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Theoretical studies of the local structure and EPR parameters for Cu^{2+} centers in disodium malonate trihydrate single crystal

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ABSTRACT

The electron paramagnetic resonance (EPR) parameters (g factors g_{xx}, g_{yy}, g_{zz} and hyperfine structure constants A_{xx}, A_{yy}, A_{zz}) of the two Cu^{2+} centers in disodium malonate trihydrate (DSMT) single crystal are theoretically interpreted using the high order perturbation formulas of these parameters for a $3d^9$ ions in rhombically elongated octahedra. In the calculation, the rhombic crystal-field parameters are determined from the superposition model and the admixture of d-orbitals in the ground state wave function are taking account, the results show that although the admixture of the $|d_z^2\rangle$ state to the ground state wave function is small, it should not be neglected in calculations of the EPR parameters. The theoretical EPR parameters show good agreement with the observed values. The results are discussed.

1. Introduction

Electron paramagnetic resonance (EPR) studies on transition-metal (TM) ions doped in single crystals can give valuable information about the environmental symmetry produced by the ligands around the metal ion and to get information about the electric fields of the paramagnetic ions [1–4]. Among the TM 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 [1,5–7]. Usually, Cu^{2+} ion replaces a divalent cation present in the lattice have been widely carried out by means of EPR technique [7–10], whereas EPR studies of the impurity Cu^{2+} replaces the monovalent cation are rather scarce. For example, EPR investigations have been carried out for Cu^{2+} doped in disodium malonate trihydrate ($C_3H_2O_4Na_2 \cdot 3H_2O$; DSMT, hereafter) and the EPR parameters (g factors g_{xx}, g_{yy}, g_{zz} and hyperfine structure constants A_{xx}, A_{yy}, A_{zz}) were measured for the impurity Cu^{2+} centers [11].

Until now, however, no satisfactory interpretation to the above experimental results has been made, and information about defect structures of DSMT:Cu^{2+} has not been obtained yet. Since local structure information for an impurity ion in crystals would be helpful to understand properties and the microscopic mechanisms of the EPR behaviors for these materials with dopants, further theoretical investigations on the EPR parameters and the local structure for the above Cu^{2+} centers are of fundamental and practical significance. In this work, the high order perturbation formulas of the EPR parameters for a $3d^9$ ion under rhombically elongated octahedra are adopted in the EPR analysis of the two Cu^{2+} centers. In the calculations, the rhombic crystal-field parameters are determined from the superposition model, the covalency effect and the admixture of d-orbitals in the ground state wave function for the impurity Cu^{2+} centers in DSMT single crystal are taking into account. The theoretical results are in good agreement with the experimental values.

2. Calculations

DSMT belongs to the triclinic system (space group P_1) and contains four molecules in a unit cell. The unit cell dimensions are $a=7.643$ Å, $b=16.215$ Å, $c=6.341$ Å and the angels are $\alpha=121.27^\circ$, $\beta=78.41^\circ$ and $\gamma=109.53^\circ$ [11,12]. When Cu^{2+} is doped in DSMT, it enters the lattice and substitutes the host Na^+ site [11]. In this case, the impurity Cu^{2+} is surrounded by two water molecules in the axial position of the octahedron and the other four planar ligands being four oxygen atoms of the two-malonate groups [11]. In the octahedral crystal field, Cu^{2+} ion has a $3d^9$ electronic configuration and ^2E_g ground state [13]. However, the ground ^2E_g term normally splits up due to the Jahn–Teller effect and hence a lowering of symmetry is expected for the Cu^{2+} ion. Sometimes the excited term $^2T_{2g}$ splits up into two or three components depending on the tetragonal or rhombic fields [14,15]. For DSMZ:Cu^{2+}, from the

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experimental EPR results (*i.e.*, $g_{zz} > g_{xx}, g_{yy} > 2$ [11]), it is evident that the impurity Cu^{2+} is under rhombically elongated octahedra. Therefore, its lower orbital doublet ^2E_g would be separated into two singlets $^2A_{1g}(\theta)$ and $^2A_{1g}{}'(\varepsilon)$. Meanwhile, the higher cubic orbital triplet $^2T_{2g}$ would be split into three singlets $^2B_{1g}$ (ζ), $^2B_{2g}$ (η) and $^2B_{3g}$ (ξ) [16]. Since the states $^2A_{1g}(\theta)$ and $^2A_{1g}{}'(\varepsilon)$ belong to the same representation of rhombic symmetry group, the ground state will be neither $^2A_{1g}(\theta)$ nor $^2A_{1g}{}'(\varepsilon)$ but an admixture of both [11,15,17], *i.e.*

$$\Phi = N\left[\alpha\left|d_{x^2-y^2}\right\rangle + \beta\left|d_{3z^2-r^2}\right\rangle\right] \tag{1}$$

