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# Investigations of the $g$ factors for the orthorhombic $Co^{2+}$ center in $YBa_2Cu_{2.7}Co_{0.3}O_{7-x}$ at room temperature

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**Abstract**

The anisotropic $g$ factors $g_x$, $g_y$ and $g_z$ for the orthorhombic $Co^{2+}$ center on the Cu(1) site in $YBa_2Cu_{2.7}Co_{0.3}O_{7-x}$ at room temperature are theoretically investigated from the perturbation formulae of the g factors for a $3d^7$ ion having low spin ($S = 1/2$) under octahedra with orthorhombic distortion. In these formulae, the contributions to the g factors from the orthorhombic crystal-fields as well as the ligand orbitals and spin-orbit coupling are taken into account based on the cluster approach. This center may be attributed to $Co^{2+}$ located in a moderately compressed oxygen octahedron with additional orthorhombic distortion. The significant decline (characterized by the reduction factor $\gamma \approx 0.13$) of the energy separations due to the Jahn-Teller effect is suggested, by analyzing the experimental g factors. The calculated g factors based on the above contributions show good agreement with the observed values. In addition, the pronounced decrease in the intensity and the remarkable nonlinear increase in the $g_y$ of $Co^{2+}$ EPR spectra as the temperature is lowered from room temperature to 150 K are also mentioned, in view of the opening of the spin gap due to antiferromagnetic interactions.


*Keywords:* Electron paramagnetic resonance; Crystal fields and spin Hamiltonians; $Co^{2+}$; $YBa_2Cu_{2.7}Co_{0.3}O_{7-x}$

## 1. Introduction

$YBa_2Cu_{2.7}Co_{0.3}O_{7-x}$ exhibits superconductivity at 77 K as determined by the absence of a low dc magnetic field modulated microwave signal, which is extremely sensitive to the presence of superconductivity [1]. Substitution of Cu by paramagnetic ions (e.g., $Co^{2+}$) leads to lowering of Tc [2]. In addition, the properties of the Jahn-Teller effect and hot pressing were also studied for $La_{1-x}Ca_xMnO_3$ and $Co^{2+}$ doped YBaCuO (and $SrLaGa_3O_7$) systems [3–7]. Recently, electron paramagnetic resonance (EPR) investigations were carried out on $YBa_2Cu_{2.7}Co_{0.3}O_{7-x}$, and the anisotropic g factors $g_x \approx 2.602$, $g_y \approx 2.896$ and $g_z \approx 3.060$ were measured for the orthorhombic $Co^{2+}$ center on the Cu(1) site at room temperature [7]. Interestingly, the pronounced decrease in the intensity of $Co^{2+}$ EPR spectra as the temperature is lowered to 150 K, where the signals were almost undetectable, was regarded as opening of a spin gap [7]. Meanwhile, in the same temperature range, the remarkable nonlinear increase in the $g_y$ of the $Co^{2+}$ spectra was attributed to formation of a ground singlet, indication of the onset of antiferromagnetic spin ordering [7].

Up to now, however, the above EPR experimental results (at room temperature) have not been theoretically explained. In general, EPR spectra of $Co^{2+}$ probe in $YBa_2Cu_{2.7}Co_{0.3}O_{7-x}$ would be helpful to understand local structure, magnetism and hence superconductivity of $CuO_2$ plane [8–10]. Second, analyses on the $Co^{2+}$ EPR data can be useful to understanding of the relationship between the unusual $Co^{2+}$ EPR behaviours at low temperatures and opening of a spin gap due to the antiferromagnetic interactions. Finally, judging from the average $\bar{g}[= (g_x + g_y + g_z)/3 \approx 2.853]$ at room temperature, the studied $Co^{2+}$

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center in $YBa_2Cu_{2.7}Co_{0.3}O_{7-x}$ is quite different from the common case of a $3d^7$ ion under weak octahedral crystal-fields, associated with the ground orbital triplet $^4T_{1g}$ of high spin $S = 3/2$ and much larger $g$ values ~4.3 [11]. Meanwhile, it is also unlike the general case of a $3d^7$ ion under strong octahedral crystal-fields, associated with the ground orbital doublet $^2E_g$ of low spin $S = 1/2$ and relatively smaller g factors [11], e.g., $\bar{g} \approx 2.3 \sim 2.5$ for $Co^{2+}$ in ZnPc [12]. Therefore, the observed g factors for the unique $Co^{2+}$ EPR spectra in $YBa_2Cu_{2.7}Co_{0.3}O_{7-x}$ are worthy of further investigations.

In this work, the g factors for the $Co^{2+}$ center in $YBa_2Cu_{2.7}Co_{0.3}O_{7-x}$ at room temperature are analyzed from the perturbation formulae of the g factors for a $3d^7$ ion having low spin ($S = 1/2$) under orthorhombic environments. In these formulae, the contributions from the orthorhombic distortion and ligand orbitals and spin-orbit coupling are included based on the cluster approach. Since the experimental data of the g factors for $Co^{2+}$ at low temperatures are incomplete, only the g factors at room temperature are theoretically treated here. Particularly, the contributions to the g factors from the reductions in the energy separations due to the Jahn-Teller effect are taken into account. In addition, the abnormal $Co^{2+}$ EPR behaviours (decrease in the intensity and nonlinear increase in the $g_y$) at low temperatures are also mentioned in consideration of the opening of the spin gap due to antiferromagnetic interactions.

