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Investigations of the local structure and the EPR parameters for Cu^{2+} in $LaSrGaO_4$

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ABSTRACT

The local structure and the spin Hamiltonian parameters (g factors and the hyperfine structure constants) for the tetragonal Cu^{2+} center in $LaSrGaO_4$ are theoretically investigated from the high order perturbation formulas of these parameters for a $3d^9$ ion in tetragonally elongated octahedra. According to these studies, the impurity Cu^{2+} is found to be surrounded by a tetragonal oxygen octahedron with the bond lengths $R_{//}\approx 2.233$ Å and $R_{\perp}\approx 1.982$ Å. The theoretical spin Hamiltonian parameters based on the above local structure show good agreement with the experimental data.

Key words: Electron paramagnetic resonance（EPR), spin hamiltonians, Cu^{2+}, $LaSrGaO_4$

INTRODUCTION

$LaSrGaO_4$ belongs to the group of $ABCO_4$ compounds(where A=Ca, La; B= Y and C =Al, Ga or some tansition-metal elements)[1] and crystallizes generally in a perovskite-like tetragonal $KNiF_4$-type structure of I4/mmm space group[2]. $LaSrGaO_4$ has extensively been studied due to its low dielectric constant and chemical stable property and applications as promising substrate for high-temperature superconduc- ting thin films[2][3]. Many studies have been performed on this material doped with tansition-metal ions by means of EPR technique[2][3], which may be helpful to understand the effect of the local distortion around impurity ions. For example, EPR experiment of Cu^{2+} in $LaSrGaO_4$ were performed and the spin Hamiltonian g factors ($g_{//}$, $g_{\perp}$) and the hyperfine structure constants ($A_{//}$, $A_{\perp}$) were measured in Ref[1]. Until now, however, these experimental results have not been theoretically explained. In this work, the EPR parameters are calculated from the high-order perturbation formulas of $3d^9$ ion in tetragonally elongated octahedra. Since the EPR parameters are sensitive to the local structure of a paramagnetic impurity center, the local structure of Cu^{2+} in $LaSrGaO_4$ can be quantitatively determined based on the EPR analysis. The results are discussed.

MATERIALS AND METHODS

In $LaSrGaO_4$, the Ga^{3+} is surrounded by a tetragonal oxygen octahedron. When the impurity Cu^{2+} ion enters to the lattice of $LaSrGaO_4$, it may occupy the Ga^{3+} site due to similar ionic radius, and local charge mismatch may be introduced. According to the axiality of the experimental results and the relationship $g_{//} > g_{\perp}$, the impurity ion Cu^{2+} is surrounded by a tetragonally elongated octahedra[4]. For Cu^{2+} ($3d^9$) ion in tetragonally elongated octahedra, the lower ^2E irreducible representation may be separated into two orbital singlets $^2A_1(|z^2>)$ and $^2B_1(|x^2-y^2>)$, with the later lying lowest, while the upper $^2T_2$ representation would split into an orbital singlet $^2B_2(|xy>)$ and a doublet $^2E(|xz>, |yz>)$[5]. The perturbation formulas of the spin Hamiltonian parameters of the $^2B_1$ ground state for a $3d^9$ ion in tetragonal symmetry can be expressed as follows[6]

$$g_{//} = g_e + 8k\zeta_d/E_1 + k\zeta_d^2/E_2^2 + 4k\zeta_d^2/E_1E_2 - g_e\zeta_d^2(1/E_1^2 - 1/2E_2^2)$$
$$+k\zeta_d^3(4/E_1 - 1/E_2)/E_2^2 - 2k\zeta_d^3(2/E_1E_2 - 1/E_2^2)/\ E_1 + g_e\zeta_d^3(1/E_1E_2^2 - 1/2E_2^3)$$
$$g_\perp = g_e + 2k\zeta_d/E_2 - 4k\zeta_d^2/E_1E_2 + k\zeta_d^2(2/E_1 - 1/E_2)/E_2 + 2g_e\zeta_d^2/E_1^2$$
$$+k\zeta_d^3(2/E_1 - 1/E_2)\times(1/E_2 + 2/E_1)/2E_2 - g_e\zeta_d^3(1/E_1^2 - 1/E_1E_2 + 1/E_2^2)/2E_2$$
$$A_{//} = P(-\kappa - 4/7) + P(8k\zeta_d/E_1 + 6k\zeta_d/7E_2 - 3k\zeta_d^2/7E_2^2 - 40k\zeta_d^2/7E_1E_2$$
$$+\kappa\zeta_d^2/E_2^2)$$
$$A_\perp = P(-\kappa + 2/7) + P[11k\zeta_d/7E_2 + 9k\zeta_d^2/14E_2^2 - 4k\zeta_d^2/7E_1^2 + 11k\zeta_d^2/7E_1E_2$$
$$+\kappa\zeta_d^2(2/E_1^2 + 1/2E_2^2)] \qquad (1)$$

where g_e ($g_e \approx 2.0023$) is the spin-only value. k is the orbital reduction factor. κ is the core polarization constant. ζ_d and P are, respectively, the spin-orbit coupling coefficient and the dipolar hyperfine structure parameter of the $3d^9$ ion in crystals. They can be written in terms of the corresponding free-ion values, i.e., $\zeta_d \approx k\ \zeta_d^0$ and $P \approx kP_0$. In the studied system, ζ_d^0, P_0 are about 829 cm^{-1} [7] and 360×10^{-4} cm^{-1} [8] for the free Cu^{2+} ion.

