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Anisotropic *g* factors of the tetragonal Cu^{2+} monomer in Tl-2223 superconductor

Zhi-Hong Zhang, Shao-Yi Wu, Min-Quan Kuang, and Chang-Chun Ding

Department of Applied Physics, School of Physical Electronics, University of Electronic Science and Technology of China, Chengdu 610054, PR China
E-mail: zhihongzhang723@163.com

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The gyromagnetic factors of the Cu^{2+} monomer in Tl-2223 superconductor are quantitatively investigated from the perturbation formulas of these factors for a $3d^9$ ion in a tetragonally elongated octahedron. The local tetragonal distortion of the system is attributable to the axial elongation along *c* axis, corresponding to the five-fold coordinated Cu^{2+}(2) site with almost 30% longer Cu–O bond length for the apical oxygen as compared to the four planar ones. The significant anisotropic behaviors of the EPR spectra perpendicular to and parallel with the *ab* (CuO_2) layers are analyzed on the basis of the local tetragonal elongation.

PACS: **71.18.+y** Fermi surface: calculations and measurements; effective mass, *g* factor.

Keywords: crystal fields and spin Hamiltonians, electron paramagnetic resonance, Cu^{2+}, Tl-2223.

Introduction

$Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl-2223) superconductor has been extensively investigated due to the interesting electrochemical [1], specific heat [2], dielectric [3], microwave [4] and superconductive [5–7] properties. It is well known that these properties may be related to the local structures and electronic states of the CuO_2 planes in Tl-2223 and can be studied by means of the electron paramagnetic resonance (EPR) technique. The EPR experiments were carried out for the Cu^{2+} monomer in Tl-2223 after air sucking at 100 °C for 12 h, with anisotropic *g* factors $g_\parallel$ and $g_\perp$ measured at room temperature [8]. Until now, however, the experimental results have not been theoretically explained.

Since the EPR behaviors and microscopic mechanism of the Cu^{2+} monomer in Tl-2223 would be useful to understand the magnetic and superconductive properties of Tl-2223, further investigations on the EPR *g* factors are of fundamental and practical significance. On the other hand, the local structure of Cu^{2+} site can be important for the analysis of the EPR behaviors of EPR. Furthermore, the changes of bond lengths bring forward the obvious influences on the crystal field and hence *g* factor. In this work, the EPR spectra of the Cu^{2+} monomer in Tl-2223 are quantitatively studied using the high order perturbation formulas of the *g* factors for a tetragonally elongated octahedral $3d^9$-cluster. In the calculations, the local structure of the five-fold coordinated Cu^{2+}(2) site is correlated to the EPR analysis from the superposition model.

Calculations

The observed EPR signal may be ascribed to the tetragonal five-fold coordinated Cu^{2+}(2) site in Tl-2223, with one longer axial Cu–O distance $R_\parallel$ (≈ 2.48 Å) and four shorter planar bond lengths $R_\perp$ (≈ 1.927 Å [9], the structural data at 295 K). This $[CuO_5]^{8-}$ complex can be described as a square pyramid (or half-octahedron without one vertex), i.e., one of original oxygen in an ideal octahedron is stretched to infinity and thus leads to an extremely elongated octahedron (see Fig. 1 of Ref. 10). For a $3d^9(Cu^{2+})$ ion in a tetragonally elongated octahedron, its original cubic ground ^2E_g level would be separated into two orbital singlets $^2A_{1g}$ and $^2B_{1g}$, with the latter lying lowest, while the cubic excited $^2T_{2g}$ state may split into an orbital singlet $^2B_{2g}$ and a doublet ^2E_g [11]. The high order perturbation formulas of the g factors for a $3d^9$ under tetragonally elongated octahedra can be expressed as [12]:

$$g_\parallel = g_s + 8k\zeta/E_1 + k\zeta^2/E_2^2 + 4k\zeta^2/(E_1E_2) + $$
$$+ g_s\zeta^2[1/E_1^2 - 1/(2E_2^2)] + k\zeta^3[4/(E_1E_2^2) - 1/E_2^3] -$$
$$- 2k\zeta^3[2/(E_1^2E_2) - 1/(E_1E_2^2)],$$

