Theoretical Investigations of the Spin Hamiltonian Parameters and the Local Structure of a Trigonal Co$^{2+}$ Center in Bi$_4$Ge$_3$O$_{12}$

Shao-Yi Wu$^{a,b}$ and Hui-Ning Dong$^{b,c}$

$^a$ Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu 610054, P.R. China
$^b$ International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110015, P.R. China
$^c$ College of Electronic Engineering, Chongqing University of Posts and Telecommunications, Chongqing 400065, P.R. China

Reprint requests to S.-Y. W.; E-mail: shaoyi_wu@163.com

Z. Naturforsch. 59a, 563–567 (2004); received June 14, 2004

The spin Hamiltonian parameters anisotropic $g$ factors $g_\parallel$, $g_\perp$ and hyperfine structure constants $A_\parallel$ and $A_\perp$, as well as the local structure of the trigonal Co$^{2+}$ center in Bi$_4$Ge$_3$O$_{12}$ (BGO) are theoretically investigated by the perturbation formulas of the spin Hamiltonian parameters for a $3d^7$ ion in trigonal symmetry, based on the cluster approach. It is found that the impurity Co$^{2+}$ substituting the host Bi$^{3+}$ undergoes an off-center displacement $\Delta Z (\approx -0.132 \, \text{Å})$ away from the center of the oxygen octahedron along the $C_3$ axis. The spin Hamiltonian parameters based on the above displacement show reasonable agreement with the observed values. The results are discussed.

**Key words:** Electron Paramagnetic Resonance (EPR); Crystal-field Theory and Spin Hamiltonians; Defect Structure; Co$^{2+}$; Bi$_4$Ge$_3$O$_{12}$ (BGO).

1. Introduction

Single crystals of Bi$_4$Ge$_3$O$_{12}$ (BGO, i.e., the 2:3 stoichiometry of bismuth germinates) have extensively investigated due to their practical applications as scintillators for the detection of high-energy photons and particles [1, 2], promising potential as nonlinear optical devices [3, 4] and solid-state laser hosts [5] as well as holographic gratings in pure crystals and transition-metal (e.g., Cr, Co, Fe and Mn) doped materials [6–8]. The above properties and applications of BGO are sensitively related to the presence of impurities [9]. For example, as regards optoelectronic applications, transition-metal-doped samples have been found to exhibit both photochromic and photorefractive effects [6–9]. To study its impurity behaviour, EPR experiments have been carried out on cobalt doped BGO, and the spin Hamiltonian parameters $g$ factors $g_\parallel$, $g_\perp$ and the hyperfine structure constants $A_\parallel$ and $A_\perp$ were measured for the trigonal Co$^{2+}$ impurity center [10]. Although the above EPR signals were attributed to the impurity Co$^{2+}$ occupying the trigonally-distorted octahedral Bi$^{3+}$ site [10], the spin Hamiltonian parameters have not been theoretically interpreted, and

![Fig. 1. Local structure of the trigonal Co$^{2+}$ center in BGO. The impurity Co$^{2+}$ replacing the host Bi$^{3+}$ ion undergoes an off-center displacement $\Delta Z$ away from the center of the oxygen octahedron along the $C_3$ axis.](http://znaturforsch.com)

the local structure for this center has not been determined either. In order to make further investigations on the spin Hamiltonian parameters and the local structure of the trigonal Co$^{2+}$ center in BGO, in this paper, we study these parameters and the local structure of this center from the perturbation formulas of the spin Hamiltonian parameters for a $3d^7$ ion in trigonal symmetry.
2. Calculations

For a $\text{Co}^{2+}$ $(3d^7)$ ion in trigonally distorted octahedra, the second-order perturbation formulas of the spin Hamiltonian parameters $g_{||}, g_\perp, A_||$ and $A_\perp$, based on the cluster approach, can be expressed as [11]

$$g_{||} = 2 + \frac{4(k\alpha + 2) \left[ \frac{3}{x^2} - \frac{4}{x^2 + 2x} \right] + 2 \left[ \frac{9}{x^2} - \frac{4}{x^2 + 2x} \right] v_1 + \left( \frac{\alpha}{\alpha'} \right)^2 v_2 - 2 \left( \frac{\alpha}{\alpha'} \right) \left[ \frac{3}{x} - \frac{4}{x + 2} \right] v_3}{\left( \frac{\alpha}{\alpha'} \right)^2 + \frac{6}{x^2 + \frac{8}{x^2 + 2x}}},$$

