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INVESTIGATIONS ON THE LOCAL STRUCTURE AND SPIN HAMILTONIAN PARAMETERS FOR THE ORTHORHOMBIC Cu^2 + CENTER IN Ca(OD)$_2$

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The local structure and the spin Hamiltonian parameters (the g factors g_i ($i = x, y, z$) and the hyperfine structure constants A_i) for Cu^{2+}-doped Ca(OD)$_2$ are theoretically investigated from the perturbation formulas of these parameters for a $3d^9$ ion in an orthorhombically elongated octahedron. From the studies, the planar Cu^{2+}—OD$^-$ bonds are found to experience the relative variation ΔR (≈ 0.014 Å) along the X and Y axes, while those parallel to the Z axis may undergo the relative elongation ΔZ (≈ 0.25 Å) due to the Jahn—Teller effect. The theoretical spin Hamiltonian parameters based on the above local lattice distortions agree well with the experimental data. As compared with the previous treatments, the improvements of the theoretical spin Hamiltonian parameters are achieved in this work by adopting the uniform calculation formulas and the tetragonal field parameters based on the superposition model.

K e y w o r d s: electron paramagnetic resonance, crystal- and ligand-field theory, Cu^{2+}, Ca(OD)$_2$.

INTRODUCTION

The Ca(OD)$_2$ (or Ca(OH)$_2$) crystals have aroused interest of researchers due to the reaction kinetics as a sorbent of SO$_2$ [1, 2]. These materials also exhibit unique structural and vibrational [3], high pressure [4, 5], and spectral properties [6—8]. In particular, local structure studies of these crystals doped with some transition metal ions (e.g., Mn^{2+}, Co^{2+}) have extensively been performed by means of the electron paramagnetic resonance (EPR) technique [9—11]. Among the transition metal ions, copper (Cu^{2+}) is a model system with a single $3d$ hole, corresponding to only one ground state and one excited state under ideal octahedral crystal fields. Thus, the EPR studies for Cu^{2+} can provide important structural and electronic information of the doped materials and are of specific significance. For example, the EPR investigations have been carried out for Cu^{2+}-doped Ca(OD)$_2$, and the spin Hamiltonian parameters (the g factors g_i ($i = x, y, z$) and the hyperfine structure constants A_i) were measured for one orthorhombic Cu^{2+} center (spectrum II) [12]. To explain the above EPR results, the simple second order perturbation formulas of the spin Hamiltonian parameters for a $3d^9$ ion under elongated octahedra were adopted in the previous work [12]. However, there are some imperfections in their treatments. First, the rough point-charge model was applied to determine the crystal field parameters, which may induce obvious errors in the final results. Meanwhile, the covalency effect of Ca(OD)$_2$:Cu^{2+} was neglected by taking the orbital reduction factor as unit. Second, the previous structure analysis assumed that two OD$^-$ groups (labeled as 3 and 6 in [12]) along the quasi-tetragonal (or Z) axis (making 48° with respect to the crystalline c axis) move towards the central Cu^{2+} by 0.234 Å, in consideration of the Jahn—Teller effect. Meanwhile, the other four nearest neighbor ligands along the X and Y axes within

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the ($1\bar{2}10$) plane were supposed to shift away from Cu^{2+} by 0.117 Å. Nevertheless, the above local structure of the defect center might actually yield an approximately tetragonally compressed octahedron, which should exhibit g factors $2 \leq g_z < g_x$, g_y [13]. Obviously, this point is opposite to the observed g factors $g_z > g_x$, $g_y > 2$ [12]. Third, the hyperfine structure constants were analyzed based on the four adjustable parameters, i.e., the dipolar hyperfine structure parameter, the core polarization constant, and two anisotropic parameters. Even though, the tetragonal approximation was adopted in the calculations, and the difference (or anisotropy) between A_x and A_y was not explained in the previous work [12]. Consequently, the previous results are not in good agreement with the experimental data, and the information on a defect structure in [12] seems insufficiently reliable for this center.