where N ($\approx k$) is the probability of finding the electron in the metal d-orbital and characteristic of the covalency of the system. α and β are the mixing coefficients due to the rhombic field components, satisfy the normalization relation

$$\alpha^2 + \beta^2 = 1. \tag{2}$$

Generally speaking, the $|d_{x^2-y^2}>$ state is dominant and so $\alpha \gg \beta$ [14,15,17,18]. Thus, from the perturbation theory, the second-order perturbation formulas of EPR g factors for d^9 in rhombic symmetry were given in Ref. [11]. The microscopic origin of the EPR parameters for d^n ions in crystals comes from both the crystal-field (CF) mechanism related to the interaction of CF excitations with the ground state and the charge–transfer (CT) mechanism related to the interaction of CT excitations with the ground state [11–13]. For the studied $[CuO_6]^{10-}$ octahedral clusters, since the CT energy levels are much higher than the CF energy levels, the contributions of CT mechanism to the EPR parameters in the studied DSMT:Cu^{2+} can be neglected. In addition, considering that the spin–orbit parameter ζ_p^0 ($\approx 150\ cm^{-1}$ [19]) of ligand O^{2-} is much smaller than that ($\approx 829\ cm^{-1}$ [20]) of the central ion Cu^{2+}. Thus, the ligand orbital and spin–orbit coupling contributions to the EPR parameters are expected to be very small and reasonably ignored for simplicity here. Then, from the perturbation theory, the high-order perturbation formulae of EPR parameters (g factors g_{xx}, g_{yy}, g_{zz} and hyperfine structure constants A_{xx}, A_{yy}, A_{zz}) for $3d^9$ ions in rhombic symmetry can be expressed as [14,15,21]:

$$g_{xx} = g_s + \frac{2k\zeta(\alpha+\sqrt{3}\beta)^2}{E_4} - \frac{2\alpha k\zeta^2(\alpha+\sqrt{3}\beta)^2}{E_2E_4} + \frac{k\zeta^2(\alpha^2-3\beta^2)}{E_3E_4} - \frac{2\alpha^2 g_s\zeta^2}{E_2^2},$$
$$- \frac{g_s\zeta^2(\alpha-\sqrt{3}\beta)^2}{2E_3^2} + \frac{2\alpha k\zeta^2(\alpha-\sqrt{3}\beta)}{E_2E_3}$$
$$g_{yy} = g_s + \frac{2k\zeta(\alpha-\sqrt{3}\beta)^2}{E_3} - \frac{2\alpha k\zeta^2(\alpha-\sqrt{3}\beta)^2}{E_2E_3} + \frac{k\zeta^2(\alpha^2-3\beta^2)}{E_3E_4} - \frac{2\alpha^2 g_s\zeta^2}{E_2^2},$$
$$- \frac{g_s\zeta^2(\alpha+\sqrt{3}\beta)^2}{2E_4^2} + \frac{2\alpha k\zeta^2(\alpha+\sqrt{3}\beta)}{E_2E_4}$$
$$g_{zz} = g_s + \frac{8\alpha^2 k\zeta}{E_2} - \frac{2\alpha k\zeta^2(\alpha-\sqrt{3}\beta)}{E_2E_3} - \frac{2\alpha k\zeta^2(\alpha+\sqrt{3}\beta)}{E_2E_4} - \frac{g_s\zeta^2(\alpha-\sqrt{3}\beta)^2}{2E_3^2},$$
$$- \frac{g_s\zeta^2(\alpha+\sqrt{3}\beta)^2}{2E_4^2} - \frac{k\zeta^2(\alpha-3\beta^2)}{E_3E_4}$$
$$A_{xx} = P\left[-\kappa+\kappa'+\frac{2}{7}+(g_{xx}-g_s)-\frac{3}{14}(g_{yy}-g_s)\right],$$
$$A_{yy} = P\left[-\kappa-\kappa'+\frac{2}{7}+(g_{yy}-g_s)-\frac{3}{14}(g_{xx}-g_s)\right],$$
$$A_{zz} = P\left[-\kappa-\frac{4}{7}+(g_{zz}-g_s)+\frac{3}{14}(g_{xx}-g_s)+\frac{3}{14}(g_{yy}-g_s)\right]. \tag{3}$$

Here g_s (≈ 2.0023) is the spin-only value. κ is the core polarization constant, and κ' is the anisotropic one due to the rhombic distortion of the Cu^{2+} centers. Taking into account the covalency effect (characterized by the covalence reduction factor N), the spin-orbit coupling parameter ζ and dipolar hyperfine constant P can be given as [22,23]

$$\zeta = N\zeta_d^0 \text{ and } P = NP_0 \tag{4}$$

here, ζ_d^0 and P_0 are the corresponding parameters of free d^n ion. For the free Cu^{2+} ion, we have ζ_d^0 ($\approx 829\ cm^{-1}$ [20]) and P_0 ($\approx 360\times10^{-4}\ cm^{-1}$ [24]).

