Investigations on the EPR Parameters for the Square Planar Cu^{2+} Centers in K_2PdX_4 (X = Cl, Br)

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The EPR parameters g factors $g_{\parallel}$, $g_{\perp}$ and the hyperfine structure constants $A_{\parallel}$ and $A_{\perp}$ for the square planar Cu^{2+} centers in K_2PdX_4 (X = Cl, Br) are theoretically investigated from the perturbation formulas of these parameters for a $3d^9$ ion under tetragonally elongated octahedra. In these formulas, not only the contributions from the conventional crystal-field (CF) mechanism, but also those from the charge-transfer (CT) mechanism are taken into account. The related molecular orbital coefficients are uniformly determined from the cluster approach, and the tetragonal field parameters Ds and Dt are obtained from the superposition model and the local structures of the systems. Based on only one adjustable parameter, the present results are in reasonable agreement with the observed values. Importance of the charge-transfer contributions is more significant for ligand Br than that for Cl due to the stronger covalency and much larger spin-orbit coupling coefficient of the former.

Key words: Crystal- and ligand fields; Electron paramagnetic resonance (EPR); Cu^{2+};
K_2PdX_4 (X = Cl, Br).

1. Introduction

Containing square planar $PdX_4{}^{2-}$ (X = Cl, Br) groups, K_2PdX_4 are interesting systems due to the properties of non-totally symmetrically distortion [1, 2], covalency [3], optical [4, 5], reacting (bonding) with some important biological molecules [6 – 8] and selective liquid membrane transport (of $PdCl_4{}^{2-}$ group) behaviours [9, 10]. On the other hand, Cu^{2+} ($3d^9$, equivalent to one 3d hole) can be regarded as a model system among the transition-metal group, having one ground state and a single excited state under regular octahedral environments. Particularly, the optical, local structure and electronic properties for square planar Cu^{2+} clusters have also been attractive subjects [11 – 14]. As is well known, electron paramagnetic resonance (EPR) is a powerful technique to study local structures and electronic states for transition-metal ions in crystals, and the corresponding experimental results can be expressed in terms of the EPR parameters (g factors $g_{\parallel}$, $g_{\perp}$ and the hyperfine structure constants $A_{\parallel}$ and $A_{\perp}$). Therefore, investigations for the square planar $CuX_4{}^{2-}$ clusters in the typical K_2PdX_4 systems are of fundamental and practical significance. For example, EPR studies were carried out on K_2PdX_4:Cu^{2+}, and the EPR parameters were also measured decades ago [13, 14].

In general, analysis of the microscopic mechanisms of the EPR parameters can reveal useful information about local structures and electronic properties of these systems. The microscopic origins of the EPR parameters for $3d^n$ ions in crystals result from both the crystal-field (CF) mechanism (related to the influence of lower CF excitations involving antibonding orbitals) and the charge-transfer (CT) mechanism (related to the influence of higher CT excitations involving bonding orbitals) [15, 16]. Usually, the CF contributions are regarded as dominant for ionic systems due to the much higher CT excitation levels. However, the energies of the CT levels for the same central ion (e. g., Cu^{2+}) decline with increasing covalency of ligand (e. g., from Cl to Br) [17]. Thus, significant CT contributions to the EPR parameters can be expected, especially for the ligands having very large spin-orbit coupling coefficient (e. g., Br). At this circumstance, interesting and instructive investigations have been carried out on

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the EPR parameters for K_2PdX_4:Cu^{2+} by means of the molecular orbital (MO) scheme [18 – 20] and diagonalizing of the complete energy matrix [21]. The detailed perturbation formulas of the EPR parameters were established in [18], by including both the CF and CT contributions in terms of various adjustable parameters (i. e., four independent MO coefficients α_0, α_1, α_2, and μ). Even though, local structures of the systems were not involved in the studies of the EPR parameters.

In order to investigate this problem to a better extent, the previous treatments of the EPR parameters based on the complicated perturbation formulas [18] may be improved so as to decrease the number of adjustable parameters and to provide more convenient theoretical analysis of EPR spectra. In this work, the improved formulas of the EPR parameters for a $3d^9$ ion under tetragonally elongated octahedra are established by considering both the CF and CT contributions. The related MO coefficients are determined from the cluster approach in a uniform way, instead of taking as adjustable parameters. Meanwhile, the local structures of the systems are correlated to the tetragonal field parameters Ds and Dt and hence to the EPR parameters.

