Trends in Applied Sciences Research

ISSN 1819-3579

Academic
Journals Inc.

www.academicjournals.com

Trends in Applied Sciences Research 1 (2): 172-175, 2006
ISSN 1819-3579

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

[1]Hui-Ning Dong, [2]Shao-Yi Wu, [1,2]Deng-Feng Li and [1]Ming Guan
[1]Institute of Applied Physics, Chongqing University of Posts and Telecommunications, Chongqing 400065, People's Republic of China
[2]Department of Applied Physics, University of Electronic Science and Technology, Chengdu 610054, People's Republic of China

Abstract: The oxygen-deficient perovskite series $LaCuO_{3-x}$ may serve as a model system with which to study the structure phase change and investigate such questions as the properties of Cu/O 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 $LaCuO_{3-x}$ 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 $LaCuO_{3-x}$ 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 $(CuO_6)^{10-}$ 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+}, $LaCuO_{3-x}$

Introduction

It is of interest for the oxygen-deficient perovskite series $LaCuO_{3-x}$ which may have tetragonal, monoclinic or orthorhombic lattice structure according to the different *x* values. In addition, its oxygen stoichiometry range ($0 \le x \le 0.5$) is the widest yet found in copper oxide compound with the copper valence to be changed from +2 to +3. This serious may thus serve as a model system with which to study the structure phase change and investigate such questions as the properties of Cu/O state and hence the superconductivity in superconductors. So many theoretical and experimental works has been done to understand the several characteristics of the $LaCuO_{3-x}$ crystals (Normand and Rice, 1997; 1996; Bringley *et al*., 1990; Matthias *et al*., 1997; Cryzyk 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 $LaCuO_{3-x}$ 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 $LaCuO_{3-x}$ are theoretically explained. The related crystal field parameters are calculated from the superposition model and the local structural parameters.

Corresponding Author: Hui-Ning Dong, Institute of Applied Physics, Chongqing University of Posts and Telecommunications, Chongqing 400065, People's Republic of China

The superposition model parameters used in this work are comparable with those for similar tetragonal $(CuO_6)^{10-}$ clusters in the previous works. The calculated results are in reasonable consistent with the experimental findings. The results are discussed.

Calculations

$LaCuO_{3-x}$ crystal has a distorted perovskite structure which belongs to the P4/m space group. For the typical tetragonal phase, there have 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):

$$\hat{H}' = \hat{H}_e + \hat{H}_{so} + \hat{H}_{CF} + \hat{H}_Z \tag{1}$$

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 $\hat{H}_{so}$ can be written as:

$$\hat{H}_{so} = \sum \zeta_d \hat{l}_i \cdot \hat{s}_i \tag{2}$$

where ζ_d is the spin-orbit coupling coefficient, for free Cu^{2+}, $\zeta_d \approx 829$ cm^{-1} (Griffith, 1964). For tetragonal symmetry, the crystal-field interaction can be expressed in terms of the irreducible tensor operators C_k^q:

$$\hat{H}_{CF} = B_{20}C_0^2 + B_{40}C_0^4 + B_{44}(C_4^4 + C_{-4}^4) \tag{3}$$

where B_{kq} are crystal field parameters. The Zeeman interaction $\hat{H}_z$ can be written as $\hat{H}_z = g_J \mu_J \hat{H} \bullet \hat{J}$, with their original meanings (Abragam and Bleaney, 1970; Griffith *et al*., 1964).

