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Investigations of the g factors and local structure for orthorhombic $Cu^{2+}(1)$ site in fresh $PrBa_2Cu_3O_{6+x}$ powders

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The electron paramagnetic resonance (EPR) g factors g_x, g_y and g_z of the orthorhombic $Cu^{2+}(1)$ site in fresh $PrBa_2Cu_3O_{6+x}$ powders are theoretically investigated using the perturbation formulas of the g factors for a $3d^9$ ion under orthorhombically elongated octahedra. The local orthorhombic distortion around the $Cu^{2+}(1)$ site due to the Jahn-Teller effect is described by the orthorhombic field parameters from the superposition model. The $[CuO6]^{10-}$ complex is found to experience an axial elongation of about 0.04 Å along c axis and the relative bond length variation of about 0.09 Å along a and b axes of the Jahn-Teller nature. The theoretical results of the g factors based on the above local structure are in reasonable agreement with the experimental data.

Key words: *crystal fields and Hamiltonians, electron paramagnetic resonance, Cu^{2+}, $PrBa_2Cu_3O_{6+x}$*

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1. Introduction

$PrBa_2Cu_3O_{6+x}$ (Pr123) compounds are useful materials with anomalous resistive and magnetic [1], vortex [2, 3], friction [4], structural [5] and superconductive [6] properties and have attracted extensive interest of researchers. These properties are largely related to the local structure and electronic behaviours near the Cu^{2+} site, which can be investigated by means of the electron paramagnetic resonance (EPR) technique. For example, EPR experiments were carried out for fresh $PrBa_2Cu_3O_{6+x}$ powders, and the anisotropic g factors g_x, g_y and g_z were also measured for the $Cu^{2+}(1)$ site [7]. Until now, however, the above experimental results have not been quantitatively interpreted, and the local structure around the $Cu^{2+}(1)$ site is not determined, either. Since the electronic properties and the local structure of the paramagnetic Cu^{2+} as well as the microscopic mechanisms of its EPR spectra would be helpful in understanding the properties of the Pr123 systems, further theoretical investigations on the g factors and the local structure of the $Cu^{2+}(1)$ site for the fresh $PrBa_2Cu_3O_{6+x}$ powders are of fundamental and practical significance. In this work, the g factors and the local structure of the fresh $PrBa_2Cu_3O_{6+x}$ powders are theoretically studied using the high order perturbation formulas of the g factors for a $3d^9$ ion in an orthorhombically elongated octahedron. In the calculations, the local orthorhombic distortion of the $Cu^{2+}(1)$ site is quantitatively involved from the superposition model in view of the Jahn-Teller effect.

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2. Calculation

In the orthorhombic phase of $PrBa_2Cu_3O_{6+x}$, the Cu^{2+}(1) site belonging to orthorhombic point symmetry (D_2) has six nearest neighbour oxygen ligands, which construct a distorted octahedron with the approximately mutually vertical Cu–O bonds of the average (or reference) distance R (≈ 1.917 Å [8]). As a Jahn-Teller ion, Cu^{2+} can suffer the Jahn-Teller effect via relaxation and compression of the Cu–O bonds parallel with and perpendicular to the c axis in terms of the relative axial elongation ΔZ. Meanwhile, the planar Cu–O bonds may suffer another relative bond length variation ΔX along a and b axes. Thus, the local structure of the orthorhombic Cu^{2+}(1) site in the fresh $PrBa_2Cu_3O_{6+x}$ powders can be characterized by axial elongation ΔZ and the perpendicular bond length variation ΔX (see figure 1).

For a $Cu^{2+}(3d^9)$ ion in an orthorhombically elongated octahedron, the original cubic ground orbital doublet ^2E_g may split into two orbital singlets $^2A_{1g}$ and $^2A'_{1g}$, with the latter lying lowest. Nevertheless, the upper cubic orbital triplet $^2T_{2g}$ can be separated into three orbital singlets $^2B_{1g}$, $^2B_{2g}$ and $^2B_{3g}$ [9]. The high order perturbation formulas of the g factors for an orthorhombically elongated octahedron can be expressed as follows [10]:

$$
\begin{aligned}
g_x &= g_s + 2k\frac{\zeta}{E_2} + k\zeta^2\left[\frac{2}{E_1E_2} - \frac{1}{E_2E_3} - \frac{4}{E_1E_3}\right] + g_s\zeta^2\left[\frac{2}{E_1^2} - \frac{1}{2E_2^2} + \frac{1}{2E_3^2}\right] \\
&\quad - k\zeta^3\left[\frac{\left(\frac{1}{E_2}-\frac{1}{E_3}\right)\left(\frac{1}{E_3}+\frac{1}{E_2}\right)}{2E_1} + \frac{\left(\frac{2}{E_1}-\frac{1}{E_2}\right)\left(\frac{2}{E_1}+\frac{1}{E_2}\right)}{2E_3} - \frac{\frac{1}{E_2}-\frac{1}{E_3}}{2E_2E_4}\right] \\
&\quad + \frac{g_s\zeta^3}{4}\left[\frac{\frac{1}{E_3}-\frac{2}{E_1}}{E_2^2} + \frac{\frac{2}{E_3}-\frac{1}{E_2}}{E_3^2} + 2\frac{\frac{1}{E_2}-\frac{1}{E_3}}{E_1^2} + 2\frac{\frac{1}{E_2^2}-\frac{1}{E_3^2}}{E_1}\right], \\
g_y &= g_s + 2k\frac{\zeta}{E_3} + k\zeta^2\left[\frac{\frac{2}{E_1}-\frac{1}{E_2}}{E_3} - \frac{4}{E_1E_2}\right] + g_s\zeta^2\left[\frac{2}{E_1^2} - \frac{1}{2E_3^2} + \frac{1}{2E_2^2}\right] \\
&\quad + k\zeta^3\left[\frac{\left(\frac{1}{E_2}-\frac{1}{E_3}\right)\left(\frac{1}{E_3}+\frac{1}{E_2}\right)}{2E_1} + \frac{\left(\frac{2}{E_1}-\frac{1}{E_3}\right)\left(\frac{2}{E_1}+\frac{1}{E_3}\right)}{2E_2} - \frac{\frac{1}{E_3}-\frac{1}{E_2}}{2E_3E_4}\right] \\
&\quad + \frac{g_s\zeta^3}{4}\left[\frac{\frac{1}{E_2}-\frac{2}{E_1}}{E_3^2} + \frac{\frac{2}{E_2}-\frac{1}{E_3}}{E_2^2} + 2\frac{\frac{1}{E_3}-\frac{1}{E_2}}{E_1^2} + 2\frac{\frac{1}{E_3^2}-\frac{1}{E_2^2}}{E_1}\right], \\
g_z &= g_s + 8k\frac{\zeta}{E_1} + k\zeta^2\left[\frac{1}{E_2E_3} + 2\left(\frac{1}{E_1E_2} + \frac{1}{E_1E_3}\right)\right] - g_s\zeta^2\left[\frac{1}{E_1^2} - \frac{\frac{1}{E_2^2}+\frac{1}{E_3^2}}{4}\right] \\
&\quad + k\zeta^3\frac{\frac{8}{E_1}-\frac{1}{E_2}-\frac{1}{E_3}}{2E_2E_3} - 2k\zeta^3\frac{\frac{1}{E_1E_2}+\frac{1}{E_1E_3}-\frac{1}{E_2E_3}}{E_1} \\
&\quad + \frac{g_s\zeta^3}{4}\left[2\frac{\frac{1}{E_2^2}+\frac{1}{E_3^2}}{E_1} - \frac{\frac{1}{E_2}+\frac{1}{E_3}}{E_2E_3}\right].
\end{aligned}
\tag{1}
$$

Here $g_s(\approx 2.0023)$ is the spin-only value. k is the orbital reduction factor, and ζ is the spin-orbit coupling coefficient of the $3d^9$ ion in crystals. The denominators E_i ($i = 1-3$) are the separations between the excited $^2B_{1g}$, $^2B_{2g}$ and $^2B_{3g}$ and the ground $^2A'_{1g}$ states, which can be obtained in terms of the cubic field parameter D_q and the orthorhombic field parameters D_s, D_t, D_ξ and D_η as [10]:

$$
\begin{aligned}
E_1 &= 10D_q, \\
E_2 &= 10D_q - 3D_s + 5D_t + 3D_\xi - 4D_\eta, \\
E_3 &= 10D_q - 3D_s + 5D_t - 3D_\xi + 4D_\eta.
\end{aligned}
\tag{2}
$$

As mentioned before, the orthorhombic distortion of the Cu^{2+}(1) site may be described as the reference distance R as well as the relative axial elongation ΔZ and the planar bond length variation ΔX.