2. Theory and Calculations

K_2PdX_4 belongs to the space group $D_{4h}{}^1$ (*P4/mmm*) with one formula unit per unit cell [22, 23]. This structure consists of square planar $[PdX_4]^{2-}$ groups stacked above each other along four fold axis. When an impurity Cu^{2+} is doped into K_2PdX_4, it may occupy host Pd^{2+} site and form a square planar $[CuX_4]^{2-}$ cluster, with tetragonal symmetry (an elongated octahedron).

2.1. Theoretical Formulas

For a $Cu^{2+}(3d^9)$ ion in tetragonally elongated octahedra, the lower ^2E_g irreducible representation would be separated into two orbital singlets $^2B_{1g}$ ($|x^2-y^2\rangle$) and $^2A_{1g}$ ($|z^2\rangle$), with the former lying lowest. Meanwhile, the upper $^2T_{2g}$ representation would split into an orbital singlet $^2B_{2g}$ ($|xy\rangle$) and a doublet $^2E_g(|xz\rangle, |yz\rangle)$ [24]. By including both the CF and CT mechanisms, the perturbation Hamiltonian for this $3d^9$ cluster under external magnetic field can be written as:

$$\begin{aligned} H' = {} & H_{SO}{}^{CF} + H_{Ze}{}^{CF} + H_{hf}{}^{CF} \\ & + H_{SO}{}^{CT} + H_{Ze}{}^{CT} + H_{hf}{}^{CT}, \end{aligned} \tag{1}$$

where H_{SO}, H_{Ze} and H_{hf} are, respectively, the spin-orbit coupling, the Zeeman term and the hyperfine interactions. The superscripts CF and CT denote the related terms for the CF and CT mechanisms, with the corresponding spin-orbit coupling coefficients (ζ_{CF}, $\zeta_{CF}{}'$ and ζ_{CT}, $\zeta_{CT}{}'$), the orbital reduction factors (k_{CF}, $k_{CF}{}'$ and k_{CT}, $k_{CT}{}'$), and the dipolar hyperfine structure parameters (P_{CF}, $P_{CF}{}'$ and P_{CT}, $P_{CT}{}'$).

Considering the contributions to the EPR parameters from the CT excitations, one can express the many-electron wave functions of CT configurations in terms of thirteen-electron wave functions out of $t_2{}^n$, e^a and e^b forms. Here t_2 and e stand for the irreducible representations of cubic (Oh) group. The superscripts n, a and b denote the non-bonding orbitals, anti-bonding orbitals (corresponding to the CF mechanism) and bonding orbitals (corresponding to the CT mechanism), respectively. Thus, the ground state $^2B_{1g}$ of the $3d^9$ cluster can be written as:

$$|{}^2B_{1g}\tfrac{1}{2}b_1\rangle = [\xi^2\eta^2\zeta^2\theta^2\varepsilon^+|\theta^2\varepsilon^2]. \tag{2}$$

In the square bracket on the right hand of (2), the letters (ξ, η, ζ and θ, ε) on the left column denote $t_2{}^n$ and e^a orbitals and those (θ, ε) on the right column denote e^b orbitals. Under tetragonal symmetry, there are only two irreducible representations $^2B_{2g}{}^b$ and $^2E_g{}^b$ (arising from the tetragonal splitting of $^2T_{2g}{}^b$ $[(t_2{}^n)^6$ $(e^a)^4$ $(e^b)^3]$ state) having non-zero spin-orbit coupling interaction with the ground state $^2B_{1g}$. Thus, these CT energy levels can be similarly expressed as:

$$\begin{aligned} |{}^2B_{2g}{}^b\tfrac{1}{2}b_2\rangle &= [\xi^2\eta^2\theta^2\varepsilon^2\zeta^+\zeta^-|\theta^2\varepsilon^+], \\ |{}^2E_g{}^b\tfrac{1}{2}\theta\rangle &= -\frac{\sqrt{3}}{2}[\eta^2\zeta^2\theta^2\varepsilon^2\xi^+\xi^-|\theta^+\varepsilon^2] \\ &\quad -\frac{1}{2}[\eta^2\zeta^2\theta^2\varepsilon^2\xi^+\xi^-|\theta^2\varepsilon^+], \\ |{}^2E_g{}^b\tfrac{1}{2}\varepsilon\rangle &= \frac{\sqrt{3}}{2}[\eta^2\zeta^2\theta^2\varepsilon^2\xi^+\xi^-|\theta^+\varepsilon^2] \\ &\quad -\frac{1}{2}[\eta^2\zeta^2\theta^2\varepsilon^2\xi^+\xi^-|\theta^2\varepsilon^+]. \end{aligned} \tag{3}$$

