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Investigations on the local structure and the EPR parameters for the tetragonal Cu^{2+} center in $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}$ crystal

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The electron paramagnetic resonance (EPR) parameters (g factors $g_{\parallel}$, $g_{\perp}$ and hyperfine structure constants $A_{\parallel}$, $A_{\perp}$) and the local structure of the tetragonal Cu^{2+} center in trigonal $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}$ crystal are theoretically investigated from the perturbation formulas of these parameters for a $3d^9$ ion in tetragonally elongated octahedra. In the calculated formulas, the contributions to the EPR parameters from ligand orbital and spin-orbit coupling are included on the basis of the cluster approach in view of moderate covalency of the studied systems, the required crystal-field parameters are estimated from the superposition model which enables correlation of the crystal-field parameters and hence the EPR parameters with the tetragonal distortion of the studied $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ cluster. According to the calculations, the ligand octahedra around Cu^{2+} are suggested to suffer relative elongation τ ($\approx 0.085 \text{ \AA}$) along the $[001]$ (or C_4) axis for the tetragonal Cu^{2+} centers in $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}$ crystal, due to the Jahn-Teller effect. The results are discussed.

Keywords. Electron paramagnetic resonance (EPR); Crystal fields; Local structure; Cu^{2+} ; $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}$
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1. Introduction

$\text{ZnMF}_6 \cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Ge}, \text{Se}, \text{Si}, \text{Zr}$) belongs to the family of isostructural fluosilicate hexahydrates having the CsCl-type structure with space group $R\bar{3}$. In these crystals, Zn^{2+} ion and M^{4+} ion occupies a trigonally distorted $\text{Zn}(\text{H}_2\text{O})_6$ and MF_6 octahedra and its site symmetry is C_{3i} [1, 2]. It is believed that the local crystal structure around an impurity in doped crystals may be unlike the corresponding structure in the host crystals. The electron paramagnetic resonance (EPR) technique is a powerful tool to investigate the defect structure of impurity centers because the EPR parameters of a paramagnetic impurity in crystals measured by EPR spectra are sensitive to its immediate environment [3, 4]. EPR experimental of the divalent $3d^n$ impurities M^{2+} ($\text{M} = \text{V}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$, et al) in $\text{ZnMF}_6 \cdot 6\text{H}_2\text{O}$ crystals substitute for the Zn^{2+} ions and form the $\text{M}(\text{H}_2\text{O})_6^{2+}$ impurity centers have attracted extensive interest [5-8]. Since no charge compensation is required, the symmetry of these impurity centers remains unchanged (*i.e.* trigonal symmetry) although the trigonal distortion in the impurity centres may often be different from that in the host $\text{ZnMF}_6 \cdot 6\text{H}_2\text{O}$ crystal. When a Cu^{2+} ion is doped into the lattice of $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}$, it may locate substitutionally on the Zn^{2+} site due to the same charge [9]. For a Cu^{2+} ($3d^9$) ion under octahedra, its ground state is the orbital doublet ${}^2\text{E}$. Nevertheless, the degenerate ground state is unstable and will undergo a tetragonal Jahn-Teller distortion, which can split the orbital doublet ${}^2\text{E}$ into two singlet ${}^2\text{B}_{1g}$ ($|x^2-y^2\rangle$) and ${}^2\text{A}_{1g}$ ($|z^2\rangle$), with the former or latter lying lowest for elongated or compressed tetragonal distortion [10-12]. This point is also supported by the studies for Cu^{2+} on the original trigonally distorted $\text{Ca}^{2+}(5)$ site in $\beta\text{-Ca}_3(\text{PO}_4)_2$ [13] and Mg^{2+} site in $\text{A}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ ($\text{A} = \text{La}, \text{Bi}$) [12], which actually shows tetragonal elongation distortion due to the Jahn-Teller effect.