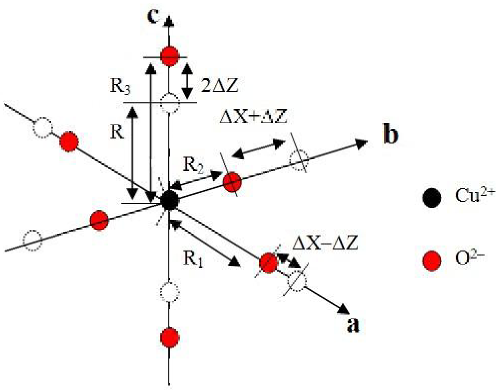

Figure 1. The local structure of the Cu^{2+}(1) site in the fresh $PrBa_2Cu_3O_{6+x}$ powders. The local Cu–O bond lengths R_i are described as the reference distance R in terms of the relative axial elongation ΔZ and the planar bond length variation ΔX.

Thus, the Cu–O bond lengths along a, b and c axes are expressed as: $R_1 = R - \Delta Z + \Delta X$, $R_2 = R - \Delta Z - \Delta X$ and $R_3 = R + 2\Delta Z$, respectively (see figure 1). This means that the Cu–O bonds suffer a relative elongation and compression of $2\Delta Z$ and ΔZ along c and a (or b) axes, respectively. Meanwhile, the planar Cu–O bonds undergo an additional relative bond length variation of ΔX along a and b axes.

Usually, the crystal-field parameters can be determined from the superposition model which has been extensively adopted for transition-metal ions in crystals [11]. Moreover, this model can also be used for powder or polycrystal systems (e.g., the superposition model analysis of the EPR spectra for Fe^{3+} modified polycrystalline $PbTiO_3$ [12] and $PbZrO_3$ [13] and Eu^{2+} in polycrystalline A zeolite [14]) and may be suitably applied to the fresh $PrBa_2Cu_3O_{6+x}$ powders studied here. From the local geometry and the superposition model [11], the orthorhombic field parameters can be determined as follows:

$$\begin{aligned}
D_s &\approx -2\overline{A}_2\left[(R/R_1)^{t2} + (R/R_2)^{t2} - 2(R/R_3)^{t2}\right]/7,\\
D_\xi &\approx 2\overline{A}_2\left[(R/R_1)^{t2} - (R/R_2)^{t2}\right]/7,\\
D_t &\approx 8\overline{A}_4\left[2(R/R_3)^{t4} - (R/R_1)^{t4} - (R/R_2)^{t4}\right]/21,\\
D_\eta &\approx 5\overline{A}_4\left[(R/R_1)^{t4} - (R/R_2)^{t4}\right]/21.
\end{aligned} \tag{3}$$

It is noted that the angular dependence is reduced due to the Cu–O bond angles (0, $\pi/2$ and π related to Z axis and 0, $\pi/2$, π and $3\pi/2$ related to X axis) and thus only the bond lengths R_i are reserved in the above formulas. Here $t_2 \approx 3$ and $t_4 \approx 5$ are the power-law exponents [11] and they are the intrinsic parameters. For $3d^n$ ions in octahedra, the relationships $\overline{A}_4 \approx 3D_q/4$ and $\overline{A}_2 \approx 10.8\overline{A}_4$ [11, 15, 16] were proved to be valid for many crystals and are suitably adopted here. Thus, the g factors (especially the axial anisotropy $\Delta g = g_z - (g_x + g_y)/2$ and the perpendicular anisotropy $\delta g = g_x - g_y$) are correlated with the orthorhombic field parameters and hence with the local structure of the system studied.

From the optical spectra for Cu^{2+} in some oxides [17], the spectral parameters $D_q \approx 1400$ cm^{-1} and $k \approx 0.77$ are obtained for the Cu^{2+} center in the fresh $PrBa_2Cu_3O_{6+x}$ powders here. The spin-orbit coupling coefficient is usually expressed as $\zeta \approx k\zeta_0$, where ζ_0(≈ 829 cm^{-1} [18]) is the corresponding free-ion value. Substituting these values into equation (1) and fitting the calculated g factors (especially the anisotropies) to the experimental data, one can determine the local axial elongation and the planar bond length variation:

$$\Delta Z \approx 0.04 \text{ Å} \quad \text{and} \quad \Delta X \approx 0.09 \text{ Å}. \tag{4}$$

The corresponding theoretical g factors are shown in table 1.