From the cluster approach, the MO orbitals

$$\begin{aligned} |\psi_t{}^x\rangle &= (N_t{}^x)^{1/2}(|\varphi_t\rangle - \lambda_t{}^x|\chi_{pt}\rangle), \\ |\psi_e{}^x\rangle &= (N_e{}^x)^{1/2}(|\varphi_e\rangle - \lambda_e{}^x|\chi_{pe}\rangle - \lambda_s{}^x|\chi_s\rangle) \end{aligned} \tag{4}$$

can be taken as the one-electron wave functions for the octahedral $3d^9$ clusters. The subscript γ (= t_{2g} or e_g)

stands for the irreducible representation of Oh group, and the superscript x (= a or b) denotes the antibonding and bonding orbitals. $|\varphi_\gamma\rangle$ are the metal 3d orbitals, and $|\chi_{p\gamma}\rangle$ and $|\chi_s\rangle$ are the ligand p- and s-orbitals. $N_\gamma{}^x$ and $\lambda_\gamma{}^x$ are the normalization factors and the orbital admixture coefficients, respectively. Thus, we have the normalization condition:

$$\begin{aligned}
&(N_t{}^x)[1-2\lambda_t{}^x S_{dpt}+(\lambda_t{}^x)^2]=1,\\
&(N_e{}^x)[1-2\lambda_e{}^x S_{dpe}-2\lambda_s{}^x S_{ds}\\
&\qquad +(\lambda_e{}^x)^2+(\lambda_s{}^x)^2]=1.
\end{aligned}\tag{5}$$

Meanwhile, the approximate relationships

$$\begin{aligned}
N^2 &= (N_t{}^a)^2[1+(\lambda_t{}^a)^2 S_{dpt}{}^2-2\lambda_t{}^a S_{dpt}],\\
N^2 &= (N_e{}^a)^2[1+(\lambda_e{}^a)^2 S_{dpe}{}^2+(\lambda_s{}^a)^2 S_{ds}{}^2\\
&\qquad -2\lambda_e{}^a S_{dpe}-2\lambda_s{}^a S_{ds}]
\end{aligned}\tag{6}$$

are satisfied by the anti-bonding orbitals. Here N is the average covalency factor, characteristic of the covalency or metal-ligand orbital admixtures in a crystal. In addition, the orthogonality relationships

$$\lambda_\gamma{}^b \approx (\lambda_\gamma{}^a S_{dp\gamma}-1)/(S_{dp\gamma}-2\lambda_\gamma{}^a)\tag{7}$$

are held for the bonding and antibonding orbitals. In general, the orbital admixture coefficients increase with increasing the group overlap integrals, and one can approximately adopt the proportional relationship between the orbital admixture coefficients and the related group overlap integrals, i. e., $\lambda_e{}^x/S_{dpe} \approx \lambda_s{}^x/S_{ds}$ (where x = a and b) within the same irreducible representation e_g.

Applying the perturbation Hamiltonian (1) to the ground and excited states (2) and (3), the improved perturbation formulas of the EPR parameters for a $3d^9$ ion under tetragonally elongated octahedra are established from the one-electron wave functions (4). Thus, we have