Until now, however, no theoretical calculations concerning the above trigonal to tetragonal distortion for the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ cluster in $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}$ crystal have been made. Considering that (i) information about local structures and electronic states for Cu^{2+} in $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}$ crystal would be helpful to understand the microscopic mechanisms of the EPR behaviors of this material containing Cu^{2+} dopants

and (ii) the EPR parameters in crystals are sensitive to its immediate environment (and hence to the defect structure of d^9 impurity center). Thus, the studies of EPR parameters for Cu^{2+} in $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}$ crystal can obtain the tetragonal distortion (characterized by $\Delta R = R_{\parallel} - R_{\perp}$, where $R_{\parallel}$ and $R_{\perp}$ represent the metal-ligand distances parallel with and perpendicular to the C_4 -axis) of the studied $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ cluster. In this work, based on the cluster approach, we calculate the EPR parameters for $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}:\text{Cu}^{2+}$ from the high-order perturbation formulas of the EPR parameters for a $3d^9$ ion under tetragonal elongated octahedral. In the calculations, the local lattice distortions around the impurity due to Jahn-Teller effect are included, and contributions from the ligand orbital and spin-orbit coupling interactions are taken into account from the cluster approach. The results are discussed.

2. Calculations

From the cluster approach, the one-electron basis functions for an octahedral d^n cluster can be expressed as [14]:

$$\begin{aligned}\Psi_t &= N_t^{1/2}(\varphi_t - \lambda_t \chi_{pt}) \\ \Psi_e &= N_e^{1/2}(\varphi_e - \lambda_e \chi_{pe} - \lambda_s \chi_s)\end{aligned}\quad (1)$$

where φ_{γ} ($\gamma = t_{2g}$ and e_g represents the irreducible representation of the O_h group) are the d orbitals of the central ion. N_{γ} and λ_{γ} (or λ_s) are respectively, the normalization factors and the orbital admixture coefficients. $\chi_{p\gamma}$ and χ_s stand for the p - and s -orbitals of the ligands. By adopting the cluster approach [15-18], these molecular orbital coefficients can be determined from the normalization conditions

$$\begin{aligned}N_t(1 - 2\lambda_t S_{dpt} + \lambda_t^2) &= 1, \\ N_e(1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) &= 1,\end{aligned}\quad (2)$$

and the approximate relationships

$$\begin{aligned}N^2 &= N_t^2(1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}), \\ N^2 &= N_e^2(1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}).\end{aligned}\quad (3)$$

here S_{dpy} (and S_{ds}) are the group overlap integrals. N is the average covalency factor, characteristic of

the covalency of the systems. Since orbital admixture and overlap between the central ion and ligands have consistent dependence on bond length, one can reasonably adopt the proportional relationship $\lambda_e/S_{dpe} \approx \lambda_s/S_{ds}$ for the same irreducible representation e_g .

Based on the cluster approach [15-18], the orbital reduction factors k (and k'), the spin-orbit coupling coefficients ζ (and ζ') and the dipolar hyperfine constants P (and P') can be determined as follow:

$$\begin{aligned}\zeta &= N_t(\zeta_d^0 + \lambda_t^2 \zeta_p^0 / 2), & \zeta' &= \sqrt{N_t N_e}(\zeta_d^0 - \lambda_t \lambda_e \zeta_p^0 / 2) \\ k &= N_t(1 + \lambda_t^2 / 2), & k' &= \sqrt{N_t N_e}[1 - \lambda_t(\lambda_e + \lambda_s A) / 2]. \\ P &= N_t P_0 & P' &= (N_t N_e)^{1/2} P_0\end{aligned}\quad (4)$$

where ζ_d^0 ($\approx 829 \text{ cm}^{-1}$) [19-21] and ζ_p^0 ($\approx 150 \text{ cm}^{-1}$) [22] are the spin-orbit coupling coefficients of the free center ion Cu^{2+} and the ligand ions O^{2-} , respectively. P_0 ($\approx 388 \times 10^{-4} \text{ cm}^{-1}$ [23, 24]) is the dipolar hyperfine structure parameter for the free Cu^{2+} . A denotes the integral $R \langle n s | \frac{\partial}{\partial y} | n p_y \rangle$, where R is the reference impurity-ligand distance of the studied systems.