Since the local structure information for an impurity ion in crystals would be helpful to understand the properties and microscopic mechanisms of the EPR behavior of these materials with dopants, further theoretical investigations on the EPR spectra and the local structure for the above Cu^{2+} center are of fundamental and practical significance. In this work, the high (fourth) order perturbation formulas of the spin Hamiltonian parameters for a $3d^9$ ion under orthorhombically elongated octahedra are adopted in the EPR analysis of this Cu^{2+} center. Importantly, the covalency effect is quantitatively included and the orthorhombic crystal field parameters are determined from the more valid superposition model. In addition, the local lattice distortions due to the Jahn—Teller effect are taken into account in a uniform way. The theoretical results and the local structure of this impurity center are discussed.

CALCULATIONS

Ca(OD)$_2$ has a trigonal structure (P_3 (D_{3d}^3) space group) with deutoxide ions on two adjacent layers perpendicular to the C$_3$ axis and parallel to the Ca^{2+} layer [14]. The Ca^{2+} ion is in the center of the deutoxide octahedron formed by six OD$^-$ ligands, with the average cation-anion distance $R \approx 2.37$ Å [14]. When a Cu^{2+} ion is doped into the Ca(OD)$_2$ lattice, it may locate substitutionally on the Ca^{2+} site due to the same charge [12]. As a Jahn—Teller ion, Cu^{2+} within the deutoxide octahedron may suffer the Jahn—Teller distortions via the vibration interaction and exhibit the local structure different from that of the host Ca^{2+} site in a pure crystal. For example, parallel Cu^{2+}—OD$^-$ bonds can be stretched by an amount ΔZ relative to the reference distance R along the Z axis, and the planar impurity ligand bonds may experience the relative variation ΔR along the X and Y axes. The above distortions of the Jahn—Teller nature may lead to an orthorhombically elongated Cu^{2+} center, despite the original trigonal symmetry of the host Ca^{2+} site in Ca(OD)$_2$. This point is also supported by the investigations for Cu^{2+} on the original trigonally distorted Cd^{2+} site in CsCdCl$_3$ [15], which is actually surrounded by a tetragonally elongated octahedron. Thus, the local structure of the impurity center can be described as the elongation ΔZ along the Z axis and the planar bond length variation ΔR along the X and Y axes.

For a $3d^9$(Cu^{2+}) ion in orthorhombically elongated octahedra, its lower orbital doublet ^2E_g would be separated into two singlets: $^2A_{1g}(\theta)$ and $^2A_{1g}{}'(\varepsilon)$, with the latter lying lowest. Nevertheless, the higher cubic orbital triplet $^2T_{2g}$ would be split into three singlets: $^2B_{1g}(\zeta)$, $^2B_{2g}(\eta)$ and $^2B_{3g}(\xi)$ [13]. In the previous work [12], the spin Hamiltonian parameters were not suitably related to the local structure of the impurity center, and the X and Y components of the calculated hyperfine structure constants were not distinguished due to the tetragonal approximation. In order to better study the EPR spectra and the local structure of the orthorhombic Cu^{2+} center in Ca(OD)$_2$, the high (fourth) order perturbation formulas of the spin Hamiltonian parameters [16] for an orthorhombically elongated $3d^9$ cluster are adopted here. Since the studied Ca(OD)$_2$:Cu^{2+} has insignificant covalency and a very weak ligand spin-orbit coupling interaction, the formulas based on the conventional crystal field model [16] by considering merely the central ion orbital and spin-orbit coupling contributions may be regarded as reasonable. Thus, the perturbation formulas of the spin Hamiltonian parameters for a $3d^9$ ion under orthorhombically elongated octahedra can be expressed as follows [16]:

$$g_x = g_s + 2k\zeta/E^{2+}k\zeta^2[(2/E_1 - 1/E_3)/E_2 - 4/(E_1 E_3)] + g_s\zeta^2[\,2/E_1^2 - (1/E_2^2 - 1/E_3^2)/2\,] - k\zeta^3 \times$$
$$\times \{(1/E_2 - 1/E_3)(1/E_3 + 1/E_2)/(2E_1) + (2/E_1 - 1/E_2)(2/E_1 + 1/E_2)/2E_3 - (1/E_2 - 1/E_3)/(2E_2 E_4)\} +$$
$$+ (g_s\zeta^3/4)[(1/E_3 - 2/E_1)/E_2^{2+}(2/E_3 - 1/E_2)/E_3^{2+}2(1/E_2 - 1/E_3)/E_1^{2+}2(1/E_2^2 - 1/E_3^2)/E_1\,],$$

$$g_y = g_s + 2k\zeta/E_3 + k\zeta^2[(2/E_1 - 1/E_2)/E_3 - 4/(E_1E_2)] + g_s\zeta^2[\,2/E_1^2 - (1/E_3^2 - 1/E_2^2)/2\,] + k\zeta^3\times$$
$$\times\{(1/E_2 - 1/E_3)(1/E_3 + 1/E_2)/(2E_1) + (2/E_1 - 1/E_3)(2/E_1 + 1/E_3)/2E_2 - (1/E_3 - 1/E_2)/(2E_3E_4)\} +$$
$$+ (g_s\zeta^3/4)[(1/E_2 - 2/E_1)/E_3^{2+}(2/E_2 - 1/E_3)/E_2^{2+}2(1/E_3 - 1/E_2)/E_1^{2+}2(1/E_3^2 - 1/E_2^2)/E_1\,],$$

$$g_z = g_s + 8k\zeta/E_1 + k\zeta^2[1/(E_3E_2) + 2(1/E_1E^{2+}1/E_1E_3)] - g_s\zeta^2[\,1/E_1^2 - (1/E_2^{2+}1/E_3^2)/4\,] +$$
$$+ k\zeta^3[\,8/E_1 - (1/E^{2+}1/E_3)]/(2E_2E_3) - 2k\zeta^3[\,1/(E_1E_2) + 1/(E_1E_3) - 1/(E_2E_3)]/E_1 +$$
$$+ (g_s\zeta^3/4)[\,2(1/E_2^{2+}1/E_3^2)/E_1 - (1/E^{2+}1/E_3)/(E_2E_3)],$$

$$A_x = P[-\kappa + \kappa' - 2N/7 + 15(g_x - g_s)/14],$$
$$A_y = P[-\kappa - \kappa' - 2N/7 + 15(g_y - g_s)/14],$$
$$A_z = P[-\kappa + 4N/7 - (g_x + g_y - 2g_s)/14\,]. \tag{1}$$

Here g_s (≈ 2.0023) is the spin-only value, k is the orbital reduction factor, ζ and P are, respectively, the spin-orbit coupling coefficient and the dipolar hyperfine structure parameter for the $3d^9$ ion in crystals. The κ and κ' values are the isotropic and anisotropic core polarization constants respectively [17]. N ($\approx k$) is the average covalency factor that is characteristic of the covalency effect of the studied system. The denominators E_i ($i = 1$—4) stand for the energy separations between the excited $^2A_{1g}(\theta)$, $^2B_{1g}(\zeta)$, $^2B_{2g}(\eta)$, and $^2B_{3g}(\xi)$ and the ground $^2A'_{1g}(\varepsilon)$ states respectively. They are determined from the energy matrix for a $3d^9$ ion under orthorhombic symmetry in terms of the cubic field parameter Dq and the orthorhombic field parameters Ds, Dt, D_ξ, and D_η

$$E_1 \approx 4Ds + 5Dt,$$
$$E_2 \approx 10Dq,$$
$$E_3 \approx 10Dq - 3Ds + 5Dt + 3D_\xi - 4D_\eta,$$
$$E_4 \approx 10Dq + Ds + 10Dt - 3D_\xi + 4D_\eta. \tag{2}$$

