(B_{44}\), which are in the following forms [22]:

\[
\begin{align*}
B_{20} &= \frac{1}{2} \sum_i G_2(\alpha)(3 \cos^2 \theta_i - 1), \\
B_{40} &= \frac{1}{8} \sum_i G_4(\alpha)(35 \cos^4 \theta_i - 30 \cos^2 \theta_i + 3), \\
B_{34} &= \frac{\sqrt{35}}{4} \sum_i G_4(\alpha)(\sin^3 \theta_i \cos \theta_i \cos 3 \varphi_i), \\
B_{44} &= \frac{\sqrt{70}}{16} \sum_i G_4(\alpha) \sin^4 \theta_i \cos 4 \varphi_i,
\end{align*}
\]

where \(G_2(\alpha)\) and \(G_4(\alpha)\) are expressed as

\[
G_2(\alpha) = -q_{e} e G^2(\alpha), \quad G_4(\alpha) = -q_{e} e G^4(\alpha).
\]

(4)

By using the Van approximation [23], we may obtain the following relations:

\[
G_2(\alpha) = -\frac{q_{e} e (\gamma^2)}{R_{\gamma}^3} = \frac{A_2}{R_{\gamma}^3}, \quad G_4(\alpha) = -\frac{q_{e} e (\gamma^4)}{R_{\gamma}^5} = \frac{A_4}{R_{\gamma}^5}.
\]

(5)

The ratio of \((\gamma^2)/\gamma^4) = 0.097 \) is obtained from the radial wave function of \(Fe^{3+}\) ions in the trigonal or tetragonal ligand field may be analysed by employing the spin Hamiltonian [25,26]:

\[
\begin{align*}
\hat{H}_{\text{S(trig)}} &= g \beta H \cdot \hat{S} + \frac{1}{3} b_0^0 \hat{O}_0^0 + \frac{1}{60} (b_0^0 \hat{O}_0^0 + b_2^0 \hat{O}_2^0), \\
\hat{H}_{\text{S(tet)}} &= g \beta H \cdot \hat{S} + \frac{1}{3} b_0^0 \hat{O}_0^0 + \frac{1}{60} (b_0^0 \hat{O}_0^0 + b_4^0 \hat{O}_4^0),
\end{align*}
\]

(6)

where \(\hat{O}_m^m\) is the standard Stevens spin operator and the \(Z\)-axis is taken to be along the \(C_2\)- and \(C_3\)-axes; \(b_0^m\) is EPR zero-field splitting parameter. From above formula (6), the zero-field-splitting energies \(\Delta E_1\) and \(\Delta E_2\) in the ground state \(^4A_1\) are expressed as functions of the EPR parameter \(b_2^0, b_4^0\) and \(b_6^0\) \((m = 3, 4)\) as follows:

\[
\begin{align*}
\Delta E_{1(\text{trig})} &= E\left(\pm \frac{5}{2}\right) - E\left(\pm \frac{1}{2}\right), \\
\Delta E_{2(\text{trig})} &= E\left(\pm \frac{3}{2}\right) - E\left(\pm \frac{1}{2}\right), \\
\Delta E_{1(\text{tet})} &= E\left(\pm \frac{5}{2}\right) - E\left(\pm \frac{1}{2}\right), \\
\Delta E_{2(\text{tet})} &= E\left(\pm \frac{3}{2}\right) - E\left(\pm \frac{1}{2}\right),
\end{align*}
\]

where \(b_2^0\) and \(b_4^0\) are almost independent of \(b_6^0\) \((m = 3, 4)\). It should be noticed that there exist the relations between \(b_0^m\) and \(D, a, F\) (used conventionally in the literature) as follows [25–28]:

\[
\begin{align*}
\text{Trig:} & \quad b_2^0 = D, \quad b_0^0 = -\frac{a - F}{3}, \quad b_4^0 = -\frac{20 \sqrt{2}}{3} a, \\
\text{Tet:} & \quad b_2^0 = D, \quad b_0^0 = \frac{a}{2} + \frac{F}{3}, \quad b_4^0 = \frac{5}{2} a.
\end{align*}
\]

(8)