$$g_\perp = \frac{4 \left[ \frac{\alpha}{\alpha'} \right]^2 + 2k\alpha + 12}{x^2 + \left( x + 2 \right)^2} + \frac{8}{x^2 + \left( x + 2 \right)^2} v_4 + \frac{12}{x(x + 2)} v_5 + \frac{12}{x(x + 2)} v_6 - \left( \frac{\alpha}{\alpha'} \right) \frac{4}{x + 2} v_7,$$

$$A_|| = P \left\{ \frac{-\kappa}{2} \left[ \frac{8}{x^2} \left( \frac{3}{x^2} - \frac{4}{x^2 + 2x} \right) \right] + \frac{4k\alpha}{\alpha'} \left( \frac{3}{x^2} - \frac{4}{x^2 + 2x} \right) \right\},$$

$$A_\perp = P \frac{-2\kappa \left[ \frac{\alpha}{\alpha'} \right]^2 + \frac{12}{x^2 + \left( x + 2 \right)^2} + \frac{8k\alpha}{\alpha'} \frac{8}{x^2 + \left( x + 2 \right)^2}}{\left( \frac{\alpha}{\alpha'} \right)^2 + \frac{6}{x^2 + \frac{8}{x^2 + 2x}}} + P' \frac{-\kappa \left[ \frac{\alpha}{\alpha'} \right]^2 + \frac{12}{x^2 + \left( x + 2 \right)^2} + \frac{12}{x(x + 2)} W_x - \frac{32}{x^2 + \left( x + 2 \right)^2} W_{xy} - \frac{4}{x^2 + \left( x + 2 \right)^2} W_{xz}}{\left( \frac{\alpha}{\alpha'} \right)^2 + \frac{6}{x^2 + \frac{8}{x^2 + 2x}}}.$$
Table 1. The spin Hamiltonian parameters $g_1$, $g_\perp$, $A_i$ and $A_\perp$ for the trigonal Co$^{2+}$ center in BGO.

<table>
<thead>
<tr>
<th></th>
<th>$g_1$</th>
<th>$g_\perp$</th>
<th>$A_1$ $(10^{-4}$ cm$^{-1}$)$^*$</th>
<th>$A_\perp$ $(10^{-4}$ cm$^{-1}$)$^*$</th>
<th>$\Delta A$ $(10^{-4}$ cm$^{-1}$)$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calc.$^a$</td>
<td>3.174</td>
<td>5.021</td>
<td>6.3</td>
<td>187.9</td>
<td>−181.6</td>
</tr>
<tr>
<td>Calc.$^b$</td>
<td>2.813</td>
<td>5.175</td>
<td>−2.362</td>
<td>−8.6</td>
<td>195.0</td>
</tr>
<tr>
<td>Expt.$^{[10]}$</td>
<td>2.765 (5)</td>
<td>5.160 (10)</td>
<td>−2.395 (6)</td>
<td>196 (6)</td>
<td>196.6 (102)</td>
</tr>
</tbody>
</table>

$^a$ Calculations based on the impurity Co$^{2+}$ at the ideal Bi$^{3+}$ site, i.e., $\Delta Z = 0$. $^b$ Calculations based on the local structural parameters in (9) due to the displacement $\Delta Z$. $^*$ The signs of $A_1$ and $A_\perp$ were not given in [10]. According to the studies in this work, we suggest that $A_1$ is negative and $A_\perp$ is positive.

and the approximate relation [11, 12]

$$f_y = N_y^2[1 + \lambda_y^2 S_{dp}(\gamma) - 2 \lambda_y S_{dp}(\gamma)],$$

where $f_y \approx (B/B_0 + C/C_0)/2$ is the ratio of the Racah parameters for a 3$d^7$ ion in the crystal to those of the free ion. $S_{dp}(\gamma)$ are the group overlap integrals.

$$V = (9/7)\bar{A}_2(R) \sum_i (R/R_i)^{\lambda_i}(3 \cos^2 \beta_i - 1)
+ \bar{A}_1(R) \sum_i (R/R_i)^{\lambda_i}[20/(21)(35 \cos^2 \beta_i - 30 \cos^2 \beta_i + 3) + (20 \sqrt{2}/3) \sin \beta_i \cos \beta_i],$$

$$V' = (-3 \sqrt{2}/7)\bar{A}_2(R) \sum_i (R/R_i)^{\lambda_i}(3 \cos^2 \beta_i - 1)
+ \bar{A}_4(R) \sum_i (R/R_i)^{\lambda_i}[(5 \sqrt{2}/21)(35 \cos^2 \beta_i - 30 \cos^2 \beta_i + 3) + (10/3) \sin \beta_i \cos \beta_i],$$