For convenience, the orthorhombic distortions of the Cu^{2+} center can be characterized by the reference distance R, the elongation ΔZ, and the planar bond length variation ΔR. Thus, the impurity ligand bond lengths are divided into three groups, i.e., the planar ones are labeled as 1 and 2 due to the bond length variation ΔR and the residual parallel ones as 3. Thus, we have

$$R_1 \approx R - \Delta Z - \Delta R, \quad R_2 \approx R - \Delta Z + \Delta R, \quad R_3 \approx R + 2\Delta Z. \tag{3}$$

From the superposition model [18] and the local geometrical relationship of the studied impurity center, the orthorhombic field parameters are determined as follows:

$$D_s \approx (4/7)\overline{A}_2(R)[2(R/R_3)^{t_2} - (R/R_1)^{t_2} - (R/R_2)^{t_2}],$$
$$D_\xi \approx (4/7)\overline{A}_2(R)[(R/R_1)^{t_2} - (R/R_2)^{t_2}],$$
$$D_t \approx (4/21)\overline{A}_4(R)[2(R/R_3)^{t_4} - (R/R_1)^{t_4} - (R/R_2)^{t_4}],$$
$$D_\eta \approx (20/21)\overline{A}_4(R)[(R/R_1)^{t_4} - (R/R_2)^{t_4}]. \tag{4}$$

Here $t_2 \approx 3$ and $t_4 \approx 5$ [18] are the power-law exponents due to the dominant ionic nature of the bonds. $\overline{A}_2(R)$ and $\overline{A}_4(R)$ are the intrinsic parameters, with the reference distance R in $Ca(OD)_2$. For octahedral $3d^n$ clusters, the relationships $\overline{A}_4(R) \approx (3/4)Dq$ and $\overline{A}_2(R) \approx 9\overline{A}_4(R)$ [18—20] have been proved valid in many crystals and are reasonably applied here. It is noted that the shortcomings of the previous calculations [12] due to acquiring the crystal field parameters from the invalid point charge model are thus overcome in this work by adopting the more powerful superposition model. Thus, the spin Hamiltonian parameters (especially the axial and perpendicular anisotropies $\Delta g = g_z - (g_x + g_y)/2$ and $\delta g = g_y - g_x$) are correlated to the orthorhombic field parameters, and hence, to the local structure of the impurity center. According to the optical spectral studies for Cu^{2+} in oxides [21, 22], the cubic field parameters $Dq \approx 1150$ cm^{-1} and $N \approx 0.82$ are obtained for the studied system here. Then the spin-orbit coupling coefficient ζ for $Ca(OD)_2:Cu^{2+}$ is acquired as the free-ion value ζ_0 (≈ 829 cm^{-1} [23]) multiplying N.

The anisotropic g factors and the hyperfine structure constants (in 10^{-4} cm^{-1}) for the orthorhombic Cu^{2+}
center in Ca(OD)$_2$

	g_x	g_y	g_z	A_x	A_y	A_z
Cal. [a]	2.0727	2.0675	2.3958	6.2	6.2	−141.9
Cal. [b]	2.0690	2.0715	2.3933	5.3	−7.3	−140.6
Expt. [12]	2.0691(2)	2.0714(2)	2.3960(2)	4.1 (16)	−8.7(32)	−141.9(11)

[a] Calculations based on the simple formulas and the crystal field parameters determined from the point-charge model and the various adjustable parameters in the previous work [12].

[b] Calculations based on the high order perturbation formulas in Eq. (1) and the local planar bond length variation ΔR and the axial elongation ΔZ due to the Jahn—Teller effect in this work.