3. The defect structure calculation of \(Fe^{3+}\) centres in \(YGG\)

Based on the generalities about the garnet crystal structure, the general formula is \(A_3B_2C_3O_{12}\), with ideal \(O_1^{10}\) – Ia3d space group [29–32]. When \(Fe^{3+}\) ions enter \(YGG\), it will substitute \(Ga^{3+}\) ions and occupy the centre of oxygen octahedron with six \(O^2-\) ligands and the centre of oxygen tetrahedron with four \(O^2-\) ligands. In order to describe the structure distortion, the \(Z\)-axis are chosen along the \(C_2\)- and \(C_3\)-axes, as shown in Figure 2, and the distortion can be described by employing two parameters \(\Delta R\) and \(\Delta \theta\). If one uses \(R_0\) and \(\theta_0\) to represent the \(Ga-O\) bond length and the angle between \(Ga-O\) bond and \(C_2\)- and \(C_3\)-axes of the
Figure 2. The local distortion for $\text{Fe}^{3+}$ centres in YGG: $\text{Fe}^{3+}$ system. (a) for octahedron at 4.2 K, (b) for octahedron at 295 K, (c) for tetrahedron at 4.2 K, and (d) for tetrahedron at 295 K.

---

Figure 1. The influence of parameter $b_4^m$ on $b_2^0$ and $b_0^2$ in YGG: $\text{Fe}^{3+}$ system. (a) for octahedron at 4.2 K, (b) for octahedron at 295 K, (c) for tetrahedron at 4.2 K, and (d) for tetrahedron at 295 K.

---

(a) Oct site

(b) Tetsite

(c) $\text{Y}_3\text{Ga}_5\text{O}_{12}$ one-eighth unit cell

---

Molecular Physics

Downloaded by [National Science Library] at 07:42 15 April 2012
The ground-state splitting $\Delta E_1$, $\Delta E_2$ and EPR parameters $b^2_1$ and $b^0_4$ as functions of $\Delta R$ and $\Delta \theta$, $10^4\Delta E_1$, $10^4\Delta E_2$, $10^4b^2_1$ and $10^4b^0_4$ are in units of cm$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta R$</th>
<th>$\Delta \theta$</th>
<th>$10^4\Delta E_1$</th>
<th>$10^4\Delta E_2$</th>
<th>$10^4b^2_1$</th>
<th>$10^4b^0_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octahedral</td>
<td>$T = 4.2$ K</td>
<td>0.0199</td>
<td>0.7480</td>
<td>-7888.5</td>
<td>-2391.3</td>
<td>-1320</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Exp. [17]</td>
<td></td>
<td>-7888.5</td>
<td>-2391.7</td>
<td>-1320</td>
</tr>
<tr>
<td></td>
<td>$T = 295$ K</td>
<td>0.0177</td>
<td>0.8529</td>
<td>-7736.7</td>
<td>-2334.7</td>
<td>-1295</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Exp. [17]</td>
<td></td>
<td>-7736.7</td>
<td>-2334.8</td>
<td>-1295</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>$T = 4.2$ K</td>
<td>0.0106</td>
<td>4.4685</td>
<td>-5299.6</td>
<td>-1850.2</td>
<td>-8799.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Exp. [17]</td>
<td></td>
<td>-5299.7</td>
<td>-1850.2</td>
<td>-880</td>
</tr>
<tr>
<td></td>
<td>$T = 295$ K</td>
<td>0.00905</td>
<td>4.4732</td>
<td>-5330.2</td>
<td>-1861.8</td>
<td>-885</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Exp. [17]</td>
<td></td>
<td>-5330.1</td>
<td>-1861.9</td>
<td>-885</td>
</tr>
</tbody>
</table>

Notes: $10^4b^2_1 = -1781.9$ cm$^{-1}$ for octahedron (4.2 K) [17], $10^4b^2_1 = -1744.2$ cm$^{-1}$ for octahedron (295 K) [17], $10^4b^0_4 = 155$ cm$^{-1}$ for tetrahedron (4.2 K) and (295 K) [17].

Table 2. The observed and calculated optical spectra for Fe$^{3+}$ ions in octahedral and tetrahedral sites with $\zeta = 0$, the units in cm$^{-1}$.

