Theoretical Explanation of the EPR g Factors for Cu$^{2+}$ Ion in LaCuO$_{3x}$

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Abstract: The oxygen-deficient perovskite series LaCuO$_{3x}$ may serve as a model system with which to study the structure phase change and investigate such questions as the properties of CuO$^-$ state and hence the superconductivity in superconductors. Since electron paramagnetic resonance is a powerful tool to analyze the electronic properties and the local structure, EPR parameters g factors of tetragonal Cu$^{2+}$ center in LaCuO$_{3x}$ crystal have been measured by Mehran et al. (1991), but up to now, there is no theoretical explanation to these useful experimental data. In this paper, EPR parameters g factors g$_{||}$, g$_{\perp}$ for the tetragonal Cu$^{2+}$ center in LaCuO$_{3x}$ are theoretically explained by the method of diagonalizing the full Hamiltonian matrix. The related crystal field parameters are calculated from the superposition model and the local structural parameters. The superposition model parameters used in this work are comparable with those for similar tetragonal (CuO)$_{3y}$ clusters in the previous works. The calculated results are in reasonable agreement with the observed values. The results are discussed. PACS: 76.30.Fc, 74.70, 71.70.Ch

Key words: Electron paramagnetic resonance, crystal field theory, Cu$^{2+}$, LaCuO$_{3x}$

Introduction

It is of interest for the oxygen-deficient perovskite series LaCuO$_{3x}$ which may have tetragonal, monoclinic or orthorhombic lattice structure according to the different x values. In addition, its oxygen stoichiometry range (0<x<0.5) is the widest yet found in copper oxide compound with the copper valence to be changed from +2 to +3. This series may thus serve as a model system with which to study the structure phase change and investigate such questions as the properties of CuO$^-$ state and hence the superconductivity in superconductors. So many theoretical and experimental works has been done to understand the several characteristics of the LaCuO$_{3x}$ crystals (Normand and Rice, 1997; 1996; Bringley et al., 1990; Matthias et al., 1997; Cryzky and Sawatzky, 1994; Okada and Kotani, 1999; Yalovega et al., 2000). For instance, electron paramagnetic resonance parameters g factors g$_{||}$, g$_{\perp}$ of tetragonal Cu$^{2+}$ center in LaCuO$_{3x}$ crystal have been measured by Mehran et al. (1991) but up to now, there is no theoretical explanation to these useful experimental data. In this paper, by diagonalizing the full Hamiltonian matrix, the electron paramagnetic resonance (EPR) parameters g factors g$_{||}$, g$_{\perp}$ for the tetragonal Cu$^{2+}$ center in LaCuO$_{3x}$ are theoretically explained. The related crystal field parameters are calculated from the superposition model and the local structural parameters.

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The superposition model parameters used in this work are comparable with those for similar tetragonal (CuO$_2$)$_{10}$ clusters in the previous works. The calculated results are in reasonable consistent with the experimental findings. The results are discussed.

Calculations

LaCuO$_4$ crystal has a distorted perovskite structure which belongs to the P4/m space group. For the typical tetragonal phase, there are two apical Cu-O bonds with 1.986 Å and four in-plane Cu-O bonds with 1.909 Å, which were given by Normand and Rice (1997).

Cu$^2+$ has a 3d$^9$ electronic configuration. The Hamiltonian for a transition-metal ion in the crystal under an external magnetic field can be written as (Abragam and Bleaney, 1970; Wu et al., 2004):

$$\hat{H} = \hat{H}_e + \hat{H}_{so} + \hat{H}_{cf} + \hat{H}_z$$

(1)

where \(\hat{H}_e\) is the electron-electron repulsion term, \(\hat{H}_{so}\) is the spin-orbit coupling interaction and \(\hat{H}_{cf}\) is the crystal-field Hamiltonian \(\hat{H}_z\) can be written as:

$$\hat{H}_z = \sum_{i=1}^{N} \xi_i \hat{L}_z \hat{s}_i$$

(2)

where \(\xi_i\) is the spin-orbit coupling coefficient, for free Cu$^2+$, \(\xi_i = 829 \text{ cm}^{-1}\) (Griffith, 1964). For tetragonal symmetry, the crystal-field interaction can be expressed in terms of the irreducible tensor operators \(C^\lambda_\mu\):

$$\hat{H}_{cf} = B_{2u} C^2_2 + B_{4u} C^2_4 + B_{6u} (C^2_4 + C^4_4)$$

(3)

where \(B_{4u}\) are crystal field parameters. The Zeeman interaction \(\hat{H}_z\) can be written as \(\hat{H}_z = g, \mu_B, \hat{B} \cdot \hat{J}\), with their original meanings (Abragam and Bleaney, 1970; Griffith et al., 1964).

By diagonalizing the complete energy matrix, we can obtain the energy levels eigenvalues. For the tetragonal (CuO$_2$)$_{10}$ cluster, the EPR spectra of Cu$^2+$ in octahedra are typical of an effective spin, \(S^e = 1/2\) the wave functions of ground Kramers doublets can be written as \(|\pm 1/2\rangle\), which can be obtained by diagonalizing the energy matrix, then the g-factors \(g_0\) and \(g_\perp\) can be expressed as (Abragam and Bleaney, 1970; Griffith et al., 1964).

$$g_\parallel = 2 <\frac{1}{2} | N^2 \hat{L}_z + g, \hat{S}_z | \frac{1}{2}>$$

$$g_\perp = 2 <\frac{1}{2} | N^2 \hat{L}_z + g, \hat{S}_z | \frac{1}{2}>$$

(4)

where \(g_\parallel \approx 2.0023\) is the free spin g-value, \(k\) is the orbital reduction factor due to the covalency reduction effect. \(\hat{L}_z\), and \(\hat{S}_z\) are, respectively, the orbital and spin angular momenta.