Table 1. The anisotropic g factors for the $Cu^{2+}(1)$ site in the fresh $PrBa_2Cu_3O_{6+x}$ powders.

	g_x	g_y	g_z	Δg	δg
Cal.	2.056	2.088	2.224	0.152	0.032
Expt. [7]	2.050(4)	2.094(4)	2.222(4)	0.15(8)	0.044(8)

3. Discussion

Table 1 reveals that the theoretical g factors and the anisotropies for the fresh $PrBa_2Cu_3O_{6+x}$ powders based on the local structural parameters ΔZ and ΔX are in good agreement with the experimental data. Therefore, the EPR spectra are satisfactorily interpreted for the fresh $PrBa_2Cu_3O_{6+x}$ powders in this work.

The EPR g factors of the fresh $PrBa_2Cu_3O_{6+x}$ powders can be characterized by the axial and perpendicular anisotropies Δg (≈ 0.15) and δg (≈ 0.044), which are ascribed to the local axial elongation ΔZ (≈ 0.04 Å) and the planar bond length variation ΔX (≈ 0.09 Å), respectively. Thus, the $Cu^{2+}(1)$ site exhibits a moderate orthorhombic distortion of the Jahn-Teller nature. Similar axial elongations and planar bond length variations due to the Jahn-Teller effect were also found for some Jahn-Teller ions (e.g., Cr^{5+} and Ti^{3+} with the same spin $S = 1/2$) in oxygen octahedra [19, 20]. It seems that Cu^{2+} prefers to exhibit elongation distortions (i.e., orthorhombically elongated octahedra) under oxygen environments.

There are some errors in the above calculations. First, the approximations of the theoretical model and formulas may bring about some errors in this work. Second, the errors also arise from the approximation of the relationship $\overline{A}_2(R) \approx 10.8\overline{A}_4(R)$ [11, 15, 16], which would somewhat affect the orthorhombic field parameters and the final results. The errors for the local structural parameters ΔZ and ΔX are estimated to be no more than 1% as the ratio $\overline{A}_2(R)/\overline{A}_4(R)$ changes by 10%. Third, the present calculations are based on the conventional crystal-field model containing only the central ion orbital and spin-orbit coupling contributions, while the ligand orbital and spin-orbit coupling contributions are not taken into account. Fortunately, although the studied system has some covalency (characterized by the covalency factor $N \approx 0.77 < 1$), the spin-orbit coupling coefficient (≈ 151 cm^{-1} [21]) of the ligand O^{2-} is much smaller than that (≈ 829 cm^{-1} [18]) of Cu^{2+}. According to various EPR studies for Cu^{2+} under oxygen octahedra [22–24], the ligand contributions to the g factors may be very small and negligible. So, the present theoretical calculations can be regarded as reasonable. Moreover, the investigations in this work would be helpful in carrying out structural and magnetic studies on $PrBa_2Cu_3O_{6+x}$ superconductors as well as applicable to other similar R123 systems.

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Дослідження g факторів і локальної структури орторомбічного вузла в чистому порошку $PrBa_2Cu_3O_{6+x}$

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g фактори g_x, g_y і g_z електронного парамагнітного резонансу для орторомбічного вузла $Cu^{2+}(1)$ в чистому порошку $PrBa_2Cu_3O_{6+x}$ теоретично досліджуються, використовуючи формалізм теорії збурень для цих параметрів для $3d^9$ іона в орторомбічному видовженому октаедрії. Локальна орторомбічна дисторсія навколо вузла $Cu^{2+}(1)$, спричинена ефектом Яна-Теллера, описується за допомогою параметрів орторомбічного поля із суперпозиційної моделі. Знайдено, що комплекс $[CuO6]^{10-}$ піддається аксіальному видовженню близько 0.04 Å вздовж c осі і відносна зміна довжини зв'язку природи Яна-Теллера є приблизно 0.09 Å вздовж осей a і b. Теоретичні результати для g факторів, що базуються на вище згаданій локальній структурі, непогано узгоджуються з експериментальними даними.

Ключові слова: *кристалічні поля і гамільтоніани, електронний парамагнітний резонанс, Cu^{2+}, $PrBa_2Cu_3O_{6+x}$*