For a $3d^9(\text{Cu}^{2+})$ ion in tetragonally elongated octahedral environment, the cubic orbital doublet 2E_g would be separated into two orbital singlets ${}^2B_{1g}(x^2-y^2)$ and ${}^2A_{1g}(z^2)$, with the former lying lowest [15, 22]. Meanwhile, the higher cubic orbital triplet ${}^2T_{2g}$ may split into an orbital singlet ${}^2B_{2g}(xy)$ and a doublet ${}^2E_g(xy, yz)$ [12, 25]. The perturbation formulas of $3d^9$ complex with tetragonal elongation distortion are established as follows [12, 15]:

$$\begin{aligned}g_{\parallel} &= g_s + 8k'\zeta' / E_1 + k\zeta'^2 / E_2^2 + 4k'\zeta\zeta' / E_1 E_2 + g_s\zeta'^2(1/E_1^2 - 1/2E_2^2) - k\zeta\zeta'^2(4/E_1 E_2^2 - 1/E_2^3) \\ &\quad - 2k'\zeta\zeta'^2(2/E_1^2 E_2 - 1/E_1 E_2^2) - g_s\zeta\zeta'^2(1/E_1 E_2^2 - 1/2E_2^3) \\ g_{\perp} &= g_s + 2k'\zeta' / E_2 - 4k\zeta'^2 / E_1 E_2 + k'\zeta\zeta'(2/E_1 E_2 - 1/E_2^2) + 2g_s\zeta'^2 / E_1^2 + \zeta\zeta'(k\zeta' - k'\zeta) / E_1 E_2^2 \\ &\quad - (2k\zeta\zeta'^2 / E_1 + k'\zeta^2\zeta' / E_2)(1/2E_2^2 - 1/E_1 E_2) - g_s\zeta\zeta'^2(1/2E_1^2 E_2 - 1/2E_1 E_2^2 + 1/2E_2^3) \\ A_{\parallel} &= P(-\kappa - 4N/7) + P'[(g_{\parallel} - g_s) + 3(g_{\perp} - g_s)/7] \\ A_{\perp} &= P(-\kappa + 2N/7) + 11P'/14(g_{\perp} - g_s)\end{aligned}\quad (5)$$

In the above formula, g_s (≈ 2.0023) is the spin-only value. ζ (ζ') and k (k') are the spin-orbit coupling

coefficients and the orbital reduction factors, respectively. P and P' are the dipolar hyperfine constants related to the interaction within t_{2g} states and the interaction between t_{2g} and e_g states, respectively. κ is the core polarization constant for the $3d^9$ ion in crystals, which can be determined from the empirical relationship $\kappa \approx -2\chi/(3N\langle r^{-3} \rangle)$ [23], where χ is characteristic of the density of unpaired spins at the nucleus of the central ion and $\langle r^{-3} \rangle$ is the expectation value of the inverse cube of the 3d radial wave function. By using $\langle r^{-3} \rangle \approx 8.252$ a.u. [26] and $\chi \approx -3.12$ a.u. [23] for Cu^{2+} in some oxides with similar $[\text{CuO}_6]^{10-}$ cluster, the value $\kappa \approx 0.32$ may be estimated.

In Eq.(5), E_1 and E_2 are the energy separations between the excited ${}^2B_{2g}$ and 2E_g and the ground ${}^2B_{1g}$ states. They can be expressed in terms of the cubic field parameter Dq and the tetragonal field parameters Ds and Dt :

$$E_1 = 10Dq$$

$$E_2 = 10Dq + 3Ds - 5Dt. \quad (6)$$

Since the superposition model [27] enables correlation of the crystal-field parameters and the structure data of d^n clusters in crystals, we can calculate the tetragonal field parameters Ds and Dt from this model. Then, we have:

$$Ds = (4/7)\bar{A}_2(R)\left[(R/R_\perp)^{t_2} - (R/R_\parallel)^{t_2}\right]$$

$$Dt = (16/21)\bar{A}_4(R)\left[(R/R_\perp)^{t_4} - (R/R_\parallel)^{t_4}\right] \quad (7)$$

here $t_2 \approx 3$ and $t_4 \approx 5$ are the power-law exponents [10-13]. $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters, with the reference bond length R taken as the metal-ligand distance for the Zn^{2+} site of the host $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}$. Detailed X-ray studies of $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}$ are not available, so R (≈ 2.080 Å) is extrapolated from R in $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ and $\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$ based on the ionic radii of Si^{4+} (0.42 Å [28]), Ti^{4+} (0.68 Å [28]) and Se^{4+} (0.54 Å [29]). Then, the group overlap integrals S_{dpy} (as well as the integrals S_{ds} and A) can be calculated from the Slater-type self-consistent field (SCF) functions [30] with the distance R . These values are shown in Table 1. For d^n ions in octahedral clusters, $\bar{A}_4(R) \approx (3/4)Dq$ [10,