<table>
<thead>
<tr>
<th>Octahedral site</th>
<th>Calculated</th>
<th>Observed [16]</th>
<th>Tetrahedral site</th>
<th>Calculated</th>
<th>Observed [16]</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>10300</td>
<td>10300</td>
<td>13800</td>
<td>13800</td>
<td>4$E^1T_{1g}(G)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14765</td>
<td>15400</td>
<td>20240</td>
<td>20160</td>
<td>4$A_1^1T_{2g}(G)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20609</td>
<td>20600</td>
<td>22895</td>
<td>22730</td>
<td>4$A_1(G),2E(G)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22199</td>
<td>21640</td>
<td>25447</td>
<td>25460</td>
<td>4$T_{2}(D)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24235</td>
<td>23950</td>
<td>28333</td>
<td>29000</td>
<td>4$T(E)$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: $B = 530$ cm$^{-1}$, $C = 3100$ cm$^{-1}$ for octahedral site, $B = 744$ cm$^{-1}$, $C = 2560$ cm$^{-1}$ for tetrahedral site.

Table 3. The calculated values of $R$ in (Å), $\theta$ in (deg) for (FeO$_6$)$^{9-}$, (FeO$_4$)$^5$-clusters in YGG:Fe$^{3+}$ system.

<table>
<thead>
<tr>
<th></th>
<th>Octahedron</th>
<th>Tetrahedron</th>
</tr>
</thead>
<tbody>
<tr>
<td>YGG: Fe$^{3+}$</td>
<td>$4.2$ K</td>
<td>$295$ K</td>
</tr>
<tr>
<td>$R$</td>
<td>2.0149</td>
<td>1.9357</td>
</tr>
<tr>
<td>$\theta$</td>
<td>51.1039</td>
<td>51.2088</td>
</tr>
</tbody>
</table>

Note: $R = 2.019$ Å for octahedral site, $R = 1.866$ Å for tetrahedral site in YIG [33].

The local defect structures of Fe$^{3+}$ replacing Ga$^{3+}$ in both octahedral and tetrahedral sites exhibit expansion distortions, this tendency may be ascribed to the fact that the radius of Fe$^{3+}$ ($r = 0.64$ Å) is larger than that of
Ga$^{3+}$ ($r = 0.62 \text{Å}$) and the Fe$^{3+}$ will push the O$^{2-}$ outward. Subsequently, we find that at the same site but different temperatures the defect structures are very similar, which indicates that the crystals are independent of temperature. Moreover, the distortion parameters $R$ and $\theta$ are listed in Table 3 deduced by equations in (9), from which we can know the values of $R$ and $\theta$ on the both sites at different temperature are close to those of YIG, respectively.

In Figure 3, we plot the curves $\Delta E_1$, $\Delta E_2$ as functions of the structure parameter $\theta$ for octahedral and tetrahedral Fe$^{3+}$ centres in YGG at different temperatures 4.2 and 295 K, respectively. From which we can see that the two figures have similar change trend for the same site at different temperature, this may indicate that the temperature has few influence on the YGG crystal. Meanwhile, we notice that when the value exceeds 54.7356, the values of $\Delta E_1$, $\Delta E_2$ change rapidly with structure parameter $\theta$ for tetrahedral Fe$^{3+}$ centre in YGG.

4. Conclusions

Using the unified crystal-field-coupling scheme, the inter-relation between the molecular structure and electronic structure has been established in trigonal and tetragonal ligand fields. By simulating the experimental EPR parameters $b_0^0$ and $b_0^2$, the local defect structure parameters $R$ and $\theta$ of octahedral (FeO$_6$)$^{5-}$ and tetrahedral (FeO$_4$)$^{5-}$ clusters are determined. The calculated results indicate that the local lattice structures around Fe$^{3+}$ centres display the same expansion distortions along the crystalline axis in the two sites. Finally, the curve of the zero-field energies in the ground state $^6A_1$ as functions of the local structure distortion parameter $\theta$ are plotted and discussed.

Acknowledgements

The authors are grateful to the National Natural Science Foundation of China (No. 10774103) and the Doctoral Education Fund of Education Ministry of China (No. 20050610011).

References