The denominators E_i (i=1–4) can be obtained from the energy matrices for a $3d^9$ ion under rhombic symmetry in terms of the cubic field parameter D_q and the rhombic field parameters D_s, D_t, D_ξ and D_η:

$$E_1 \approx 4D_s + 5D_t,$$
$$E_2 \approx 10D_q,$$
$$E_3 \approx 10D_q + 3D_s - 5D_t - 3D_\xi + 4D_\eta,$$
$$E_4 \approx 10D_q + 3D_s - 5D_t + 3D_\xi - 4D_\eta. \tag{5}$$

The local structures of the impurity Cu^{2+} centers in DSMT single crystal are described by the metal–ligand distance R_i (i=x, y, z). Then, from the superposition model [25] and local geometrical relationship of the impurity Cu^{2+} centers, the cubic field parameter D_q and the rhombic field parameters D_s, D_t, D_ξ and D_η can be expressed as follows:

$$D_q = \frac{2}{3}\bar{A}_4(R_0)\left[\left(\frac{R_0}{R_x}\right)^{t_4} + \left(\frac{R_0}{R_y}\right)^{t_4}\right],$$
$$D_s = \frac{2}{7}\bar{A}_2(R_0)\left[\left(\frac{R_0}{R_x}\right)^{t_2} + \left(\frac{R_0}{R_y}\right)^{t_2} - 2\left(\frac{R_0}{R_z}\right)^{t_2}\right],$$
$$D_t = \frac{8}{21}\bar{A}_4(R_0)\left[\left(\frac{R_0}{R_x}\right)^{t_4} + \left(\frac{R_0}{R_y}\right)^{t_4} - 2\left(\frac{R_0}{R_z}\right)^{t_4}\right],$$
$$D_\xi = \frac{2}{7}\bar{A}_2(R_0)\left[\left(\frac{R_0}{R_x}\right)^{t_2} - \left(\frac{R_0}{R_y}\right)^{t_2}\right],$$
$$D_\eta = \frac{10}{21}\bar{A}_4(R_0)\left[\left(\frac{R_0}{R_x}\right)^{t_4} - \left(\frac{R_0}{R_y}\right)^{t_4}\right]. \tag{6}$$

Here $t_2 \approx 3$ and $t_4 \approx 5$ are the power-law exponents due to the dominant ionic nature of the bonds [14,16,25–27]. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters with the reference distance R_0 taken as $R_0 = \bar{R} = (R_x+R_y+R_z)/3$. For $3d^n$ ions in the octahedral clusters, the ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0) \approx 12$ are proved to be valid in many crystals [22,26,28,29] and reasonably adopted here.

According to the optical spectral studies for Cu^{2+} in oxides with similar $[CuO_6]^{10-}$ cluster, $\bar{A}_4(R_0) \approx 900\ cm^{-1}$ can be obtained and used for the studied system here [30]. Then, for the two Cu^{2+} centers I and II, respectively, in DSMT single crystal, we take the Cu^{2+}–O^{2-} bond lengths as:

$$R_x^I \approx 1.92,\ R_y^I \approx 2.01,\ R_z^I \approx 2.20\ \text{Å}.$$

Table 1
Theoretical and experimental anisotropic g factors and the hyperfine structure constants (in $10^{-4}\ cm^{-1}$) for the impurity Cu^{2+} centers in $C_3H_2O_4Na_2\cdot3H_2O$ single crystal.

	g_{xx}	g_{yy}	g_{zz}	A_{xx}	A_{yy}	A_{zz}
Center I						
Cal.[a]	2.057	2.064	2.341	51.4	9.6	−140.5
Cal.[b]	2.079	2.091	2.337	56.6	16.7	−138.2
Expt. [11]	2.078	2.090	2.336	59.0	17.4	134.2
Center II						
Cal.[a]	2.083	2.107	2.399	37.8	62.0	−127.8
Cal.[b]	2.071	2.091	2.339	30.1	54.0	−139.6
Expt. [11]	2.068	2.090	2.340	31.4	53.4	135.6

[a] Calculations based on the perturbation formulae but omission of the admixture $^2A_{1g}(\theta)$ and $^2A_{1g}{}'(\varepsilon)$ states (*i.e.*, taking α=1, β=0).
[b] Calculations based on the perturbation formulae and considering the admixture between $^2A_{1g}(\theta)$ and $^2A_{1g}{}'(\varepsilon)$ states.