By diagonalizing the complete energy matrix, we can obtained the energy levels eigenvectors. For the tetragonal $(CuO_6)^{10-}$ cluster, the EPR spectra of Cu^{2+} in octahedra are typical of an effective spin, S' = 1/2 the wave functions of ground Kramers doublets can be written as $|\varepsilon, \pm 1/2>$, which can be obtained by diagonalizing the energy matrix, then the g-factors $g_{//}$ and $g_\perp$ can be expressed as (Abragam and Bleaney, 1970; Griffith *et al*., 1964).

$$\begin{aligned} g_{//} &= 2 < \varepsilon, \frac{1}{2} | N^2 \hat{L}_x + g_e \hat{S}_x | \varepsilon, -\frac{1}{2} > \\ g_\perp &= 2 < \varepsilon, \frac{1}{2} | N^2 \hat{L}_z + g_e \hat{S}_z | \varepsilon, \frac{1}{2} > \end{aligned} \tag{4}$$

$\hat{S}_i$

where g_e (≈ 2.0023) is the free spin g-value. k is the orbital reduction factor due to the covalency reduction effect. $\hat{L}_i$ and (i = x, z) are, respectively, the orbital and spin angular momenta.

The hyperfine structure constants $A_{//}$ and $A_\perp$ can be derived as (Rao and Narayana, 1964; Huang *et al*., 2003; Dong *et al*., 2004).

Table 1: EPR g-factors and hyperfine structure parameters for Cu^{2+} in $LaCuO_{3-x}$ crystal

			$^{63}Cu^{2+}$		$^{65}Cu^{2+}$	
	$g_{//}$	$g_{\perp}$	$A_{//}$	$A_{\perp}$	$A_{//}$	$A_{\perp}$
Cal.	2.6283	1.9543	99.4	52.7	106.6	56.5
Expt.[ ]	2.65	1.91				

$$A_{//} = P[-\kappa - \frac{4}{7}N^2 + (g_z - g_e) + \frac{3}{7}(g_{\perp} - g_e)]$$
$$A_{\perp} = P[-\kappa + \frac{2}{7}N^2 + \frac{11}{14}(g_{\perp} - g_e)] \quad (5)$$

where κ is the core polarization constant, which is near the value 0.3 for $3d^n$ ions in crystals (Dong *et al*., 2004)). P is the dipolar hyperfine parameter for Cu^{2+} in the crystal, $P = P_0$ (where P_0 is the free-ion value, i.e., $P_0 \approx 388\times10^{-4}cm^{-1}$ for $^{63}Cu^{2+}$ and $P_0 \approx 416\times10^{-4}cm^{-1}$ for $^{65}Cu^{2+}$, 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:

$$B_{kq} = \sum_{j=1}^{n} \bar{A}_k(R_0)(R_0 \mid R_j)^{t_k} K_k^q(\theta_j, \phi_j) \quad (6)$$

where t_k is the power-law exponent and $\bar{A}_k(R_0)$is the intrinsic parameter with the reference distance R_0. Usually, $t_2 \approx 3$ and $t_4 \approx 5$ because of the ion nature of the bonds (Newman and Ng, 1989; Edgar, 1976). For the $(CuO_6)^{10-}$ octahedron cluster, $\bar{A}_4(R_0) \approx 615\ cm^{-1}$ with $R_0 \approx 2.153$Å (Petrosyan *et al*., 1984). Since the ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0)$ is in the range of 9~12 for $3d^n$ ions in many crystals (Yeung and Newman, 1986; Edgar, 1976), we take $\bar{A}_2(R_0) \approx 11\ \bar{A}_4(R_0)$ here. The coordination factor $K_k(\theta_j, \phi_j)$ can be obtained from the local structural parameters of the studied system (Yeung and Newman, 1986; Newman and Ng, 1989). There have two apical Cu-O bonds with $R_{//} \approx 1.986$ Å and four in-plane Cu-O bonds with $R_{\perp} \approx 1.909$ Å (Normand and Rice, 1997).

Substituting all these parameters into the above formulas and diagonalizing the complete energy matrix, the g-factors for Cu^{2+} ion and the hyperfine structure constants A factors for $^{63}Cu^{2+}$ and $^{65}Cu^{2+}$ isotopes in $LaCuO_{3-x}$ 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 $g_{//}$, $g_{\perp}$ for the tetragonal Cu^{2+} center in $LaCuO_{3-x}$ crystal. One can find that the calculated EPR parameters g_i factors in $LaCuO_{3-x}$ 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 $A_{//}$ and $A_{\perp}$ for tetragonal Cu^{2+} center in $LaCuO_{3-x}$ were not reported. These calculated results (Table 1) remain to be checked by the experimental studies.