12, 15-17], where Dq is the cubic field parameter which is often obtained from the optical spectra of the studied system. According to the optical spectra for Cu^{2+} in some oxides with $[\text{CuO}_6]^{10-}$ clusters, the value $Dq \approx 710 \text{ cm}^{-1}$ [31, 32] can be obtained and adopted here. By studying the optical and EPR spectra for $3d^n$ ions in many crystals, the ratio $\bar{A}_2(R)/\bar{A}_4(R)$ is found to be in the range $8 \sim 12$ [10-13, 33-35], we take the average value, *i.e.*, $\bar{A}_2(R)/\bar{A}_4(R) \approx 10$, here. $R_{\parallel}$ and $R_{\perp}$ are the metal-ligand distances parallel with and perpendicular to the C_4 axis. Because of the Jahn–Teller effect of Cu^{2+} centers in $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}$ crystal, the bond lengths can be expressed in terms of the tetragonal elongation parameter τ as:

$$R_{\parallel} = R + 2\tau \text{ and } R_{\perp} = R - \tau. \quad (8)$$

Then, in the above formulas, if the covalency factor N is known, the related molecular orbital coefficients N_{γ} and λ_{γ} , the spin-orbit coupling coefficients ζ and ζ' and the orbital reduction factors k and k' can be determined.

Therefore, in the above formulas of the studied EPR parameters for $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}:\text{Cu}^{2+}$, only the covalency factor N and the relative axial tetragonal elongation τ are not known. Substituting these parameters into Eq. (5) and fitting the calculated EPR parameters to the experimental values, one can obtain

$$N \approx 0.76 \text{ and } \tau \approx 0.085 \text{ \AA} \quad (9)$$

for the impurity Cu^{2+} center in $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}$. Accordingly, the parallel and perpendicular $\text{Cu}^{2+}\text{-H}_2\text{O}$ bond lengths (*i.e.*, $R_{\parallel} \approx 2.250$ and $R_{\perp} \approx 1.995 \text{ \AA}$) for the studied system are obtained. These values are also listed in Table 1. The corresponding theoretical results (Cal.^b) of the EPR parameters are shown in Table 2. To clarify the importance of the ligand orbit and spin-orbit coupling contributions to the EPR parameters, the calculated results (Cal.^a) based on the conventional crystal-field model by neglecting the ligand orbital and the spin-orbit coupling contributions (*i.e.*, $k = k' = N$ and $\zeta = \zeta' = N\zeta_d^0$) are also collected in Table 2.

3. Discussion

Table 2 reveals that the calculated EPR parameters (Cal.^b) based on the perturbation formulas and inclusion of the ligand contributions show better agreement with the experimental data than those (Cal.^a) based on omission of the ligand contributions. Thus, the EPR parameters for $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}:\text{Cu}^{2+}$ are satisfactorily interpreted, and local structure of the parallel and perpendicular Cu^{2+} - H_2O bond lengths is also obtained.

1) The studied systems may exhibit significant covalency and ligand contributions due to the short Cu-O distances of the corresponding Cu^{2+} sites even under oxygen environments. This point is illustrated by the low covalency factor N ($\approx 0.76 \ll 1$) and the obvious orbital admixture coefficients λ_γ and λ_s ($\approx 0.36 \sim 0.56$) from the present cluster approach calculations. When the ligand orbital and spin-orbit coupling contributions are neglected, the results (Cal.^a) are in poor agreement with the experimental data, especially the calculated g factors and the anisotropies are much larger than the observed values. In fact, from Table 1, one can obtain that the relative deviations $\zeta/\zeta' - 1$ ($\approx 4.5\%$) and $k/k' - 1$ ($\approx 55\%$) for Cu^{2+} center in $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}$. So, the contributions to the EPR parameters from anisotropic orbital admixture (covalency effect) should be taken into account for the systems with moderate covalency.