$$g_\perp = g_s + 2k\zeta/E_2 + k\zeta^2[2/(E_1E_2) - 1/E_2^2 - 4/(E_1E_2)] +$$
$$+ 2g_s\zeta^2/E_1^2 + k\zeta^3(4/E_1^2 - 1/E_2^2)/(2E_2), \quad (1)$$

where g_s ($\approx$ 2.0023) is the pure spin value. k and ζ are, respectively, the orbital reduction factor and the spin-orbit coupling coefficient for the $3d^9$ ion in crystals. The denominators E_1 and E_2 denote the energy separations between the excited ${}^2B_{2g}$ and ${}^2E_g$ and the ground ${}^2B_{1g}$ states [12], which can be determined from the energy matrix of a $3d^9$ ion under tetragonal symmetry:

$$E_1 = 10Dq, \text{ and } E_2 = 10Dq - 3Ds + 5Dt. \qquad (2)$$

Here Dq is the cubic field parameter, and Ds and Dt are the tetragonal ones. The tetragonal field parameters may be calculated from the superposition model [12] and the local geometry of this Cu^{2+}(2) site in Tl-2223:

$$Ds \approx (4/7)\bar{A}_2 [(R/R_\perp)^{t2} - (1/2)\ (R/R_\parallel)^{t2}],$$

$$Dt \approx (16/21)\bar{A}_4[(R/R_\perp)^{t4} - (1/2)\ (R/R_\parallel)^{t4}]. \qquad (3)$$

Here t_2 ($\approx$ 3) and t_4 ($\approx$ 5) are the power-law exponents [13]. $\bar{A}_2$ and $\bar{A}_4$ are the intrinsic parameters, with the reference distance R taken as the average of the parallel and perpendicular Cu–O distance. For $3d^n$ ions in octahedra, the relationships $\bar{A}_4 \approx (3/4)\,Dq$ and $\bar{A}_2 \approx 10.8\,\bar{A}_4$ [13] have been proved valid in many crystals and are suitably employed here. So the EPR g factors, especially the anisotropy Δg (= $g_\parallel - g_\perp$), are correlated to the tetragonal field parameters and hence to the local structure of the Cu^{2+}(2) site.

From the optical absorption data for Cu^{2+} in oxides [14], the spectral parameters $Dq \approx 1260$ cm^{-1} and $k \approx 0.78$ can be obtained for the Cu^{2+}(2) site in Tl-2223. According to the free-ion value $\zeta_0 \approx 829$ cm^{-1} [11] for Cu^{2+}, the spin-orbit coupling coefficient $\zeta \approx k\zeta_0$ can be calculated. Substituting the values mentioned above into Eq. (1), the theoretical g factors as well as the anisotropy Δg are obtained and shown in Table 1.

Table 1. The g factors and anisotropy of the Cu^{2+} monomer in Tl-2223

	$g_\parallel$	$g_\perp$	Δg
Calculation	2.350	2.050	0.300
Experiment [8]	2.35	2.10	0.25

Discussion

One can find from Table 1 that theoretical g factors for the Cu^{2+} monomer in Tl-2223 based on the perturbation formulas Eq. (1) and the local structural parameters of the Cu^{2+} site show reasonable agreement with the observed values. Thus, the EPR experimental data [8] are satisfactorily interpreted for the first time in this work.

The low symmetrical (tetragonal) distortion of the system arises from the tetragonal elongation of this five-fold coordinated Cu^{2+} site in Tl-2223, i.e., one longer axial $R_\parallel$ ($\approx$ 2.48 Å) and four shorter planar $R_\perp$ ($\approx$ 1.927 Å [9]) with about 30% relative discrepancy. Although the tetragonal elongation is ascribed to the local structure of the Cu^{2+} site in Tl-2223, the influence of the Jahn–Teller effect cannot be excluded. This point was mentioned for the similar Cu^{2+} center on the octahedral Ca^{2+} site in $Ca(OH)_2$ [15].

The positive observed anisotropy Δg may be interpreted as the tetragonal elongation of the $[CuO_5]^{8-}$ complex, which results in the ground ${}^2B_{1g}$ state. Further, the significant anisotropic behaviors of the EPR spectra perpendicular to and parallel with the ab (CuO_2) layers are also understandable in view of the local tetragonal elongation. The theoretical studies in this work seem helpful to understand material microstructures and magnetic properties of CuO_2 plane in high T_c superconductors.

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