## 2. Calculations

In $YBa_2Cu_3O_{7-x}$ of orthorhombic phase, the Cu(1) site is surrounded by a distorted oxygen octahedron of orthorhombic ($D_{2h}$) point symmetry, with the Cu-O bond lengths $R_1 \approx 1.9114$ Å, $R_2 \approx 1.9436$ Å and $R_3 \approx 1.8572$ Å along $a$, $b$ and $c$ axes, respectively [13,14]. The Co doping was carried out by mixing and grinding and then pressing into pellets the appropriate molar amounts of $Y_2O_3$, $BaCO_3$, CaO and CoO for the composition $YBa_2Cu_{2.7}Co_{0.3}O_{7-x}$, as stated in Ref. [7]. When a $Co^{2+}$ ion replaces the Cu(1) ion, it may conserve the original orthorhombic point symmetry. Belonging to the case of strong crystal-fields, $Co^{2+}$ ($3d^7$) in this system has the orbital doublet $^2E_g$ ($t_{2g}^6 e_g$) with low spin ($S = 1/2$) as the ground state, which can be described as an unpaired electron in $e_g$ state [14,15]. As the octahedron is compressed, the ground $^2E_g$ state would be split into two orbital singlets $\varepsilon$ ($|x^2 - y^2\rangle$) and $\theta$ ($|z^2\rangle$), with the former lying lowest [15].

The perturbation formulae of the $g$ factors $g_{//}$ and $g_\perp$ for a $3d^7$ ion in tetragonally compressed octahedra have been established by including the contributions from the excited states via the central ion spin-orbit coupling and the cubic crystal-field interactions [15]. However, the contributions from the low symmetrical crystal-fields and the orbital reduction factor due to the covalency effect were not taken into account. Additionally, the contributions from ligand orbitals and spin-orbit coupling interactions were neglected as well. In order to investigate the EPR spectra for the orthorhombic $Co^{2+}$ center, the conventional tetragonal formulae in Ref. [15] need to be extended to the orthorhombic ones by including the above contributions based on the cluster approach. Then the total single electron wave functions can be determined, by including the contributions from both the central ion d-orbitals and the ligand s- and p-orbitals [16]. Thus, we have

$$\begin{aligned} \psi_t &= N_t^{1/2}(\varphi_t - \lambda_t \chi_{pt}), \\ \psi_e &= N_e^{1/2}(\varphi_e - \lambda_e \chi_{pe} - \lambda_s \chi_s). \end{aligned} \tag{1}$$

Here $\varphi_\gamma$ ($\gamma = e$ and $t$ denote the irreducible representations of the $O_h$ group) are the d orbitals of the central ion, and $\chi_{p\gamma}$ and $\chi_s$ stand for the p- and s- orbitals of the ligands. $N_\gamma$ and $\lambda_\gamma$ (or $\lambda_s$) are, respectively, the normalization factors and the orbital admixture coefficients. By applying the semiempirical method [16], the molecular orbital coefficients $N_\gamma$ and $\lambda_\gamma$ (or $\lambda_s$) can be expressed from the normalization conditions

$$\begin{aligned} N_t(1 - 2\lambda_t S_{dpt} + \lambda_t^2) &= 1, \\ N_e(1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) &= 1, \end{aligned} \tag{2}$$

and the approximate relationships

$$\begin{aligned} N^2 &= N_t^2[1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}], \\ N^2 &= N_e^2[1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}]. \end{aligned} \tag{3}$$

Here $S_{dp\gamma}$ (and $S_{ds}$) are the group overlap integrals. $N$ is the average covalency factor, characteristic of the covalency effect (or reduction of the Racah parameters $B$ and $C$) for the central ion in compounds. In general, the admixture coefficients increase with the increase of the group overlap integrals, and one can approximately adopt the proportional relationship between the admixture coefficients and the related group overlap integrals, i.e., $\lambda_e/S_{dpe} \approx \lambda_s/S_{ds}$ within the same irreducible representation $e_g$.

From the perturbation method similar to that in Ref. [15] and the cluster approach [16], one can obtain the formulae of the g factors for $3d^7$ ions under octahedra with orthorhombic compression distortion:

$$\begin{aligned} g_z &= g_s + 2k'\zeta'^2/E_{1z}^2 + 4k\zeta/E_z, \\ g_x &= g_s + 2k'\zeta'^2/E_{1x}^2 + k\zeta/E_x, \\ g_y &= g_s + 2k'\zeta'^2/E_{1y}^2 + k\zeta/E_y, \end{aligned} \tag{4}$$

with

$$\begin{aligned} 1/E_z &= 1/E_{3z} + 1/E_{4z} + 0.38(1/E_{3z} - 1/E_{4z}), \\ 1/E_x &= 1/E_{3x} + 1/E_{4x} + 0.38(1/E_{3x} - 1/E_{4x}), \\ 1/E_y &= 1/E_{3y} + 1/E_{4y} + 0.38(1/E_{3y} - 1/E_{4y}). \end{aligned} \tag{5}$$

Here $g_s$ (=2.0023) is the spin-only value. $E_i$ ($i = 1, 3, 4$) are the energy separations between the excited $^4T_{1b}$, $^2T_{2a}$ and $^2T_{2b}$ and the ground $^2E_g$ states of the $3d^7$ ion [15,17]. The subscripts $\alpha$ (=$x$, $y$ and $z$) denote the various compo-