where $t_2$ and $t_4$ are the power-law exponents. One can take $t_2 \approx 3$ and $t_4 \approx 5$ due to the ionic nature of the bonds [15, 16]. $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters with the reference bonding length $R$. For 3$d^7$ ions in octahedra, $\bar{A}_2(R) \approx (3/4) D_q$ [15, 16] and $\bar{A}_4(R) \approx 10.8 A_4(R)$ [16, 17]. For the Bi$^{3+}$ site in BGO, the host metal-ligand bonding lengths $R_j^0$ and the angles $\beta_j^0$ between $R_j^0$ and the $C_3$ axis are $R_j^0 \approx 2.149 \text{Å}$, $\beta_j^0 \approx 51.38^\circ$, $R_2^0 \approx 2.620 \text{Å}$, $\beta_2^0 \approx 104.62^\circ$ [18 20]. Usually, the impurity-ligand distances $R_j$ may be unlike the host metal-ligand distances $R_j^0$ in pure BGO due to the difference of ionic radii between the impurity Co$^{2+}$ and the replaced Bi$^{3+}$. However, we can estimate the distances $R_j$ from the empirical relationship [21, 22]

$$R_j \approx R_j^0 + (r_i - r_h)/2.$$  

Thus, from the intrinsic radius $r_i(\approx 0.72 \text{Å} [23])$ of Co$^{2+}$ and the radius $r_h(\approx 0.95 \text{Å} [23])$ of Bi$^{3+}$, the distances $R_j$ are obtained. Here, the average $R(\approx 2.270 \text{Å})$ is taken as the reference distance in (5), i.e., $R = \bar{R}$. By using the distance $R$ and the Slater-type SCF functions [24, 25], the group overlap integrals $S_{dp}(\xi_0) \approx 0.012$ and $S_{dp}(\xi_2) \approx 0.003$ can be calculated.

Strictly speaking, the structure around the host Bi$^{3+}$ site in BGO has C$_3$ point symmetry. For simplicity, however, one can take the C$_{3v}$ approach, as is done in many crystal-field and spin Hamiltonian calculations for paramagnetic ions in corundum-type crystals [13, 14]. With the superposition model (SPM) [15] and the local geometrical relationship of the $[\text{CoO}_6]$ $^{10-}$ cluster in BGO:Co$^{2+}$ (see Fig. 1), the trigonal field parameters $V$ and $V'$ can be expressed as

$$V \approx 810 \text{ cm}^{-1}, \quad C \approx 3780 \text{ cm}^{-1},$$

$$D_q \approx -660 \text{ cm}^{-1}$$

for the studied system. For a free Co$^{2+}$ ion [27], $B_0 \approx 1115 \text{ cm}^{-1}$ and $C_0 \approx 4366 \text{ cm}^{-1}$, thus $f_y \approx 0.80$. From (3) and (4), we have $N_1 \approx 0.893$, $N_e \approx 0.896$, $\lambda_i \approx 0.349$, $\lambda_e \approx 0.353$. Substituting the free-ion values $\xi_0^0 \approx 533 \text{ cm}^{-1}$ [27], $P_0 \approx 254 \cdot 10^{-4} \text{ cm}^{-1}$ [28] of Co$^{2+}$ and $\xi_0^0 \approx 151 \text{ cm}^{-1}$ [29] of O$^{2-}$ into (2), the parameters $k \approx 0.948$, $k' \approx 0.840$, $\zeta \approx 484 \text{ cm}^{-1}$, $\zeta' \approx 469 \text{ cm}^{-1}$, $P \approx 226 \cdot 10^{-4} \text{ cm}^{-1}$ and $P' \approx 227 \cdot 10^{-4} \text{ cm}^{-1}$ are calculated.

Substituting these parameters (including the trigonal field parameters $V$ and $V'$ based on the impurity Co$^{2+}$ at the ideal Bi$^{3+}$ site) and the core polarization constant
The Local Structure of Trigonal Co$^{2+}$ Center in Bi$_4$Ge$_3$O$_{12}$

\[ \kappa \approx 0.325 \text{ for Co}^{2+} \text{ in oxides [11, 30], the theoretical } \] 
\[ g_\parallel, g_\perp, A_1 \text{ and } A_1 \text{ for Co}^{2+} \text{ in BGO are calculated and shown in Table 1.} \]