Acknowledgement

This work was financially supported by the Science Foundations of Science and Education Committees of Chongqing (No. kj050502 and CSTC 2005BB4070).

References

Abragam, A. and B. Bleaney, 1970. Electron Paramagnetic Resonance of Transition Ions. Oxford University Press, London.

Bringley, J.F., B.A. Scott, S.J.L. Placa, R.F. Boeheme, T.M. Shaw, M.V. Mcelfresh, S.S. Trail and D.E. Cox, 1990. Synthesis of the defect perovskite series $LaCuO_{3-\delta}$ with copper valence varying from 2+ to 3+. Nature, 347: 263.

Czyzyk, M.T. and G.A. Sawatzky, 1994. Local-density functional and on-site correlations: The electronic structure of La_2CuO_4 and $LaCuO_3$. Phys. Rev., B49: 14211.

Dong, H.N., S.Y. Wu and P. Li, 2004. Theoretical explanation of EPR parameters for Cu^{2+} ion in TiO_2 crystal. Phys. Stat. Sol., 241: 1935.

Edgar, A., 1976. Electron paramagnetic resonance studies of divalent cobalt ions in some chloride salts. J. Phys. C: Solid State Phys., 9: 4303.

Griffith, J.S., 1964. The Theory of Transition-Metal Ions. Cambridge University Press, London.

Huang, P., H. Ping and M.G. Zhao, 2003. Theoretical examination of optical and EPR spectra for Cu^{2t} ion in K_2PdCl_4 crystal. J. Phys. Chem. Sol., 64: 523.

Mehran, F., T.R. McGuire, J.F. Bringley and B.A. Scott, 1991. Electron paramagnetic resonance of Cu^{2+} ions in the tetragonal perovskite $LaCuO_{3-\delta}$. Phys. Rev., B43: 11411.

Matthias, T., M.E. Zhitomirsky and L.D. Landau, 1997. Kazuo Ueda, Nearly critical ground state of $LaCuO_{2.5}$. Phys. Rev., B55: 6117.

McGarvey, B.R., 1967. The isotropic hyperfine interaction. J. Phys. Chem., 71: 51.

Normand, B. and T. M. Rice, 1996. Electronic and magnetic structure of $LaCuO_{2.5}$. Phys. Rev., B 54: 7180.

Normand, B. and T.M. Rice, 1997. Dynamical properties of an anti-ferromagnet near the quantum critical point: Application to $LaCuO_{2.5}$. Phys. Rev., B56: 8760.

Newman D.J. and B. Ng, 1989. The superposition model of crystal field. Rep. Prog. Phys., 52: 699.

Okada, K. and A. Kotani, 1999. Large-Cluster Effects on Core-Level Photoabsorption Spectrum of $LaCuO_3$. J. Phys. Soc. Jpn., 68: 666.

Petrosyan, A.K., R.M. Khachatryas and K.G. Sharoyas, 1984. The superposition parameters for Cu^{2+} ion in $LiNbO_3$ crystal. Phys. Stat. Sol., B122: 725.

Rao, T.B. and M. Narayana, 1964. A theoretical study of EPR spectra in Cu^{2+} and Mn^{2+} doped $CaCd(CH_3COO_4)$ $6H_2O$. Phys. Stat. Sol., 6: k149.

Wu, S.Y. and J. Magn, 2004. Materials, Theoretical explanations to EPR g factors for Er^{3+} ion in $La_{2-x}Sr_xCuO_4$. Superconductor, 268: 399.

Yeung, Y.Y. and D.J. Newman, 1986.Superposition-model analyses for the Cr^{3+} $^4A_2$ ground state. Phys. Rev., B34: 2258.

Yalovega, G. and A.V. Soldatov, 2000. Electronic structure of $LaCuO_3$: X-ray absorption fine structure theoretical analysis. Phys. Stat. Sol., 218: 455.