2) The calculated ΔR ($= R_{\parallel} - R_{\perp} \approx 0.255 \text{ \AA}$) for Cu^{2+} centre in $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}:\text{Cu}^{2+}$ crystal illustrated that the impurity Cu^{2+} ion is located in the distorted octahedral sites (D_{4h}) elongated along C_4 -axis, which is consistent with the expectation based on the positive anisotropy Δg ($= g_{\parallel} - g_{\perp}$) for a $3d^9$ cluster suffering the Jahn-Teller effect. This type of Jahn-Teller distortion has been found for Cu^{2+} ions in many trigonal crystals [11-13]. Moreover, the tetragonal distortion ΔR for Cu^{2+} in $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}:\text{Cu}^{2+}$ crystal is in the same order of magnitude ($\sim 10^{-1} \text{ \AA}$) as those found for many $[\text{CuO}_6]^{10-}$ Jahn-Teller systems [11-13, 36] and is very close to that ($\Delta R \approx 0.254 \text{ \AA}$ [34]) for Cu^{2+} in trigonal ZnCO_3 crystal based on the EPR analysis. Interestingly, the relative elongation τ ($\approx 0.085 \text{ \AA}$) of the ligand octahedra

around Cu^{2+} in $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}$ crystal obtained in this work is very close to that (≈ 0.083 and $0.065 \text{ \AA}$ [11]) for Cu^{2+} on the octahedral interstitial sites in the trigonal crystal $\text{Ca}(\text{OH})_2$ based on the EPR analysis and can be regarded as reasonable. So, the tetragonal elongation of the studied $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ cluster in $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}:\text{Cu}^{2+}$ obtained from the above calculations is reasonable in physics.

3) It is difficult to determine the signs of hyperfine structure constants in EPR experiment [25, 26]. So the constants A values obtained from EPR measurements are actually the absolute values. Our calculations suggest that $A_{\parallel}$ and $A_{\perp}$ is negative and positive, respectively. The signs of $A_{\parallel}$ and $A_{\perp}$ suggested here for tetragonal $[\text{CuO}_6]^{10-}$ cluster in $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}:\text{Cu}^{2+}$ are the same as those for similar tetragonal $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ cluster in many crystals [10, 12, 17, 34-36] and can be regarded as reasonable.

4. Conclusion

The EPR parameters and the local structures for $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}:\text{Cu}^{2+}$ are theoretically studied from the high order perturbation formulas of a tetragonally elongated octahedral $3d^9$ cluster. The ligand octahedra around Cu^{2+} are found to suffer the relative elongations of about $0.085 \text{ \AA}$ for $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ cluster, along the C_4 axis due to the Jahn-Teller effect, which may entirely depress the original slight trigonal distortion of the host Zn^{2+} site. It is suggested that these perturbation formulas are effective in the studies of EPR parameters and the tetragonal distortion (or defect structure) for $3d^9$ ions in crystals.

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Table 1 The reference distance R and the parallel and perpendicular bond lengths for the impurity ligands distance $R_{\parallel}$ and $R_{\perp}$ (in Å), the group overlap integrals $S_{d\gamma}$ ($\gamma = t$ and e), S_{ds} and the integral A , the optical spectra parameters D_q and N , the normalization factors N_{γ} and the orbital admixture coefficients λ_{γ} and λ_s , the spin-orbit coupling coefficients ζ and ζ' (in cm^{-1}) and the orbital reduction factors k and k' for Cu^{2+} in $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}$.

R	$R_{\parallel}$	$R_{\perp}$	S_{dpt}	S_{dpe}	S_{ds}	A	D_q	N
2.080	2.250	1.995	0.0089	0.0295	0.0236	1.3123	710	0.76
N_t	N_e	λ_t	λ_e	λ_s	ζ	ζ'	k	k'
0.7638	0.7769	0.5650	0.4490	0.3592	651.6	623.8	0.8858	0.5700

Table 2 The calculated and experimental EPR parameters of g factors and the hyperfine structure constants (in cm^{-1}) for $\text{ZnSeF}_6 \cdot 6\text{H}_2\text{O}:\text{Cu}^{2+}$.

	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$
Cal. ^a	2.5722	2.1263	-107.2	-2.19
Cal. ^b	2.4294	2.0948	-135.9	-9.35
Expt. [9]	2.4295 ± 0.0005	2.0965 ± 0.0005	131.1 ± 0.3	9.3 ± 1

^a Calculations based on the conventional formulas of the EPR parameters by neglecting the ligand orbital and spin-orbit coupling contributions (*i.e.*, $k = k' = N$ and $\zeta = \zeta' = N\zeta_d^0$) in this work.

^b Calculations results of the EPR parameters based on the high-order perturbation formulas and inclusion of the ligand orbital and spin-orbit coupling contributions from the cluster approach in this work.