$$\begin{aligned}
g_\parallel &= g_s+\Delta g_\parallel{}^{CF}+\Delta g_\parallel{}^{CT},\\
\Delta g_\parallel{}^{CF} &= 8k_{CF}'\zeta_{CF}'/E_1+k_{CF}\zeta_{CF}'^2/E_2{}^2\\
&\quad +4k_{CF}'\zeta_{CF}\zeta_{CF}'/(E_1E_2)\\
&\quad +g_s\zeta_{CF}'^2[1/E_1{}^2-1/(2E_2{}^2)]\\
&\quad -k_{CF}\zeta_{CF}\zeta_{CF}'^2(4/E_1-1/E_2)/E_2^2\\
&\quad -2k_{CF}'\zeta_{CF}\zeta_{CF}'^2[2/(E_1E_2)-1/E_2{}^2]/E_1\\
&\quad -g_s\zeta_{CF}\zeta_{CF}'^2[1/(E_1E_2{}^2)-1/(2E_2{}^3)],\\
\Delta g_\parallel{}^{CT} &= 8k_{CT}'\zeta_{CT}'/E_{CT1},\\
g_\perp &= g_s+\Delta g_\perp{}^{CF}+\Delta g_\perp{}^{CT},\\
\Delta g_\perp{}^{CF} &= 2k_{CF}'\zeta_{CF}'/E_2-4k_{CF}\zeta_{CF}'^2/(E_1E_2)\\
&\quad +k_{CF}'\zeta_{CF}\zeta_{CF}'(2/E_1-1/E_2)/E_2\\
&\quad +2g_s\zeta_{CF}'^2/E_1{}^2\\
&\quad +\zeta_{CF}\zeta_{CF}'(k_{CF}\zeta_{CF}'-k_{CF}'\zeta_{CF})/(E_1E_2{}^2)\\
&\quad -\zeta_{CF}\zeta_{CF}'(1/E_2-2/E_1)(2k_{CF}\zeta_{CF}'/E_1\\
&\quad +k_{CF}'\zeta_{CF}/E_2)/(2E_2)\\
&\quad -g_s\zeta_{CF}\zeta_{CF}'^2[1/E_1{}^2-1/(E_1E_2)\\
&\qquad\qquad +1/E_2{}^2]/(2E_2),\\
\Delta g_\perp{}^{CT} &= 2k_{CT}'\zeta_{CT}'/E_{CT2},\\
A_\parallel &= A_\parallel{}^{CF}+A_\parallel{}^{CT},\\
A_\parallel{}^{CF} &= -\kappa P_0-4P_{CF}/7+P_{CF}'[8k_{CF}'\zeta_{CF}'/E_1\\
&\quad +6k_{CF}'\zeta_{CF}'/(7E_2)-3k_{CF}\zeta_{CF}'^2/(7E_2{}^2)\\
&\quad -40k_{CF}'\zeta_{CF}\zeta_{CF}'/(7E_1E_2)+\kappa\zeta_{CF}'^2/E_2{}^2],\\
A_\parallel{}^{CT} &= P_{CT}[8k_{CT}'\zeta_{CT}'/E_{CT1}+6k_{CT}'\zeta_{CT}'/(7E_{CT2})],\\
A_\perp &= A_\perp{}^{CF}+A_\perp{}^{CT},\\
A_\perp{}^{CF} &= -\kappa P_0+2P_{CF}/7+P_{CF}'[11k_{CF}'\zeta_{CF}'/(7E_2)\\
&\quad +9k_{CF}'\zeta_{CF}\zeta_{CF}'/(14E_2{}^2)-4\zeta_{CF}'^2/(7E_1{}^2)\\
&\quad +11k_{CF}'\zeta_{CF}\zeta_{CF}'/(7E_1E_2)\\
&\quad +\kappa\zeta_{CF}'^2[2/E_1{}^2+1/(2E_1{}^2)],\\
A_\perp{}^{CT} &= 11P_{CT}'k_{CT}'\zeta_{CT}'/(7E_{CT2}).
\end{aligned}\tag{8}$$

Here g_s = 2.0023 is the spin-only value. E_1 and E_2 are the CF energy separations between the excited ${}^2B_{2g}$ and ${}^2E_g$ and ground ${}^2B_{1g}$ states: E_1 = 10 Dq and E_2 = 10 Dq + 5 Ds − 3 Dt. Here Dq is the cubic field parameter, and Ds and Dt are the tetragonal ones. E_{CT1} and E_{CT2} are the energy differences between the CT excited ${}^2B_{2g}{}^b$ and ${}^2E_g{}^b$ and ground ${}^2B_{1g}$ states. κ is the core polarization constant. In (8), the spin-orbit coupling coefficients and the orbital reduction factors of the CF mechanism are