From Table 1 it can be found that the calculated $g$ and $A$ factors based on the above structural data are inconsistent with the experimental data, particularly the anisotropies $\Delta g$ and $\Delta A$ are smaller than the observed ones. This means that the estimated trigonal distortion based on the Co$^{2+}$ ion at the exact Bi$^{3+}$ site is somewhat smaller. As pointed out by the studies on impurity ions in trigonally-distorted octahedral environments [21, 31], when the host cation is replaced by the impurity with different size and charge, it can be expected that the impurity ion does not occupy exactly the host site, but is shifted along the C$_3$ axis by an amount $\Delta Z$. Therefore, Co$^{2+}$ may undergo an off-center displacement $\Delta Z$ away from the center of the oxygen octahedron along the C$_3$ axis (see Fig. 1) so as to increase the trigonal distortion and hence the theoretical $\Delta g$ and $\Delta A$. Thus the new local structural parameters $R'_j$ and $\beta'_j$ can be determined from the $\Delta Z$. By fitting the calculated $\Delta g$ or $\Delta A$ to the experiment, one can obtain the displacement (note: the displacement direction towards the center of the oxygen octahedron is defined as positive)

\[ \Delta Z \approx -0.132 \text{ Å} \quad (8) \]

for the studied impurity center. The local structural parameters, based on the $\Delta Z$ are

\[ R_1 \approx 2.119 \text{ Å, } \beta_1 \approx 48.59^\circ, \]
\[ R_2 \approx 2.475 \text{ Å, } \beta_2 \approx 101.66^\circ. \quad (9) \]

The corresponding spin Hamiltonian parameters are also collected in Table 1.

3. Discussions

Table 1 shows that the theoretical spin Hamiltonian parameters, especially the anisotropies $\Delta g$ and $\Delta A$ based on the off-center displacement $\Delta Z$ agree better with the experimental data than those based on Co$^{2+}$ occupying the ideal Bi$^{3+}$ site (i.e., $\Delta Z = 0$).

1. The local structural parameters in (9) for Co$^{2+}$ in BGO indicate that the trigonal distortion is increased due to the outward displacement $\Delta Z$ of Co$^{2+}$, and then the [CoO$_6$]$_{10}^-$ cluster is further compressed along the C$_3$ axis. Since the impurity Co$^{2+}$ is smaller than the replaced Bi$^{3+}$, the immediate environment around the impurity may become looser. Meanwhile, the smaller charge of Co$^{2+}$ leads to a weaker electrostatic interaction acting upon the impurity than on the host. As a result, the impurity Co$^{2+}$ may be unstable at the ideal Bi$^{3+}$ site and then suffer the off-center displacement $\Delta Z$ away from the center of the oxygen octahedron. Interestingly, if one neglects $\Delta Z$ in the above calculations, good agreement between theory and experiment is difficult to achieve by modifying the ratio $A_2(R)/A_4(R)$ within the widely accepted range of $9 \sim 12$ [16] and even the values of the spectral parameters in (7). So, the displacement $\Delta Z$ obtained in this work can be regarded as suitable. Nevertheless, the structural parameters of Co$^{2+}$ obtained in the present work are different from those ($R_1 \approx 2.10(5)$ Å, $\beta_1 \approx 55(5)^\circ$, $R_2 \approx 2.2(1)$ Å and $\beta_2 \approx 125(9)^\circ$) of Mn$^{2+}$ at the same Bi$^{3+}$ site in BGO based on SPM analyses [32]. The local structure of the latter exhibits an almost regular [MnO$_6$]$_{10}^-$ octahedron due to the shift of Mn$^{2+}$ towards the center of the octahedron along the C$_3$ axis [32]. The above discrepancy seems to be attributed to different physical or chemical properties and hence different local behaviour of the two divalent ions in BGO. This point is worthy of further investigations.

2. It is noted that charge mismatching substitution of Bi$^{3+}$ by Co$^{2+}$ would possibly induce charge compensation around the impurity. Judging from the trigonal symmetry of the observed defect center, the probable means of compensation may be a Bi$^{3+}$ in the neighbourhood of the central Co$^{2+}$ substituted by a tetravalent diamagnetic impurity ion. It is however more likely that the charge compensation is far enough from the studied Co$^{2+}$ center and its influence can also be regarded as small and negligible, as pointed out for similar divalent Mn$^{2+}$ in oxides [32, 33].

3. There may be some errors in the calculated spin Hamiltonian parameters and the displacement $\Delta Z$ due to the following: (i) Approximation of the theoretical model and related calculation formulas. (ii) In order to reduce the number of the adjustable parameters, displacements of the oxygen ligands were not included in the calculations. Little change would be induced by this effect. (iii) The errors of the SPM parameters may also have some influence on the final results. We find that the theoretical results are insensitive to the choice of $A_2(R)$, when the ration $A_2(R)/A_4(R)$ changes within the range of $9 \sim 12$, the variations of the calculated trigonal field parameters $V$, $V'$ and hence of the theoretical spin Hamiltonian parameters change by not more than 4%.
In summary, the spin Hamiltonian parameters and the local structure around the trigonal $\text{Co}^{2+}$ center in BGO were theoretically investigated on the basis of a reasonable off-center displacement of the impurity ion along the $C_3$ axis.