Thus, in the formulas of the g factors there are only two unknown parameters (i.e., the elongation ΔZ and the planar bond length variation ΔR). Substituting the above values into Eq. (1) and fitting the calculated g factors to the experimental data, one can obtain

$$\Delta Z \approx 0.25 \text{ Å}, \quad \Delta R \approx 0.014 \text{ Å}. \tag{5}$$

In the calculations of the hyperfine structure constants, the dipolar hyperfine structure parameter $P \approx 388 \times 10^{-4}$ cm^{-1} for Cu^{2+} [24]. From the core polarization constant ($\approx 0.26 \sim 0.33$ [25]) for Cu^{2+} in Tutton′s salts, one can estimate $\kappa \approx 0.32$ for the system studied here. This value is also close to that (≈ 0.34) adopted in the previous work [12] and can be regarded as reasonable. Substituting these data into Eq. (1) and fitting the calculated A factors to the observed values, the anisotropic core polarization constant is obtained

$$\kappa' \approx 0.02. \tag{6}$$

The corresponding spin Hamiltonian parameters (Cal. [b]) are shown in Table 1. For comparisons, the previous theoretical results (Cal. [a]) based on various adjustable parameters and the crystal field parameters from the point charge model [12] are also collected in Table 1.

DISCUSSION

It can be found from Table 1 that the calculated spin Hamiltonian parameters (Cal. [b]) based on the axial elongation ΔZ and the planar bond length variation ΔR show good agreement with the experimental data. As compared with the previous results [12], some improvements are achieved in this work even by adopting fewer adjustable parameters. Thus, the EPR spectra of the orthorhombic Cu^{2+} center in Ca(OD)$_2$ are satisfactorily interpreted, and the information about the local structure of this impurity center is also obtained.

1) The EPR spectra for Ca(OD)$_2$:Cu^{2+} may be characterized by the axial and perpendicular anisotropies Δg and δg. According to Eqs. (1), (3), and (4), the anisotropies arise mainly from the axial (i.e., the crystal field parameters Ds and Dt due to the axial elongation ΔZ) and the perpendicular (i.e., D_ξ and D_η due to the planar bond length variation ΔR) orthorhombic distortions of the ligand octahedron arising from the Jahn—Teller effect. Thus, the relative axial elongation ratio $\Delta Z/R$ (≈ 10 %) and the relative planar bond length variation ratio $\Delta R/R$ (≈ 0.5 %) can largely account for the observed anisotropies Δg (≈ 0.33) and δg (≈ 0.0023) respectively. Despite the original trigonal symmetry of the host Ca^{2+} site in Ca(OD)$_2$, the impurity Cu^{2+} center actually exhibits orthorhombic symmetry due to the Jahn—Teller distortions. Interestingly, for substitutional Cu^{2+} on the similar trigonal Cd^{2+} (or Nb^{5+}) site in CsCdCl$_3$ (or LiNbO$_3$), the Cu^{2+}—Cl$^-$ (or Cu^{2+}—O^{2-}) combination also shows a tetragonally (or orthorhombically) elongated octahedron of the Jahn—Teller nature [15, 22]. The studied Cu^{2+} center in Ca(OD)$_2$ (or other oxides) is different from some other transition metal impurity (e.g., Mn^{2+} [9,10])

centers in the same crystal, which may exhibit the ground orbital non-degenerate $^6A_{1g}$, and thus no Jahn—Teller effect would occur. Of course, the determination of local structures for transition metal ions in crystals is actually a difficult problem that involves complicated physical and chemical properties of the impurities and the host materials. Thus, the theoretical calculations and the local structural parameters ΔZ and ΔR obtained in this work for Ca(OD)$_2$:Cu^{2+} should be regarded as tentative ones and remain to be further checked by experimental investigations.

2) The hyperfine structure constants (Cal. [b]) calculated in this work based on the local structural parameters ΔZ and ΔR in Eq. (5) and the anisotropic core polarization constant κ' in Eq. (6) show better agreement with the experimental data than those based on the tetragonal approximation in the previous work [12]. From Eq. (1), the anisotropic parts of the hyperfine structure constants (especially the difference between A$_x$ and A$_y$) arise mainly from κ' and the anisotropy δg. Second, the optimal κ' ($\approx 0.02 << \kappa \approx 0.32$) can be described as a tiny difference in the Cu^{2+} $3d$—$4s$ orbital admixture between X and Y directions. Interestingly, small κ' is also qualitatively consistent with the low ratio $\Delta R/R$ (≈ 0.5 %) and can be regarded as the suitable characteristic of the perpendicular orthorhombic contributions to the hyperfine structure constants. Moreover, only the absolute values of the A factors were determined in [12]. From the present calculations and the experimental data [25, 26] for various orthorhombic Cu^{2+} centers in some oxides, the signs of A$_y$ and A$_z$ are negative, and that of A$_x$ is positive.