In equation 1, E_1 and E_2 are the energy separations between the excited $^2B_{2g}$ and ^2E_g and the ground $^2B_{1g}$ states:

$$E_1 = E(^2B_2) - E(^2B_1) = 10Dq$$

$$E_2 = E(^2E) - E(^2B_1) = 10Dq - 3D_s + 5D_t \qquad (2)$$

Here Dq is the cubic field parameter, D_s and D_t are the tetragonal field parameters. From the superposition model [9] and the geometrical relationship of the present system, the crystal field parameters can be expressed as:

$$Dq = (4/3)\ \bar{A}_4(R_0)(R_0/R_\perp)^{t4}$$
$$D_s = (4/7)\ \bar{A}_2(R_0)\ [(R_0/R_{//})^{t2} - (R_0/R_\perp)^{t2}]$$
$$D_t = (8/21)\ \bar{A}_4(R_0)\ [(R_0/R_{//})^{t4} - (R_0/R_\perp)^{t4}] \qquad (3)$$

Here $R_{//}$ and $R_\perp$ denote the bond lengths parallel to the four-fold axis and perpendicular to the axis, respectively. t_2 and t_4 are the power-law exponents, usually, $t_2 \approx 3$ and $t_4 \approx 5$ because of the ion nature of the bonds[9]. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters, with the reference bonding length R_0. For the $(CuO_6)^{10-}$ octahedron cluster, $\bar{A}_4(R_0) \approx 615 cm^{-1}$ with $R_0 \approx 2.153$ Å [10]. 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 crystal[11], we take $\bar{A}_2(R_0) \approx 9\,\bar{A}_4(R_0)$ here.

Thus by using the formulas of the g-factors and A constants, and fitting the calculated results to the experimental values, one can obtain:

$N \approx 0.754$ $\quad R_{//} \approx 2.233$ Å $\quad R_\perp \approx 1.982$ Å $\quad \kappa \approx 0.338$

The corresponding calculated values are shown in Table 1.

Table 1 The EPR parameters for Cu^{2+} in $LaSrGaO_4$

	$g_{//}$	$g_\perp$	$A_{//}/10^{-4}\cdot cr$	$A_\perp/10^{-4}\cdot cm^{-1}$
Ca	2.3	2.0	-150.8	-5.8
Exp	2.3	2.0	143	6
Exp	2.3	2.0	146	~3

RESULTS AND DISCUSSION

From Table 1, one can find that the theoretical calculations based on the higher order perturbation formulas (Eq.1) and the geometrical relationship of the present studied system are in good agreement with the experimental values. So the spin Hamiltonian parameters and the related parameters adopted here can be regard as reasonable.

(1) the $Dq \approx 1240$ cm^{-1} obtained in this work is closed to the isostructural crystal doped with Cu^{2+} ions. For example, $Dq \approx 1260$ cm^{-1} was obtained in $SrLaAlO_4$-doped Cu^{2+} system based on EPR analysis [6]. This supports the validity of the calculations in this work.

(2) Considering that the ionic radius of the impurity Cu^{2+}(r_i≈0.72Å[12]) is different from the radius of the replaced host ion Ga^{3+}(r_h≈0.62Å[12]), the impurity- ligand distance is unlike the corresponding metal-ligand distance ($R_\perp^h$≈1.922 Å[13]) in the host crystal $LaSrGaO_4$. From the empirical relationship[14], one can reasonably estimate the $R_\perp$≈ R_h+(r_i-r_h)/2≈1.972 Å which is very closed to the value 1.982 Å obtained in this work by analysis the EPR parameters for present system. This also supports the reasonability of the theoretical results.

(3) The observed values of $A_{//}$ and $A_\perp$ from the EPR experiment given in Ref.[1] are positive. However, the theoretical calculations are negative (see Table 1). In fact, these negative signs of the hyperfine structure constants are supported by the experimental results for some similar EPR investigation on Cu^{2+} in elongated oxygen octahedral[15][16]. So the sign of the calculated results can be regard as reasonable.

(4)There are some errors in the above calculations. First, approximation of the theoretical model can lead to some errors in the final results. Second, the contributions from the ligand orbitals and spin-orbit coupling coefficient are ignored here. Fortunately, these contributions are expected to be unimportant and negligible due to the small magnitude of the spin-orbit coupling interaction for the ligand O^{2-}(ζ ≈151 cm^{-1}[17]) compared with that of the impurity Cu^{2+}(ζ≈829 cm^{-1}[7]).

CONCLUSION

In this work, the local structure and the spin Hamiltonian parameters for the tetragonal Cu^{2+} center in $LaSrGaO_4$ are theoretically investigated from the high order perturbation formulas of these parameters. It is found that the impurity Cu^{2+} is surrounded by a tetragonal oxygen octahedron with the bond lengths $R_{//}$≈2.233 Å and $R_\perp$ ≈ 1.982 Å.

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