The hyperfine structure constants \(A_{2N}\) and \(A_z\) can be derived as (Rao and Narayana, 1964; Huang et al., 2003; Dong et al., 2004).

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Table 1: EPR g-factors and hyperfine structure parameters for Cu\textsuperscript{2+} in LaCuO\textsubscript{x} crystal

<table>
<thead>
<tr>
<th></th>
<th>g\textsubscript{\textsc{e}}</th>
<th>g\textsubscript{\textsc{z}}</th>
<th>A\textsubscript{0}</th>
<th>A\textsubscript{1}</th>
<th>A\textsubscript{2}</th>
<th>A\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>60Cu\textsuperscript{2+}</td>
<td>2.6283</td>
<td>1.9543</td>
<td>59.4</td>
<td>52.7</td>
<td>106.6</td>
<td>56.5</td>
</tr>
<tr>
<td>62Cu\textsuperscript{2+}</td>
<td>2.65</td>
<td>1.91</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\begin{align*}
A\textsubscript{0} &= P[-\kappa - \frac{4}{7} N^2 + (g\textsubscript{\textsc{e}} - g\textsubscript{\textsc{z}}) + \frac{3}{7} (g\textsubscript{\textsc{e}} - g\textsubscript{\textsc{z}})] \\
A\textsubscript{1} &= P[-\kappa + \frac{2}{7} N^2 + \frac{11}{14} (g\textsubscript{\textsc{e}} - g\textsubscript{\textsc{z}})]
\end{align*} \tag{5}

where \( \kappa \) is the core polarization constant, which is near the value 0.3 for 3d\textsuperscript{2} ions in crystals (Dong et al., 2004)). \( P \) is the dipolar hyperfine parameter for Cu\textsuperscript{2+} in the crystal, \( P = P_0 \) (where \( P_0 \) is the free-ion value, i.e., \( P_0 \approx 388 \times 10^{-4} \text{ cm}^{-1} \) for 60Cu\textsuperscript{2+} and \( P_0 \approx 416 \times 10^{-4} \text{ cm}^{-1} \) for 62Cu\textsuperscript{2+}, respectively (McGarvey et al., 1967).

Based on the Newman’s superposition model (Yeung and Newman, 1986; Newman and Ng, 1989) the crystal field parameters in Eq.(3) can be expressed as:

\begin{equation}
B_{\text{ef}} = \sum_{i=1}^{3} \overline{A}_i \langle R_i | R_j \rangle^2 K_0(\theta, \phi)
\end{equation} \tag{6}

where \( t_b \) is the power-law exponent and \( \overline{A}_i (R_0) \) is the intrinsic parameter with the reference distance \( R_0 \). Usually, \( t_b = 3 \) and \( t_b = 5 \) because of the ion nature of the bonds (Newman and Ng, 1989; Edgar, 1976). For the (CuO\textsubscript{3})\textsuperscript{\textsc{2+}} octahedron cluster, \( \overline{A}_i (R_0) = 615 \text{ cm}^{-1} \) with \( R_0 = 2.153 \text{ Å} \) (Petrosyan et al., 1984). Since the ratio \( A_i (R_0)/A_i (R_0) \) is in the range of 9–12 for 3d\textsuperscript{2} ions in many crystals (Yeung and Newman, 1986; Edgar, 1976), we take \( \overline{A}_i (R_0) = 11 \overline{A}_i (R_0) \) here. The coordination factor \( K_0(\theta, \phi) \) can be obtained from the local structural parameters of the studied system (Yeung and Newman, 1986; Newman and Ng, 1989). There are two apical Cu-O bonds with \( R_0 = 1.986 \text{ Å} \) and four in-plane Cu-O bonds with \( R_0 = 1.909 \text{ Å} \) (Normand and Rice, 1997).

Substituting all these parameters into the above formulas and diagonalizing the complete energy matrix, the g-factors for Cu\textsuperscript{2+} ion and the hyperfine structure constants \( A \) factors for 60Cu\textsuperscript{2+} and 62Cu\textsuperscript{2+} isotopes in LaCuO\textsubscript{x} are obtained. The comparisons between the calculated and experimental EPR parameters are shown in (Table 1).

**Discussion**

By diagonalizing the Hamiltonian matrix, we calculated the electron paramagnetic resonance g factors \( g_0 \) and \( g_2 \) for the tetragonal Cu\textsuperscript{2+} center in LaCuO\textsubscript{x} crystal. One can find that the calculated EPR parameters g factors in LaCuO\textsubscript{x} are in reasonable agreement with the experimental findings (Table 1). This indicates that the study method and the used parameters in this paper can be regarded as reasonable.

The observed values of \( A_0 \) and \( A_1 \) for tetragonal Cu\textsuperscript{2+} center in LaCuO\textsubscript{x} were not reported. These calculated results (Table 1) remain to be checked by the experimental studies.
Acknowledgement

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References