3) The previous theoretical results [12] are not as good as those in this work. This can be ascribed to the incomplete formulas of the spin Hamiltonian parameters and the uncertainties of the various adjustable parameters (i.e., two ligand displacement parameters, dipolar hyperfine structure parameter, core polarization constant, and two anisotropic parameters) [12]. The previous studies obtained that two OD$^-$ groups along Z axis move towards Cu^{2+} by 0.234 Å, and the other four ligands along X and Y axes within the $(1\overline{2}10)$ plane move away from Cu^{2+} by 0.117 Å [12]. However, the above ligand displacements would yield an approximately tetragonally compressed octahedron (i.e., the bond lengths along the Z axis were shorter than those along the X and Y axes), which should correspond to the g factors $2 \leq g_z < g_x, g_y$ [13]. This might be obviously opposite to the observed g factors: $g_z > g_x, g_y > 2$ [12]. Meanwhile, the crystal field parameters determined from the rough point charge model and the approximation of pure ionicity (i.e., $k \approx 1$) can also induce significant errors in the final results. Fortunately, the errors due to the above approximations may be largely cancelled by the uncertainties of the adjustable parameters, and thus, qualitative consistence in the spin Hamiltonian parameters between theory and experiment was obtained in the previous studies [12].

4) There are some errors in the present calculations. First, the approximation of the theoretical model and the formulas can induce some errors for the resulting spin Hamiltonian parameters and the local structural parameters ΔZ and ΔR. Second, the calculations are based on the conventional crystal field model containing only the impurity orbital and spin-orbit coupling contributions, while those from the ligand orbitals and spin-orbit coupling coefficient are not taken into account. Fortunately, although the studied Cu^{2+} center in Ca(OD)$_2$ shows some covalency (characterized by the covalency factor $N \approx 0.82$), the spin-orbit coupling coefficient (≈ 151 cm^{-1} [27]) of oxygen in the OD$^-$ ligand is much smaller than that (≈ 829 cm^{-1} [23]) of the Cu^{2+}impurity. Thus, the ligand contributions to the spin Hamiltonian parameters are expected to be very small and reasonably ignored for simplicity here, as treated in various works for some Cu^{2+} centers in oxides [28, 29]. Third, the errors in the local structure and the spin Hamiltonian parameters also arise from the approximation of the relationship $\overline{A}_2(R) \approx 9\overline{A}_4(R)$ [18—20], which would somewhat affect the orthorhombic field parameters (Eq. (4)) and the final results. According to the calculations, the errors in the final spin Hamiltonian parameters and the local structural parameters are estimated to be not more than 1 % when the $\overline{A}_2(R)/\overline{A}_4(R)$ ratio varies by 10 %. Finally, the core polarization constants κ and κ' adopted in the calculations of the hyperfine structure constants can also lead to some errors. In view of the reasonable value of κ and the smallness of κ', the effects of the above errors on the resulting A factors can be regarded as very small and negligible.

CONCLUSIONS

The spin Hamiltonian parameters and the local structure for the orthorhombic Cu^{2+} center in Ca(OD)$_2$ are theoretically studied from the high order perturbation formulas for an orthorhombically elongated octahedral $3d^9$ cluster. The planar Cu^{2+}—OD$^-$ bonds are found to suffer the relative variation ΔR ($\approx$0.014 Å) along the X and Y axes, while those parallel to the Z axis may experience the relative elongation ΔZ ($\approx$0.25 Å) due to the Jahn—Teller effect. The theoretical results of this work show some improvements as compared with those of the previous studies.

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