$$\begin{aligned}
\zeta_{CF} &= (N_t{}^a)^2[\zeta_d{}^0+(\lambda_t{}^a)^2\zeta_p{}^0/2],\\
\zeta_{CF}' &= N_t{}^a N_e{}^a[\zeta_d{}^0-\lambda_t{}^a\lambda_e{}^a\zeta_p{}^0/2],\\
k_{CF} &= (N_t{}^a)^2[1+(\lambda_t{}^a)^2/2],\\
k_{CF}' &= N_t{}^a N_e{}^a[1+\lambda_t{}^a\lambda_e{}^a/2],\\
P_{CF} &= (N_t{}^a)^2 P_0,\\
P_{CF}' &= N_t{}^a N_e{}^a P_0,
\end{aligned}\tag{9}$$

and those of the CT mechanism are

$$\zeta_{CT}' = N_t^a N_e^b\{[\lambda_t^a - S_{dp}(e_{2g})]\zeta_d^0 + \lambda_t^a\zeta_p^0/2\},$$

$$k_{CT}' = N_t^a N_e^b\{\lambda_e^a + \lambda_t^a/2 + \lambda_t^a S_{dp}(t_{2g})S_{dp}(e_g) - \lambda_t^a\lambda_e^a S_{dp}(t_{2g})\}$$

$$P_{CT} = (N_t^b)^2 P_0,$$

$$P_{CT}' = N_t^b N_e^b P_0. \quad (10)$$

Here ζ_d^0 and ζ_p^0 are the spin-orbit coupling coefficients of the free $3d^9$ and ligand ions, respectively. P_0 is the dipolar hyperfine structure parameter of the free $3d^9$ ion.

2.2. Calculations for K_2PdX_4:Cu^{2+}

Now the above formulas are applied to K_2PdX_4:Cu^{2+}. For the square planar $[CuX_4^{2-}]$ clusters, the tetragonal field parameters can be determined from the superposition model [25] and the local geometrical relationship of the systems:

$$Ds = -(4/7)\bar{A}_2(R)(R/R_\perp)^{t_2}$$
$$Dt = -(8/21)\bar{A}_4(R)(R/R_\perp)^{t_4}, \quad (11)$$

Here $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters. $R_\perp$ denotes the planar bond length. R is the reference distance (or the metal-ligand bond length), and $R = R_\perp$ for the studied square planar clusters here. For octahedral $3d^n$ clusters, the relationships $\bar{A}_4(R) \approx (3/4)$ Dq and $\bar{A}_2(R) \approx 10.8\,\bar{A}_4(R)$ have been proved to be valid in many crystals [25–27] and reasonably applied here.

For K_2PdX_4:Cu^{2+}, the cubic field parameters $Dq \approx 1250\ cm^{-1}$ and $1150\ cm^{-1}$ for X = Cl and Br can be obtained from the spectral parameters for Cu^{2+} in halides [28]. From [29], the average covalency factor N (≈ 0.765) is acquired for Cu^{2+} in $SrLaAlO_4$. Considering that the covalency of Cu^{2+}-X^- bonds in K_2PdX_4:Cu^{2+} should be stronger than that of Cu^{2+}-O^{2-} bonds in $SrLaAlO_4$:Cu^{2+}, one can approximately acquire $N \approx 0.695$ and 0.638 for X = Cl and Br, respectively, in the studied systems. From the Cu^{2+}-X^- distances R (≈ 2.265 Å and 2.42 Å [18, 22, 23] for K_2PdCl_4 and K_2PdBr_4, respectively), the related group overlap integrals are calculated from the Slater-type self-consistent field (SCF) wave functions [30, 31]. Using (8)–(9) and the related free-ion values (i. e., $\zeta_d^0 \approx 829\ cm^{-1}$ [32] and $P_0 \approx 416 \cdot 10^{-4}\ cm^{-1}$ [33] for Cu^{2+} and $\zeta_p^0 \approx 587\ cm^{-1}$ and $2460\ cm^{-1}$ [34] for Cl^- and Br^-), the spin-orbit coupling coefficients, the orbital reduction factors and the dipolar hyperfine structure parameters can be determined for both the CF and CT mechanisms. All these values are shown in Table 1. The core polarization constants in the formulas of the hyperfine structure constants are taken as $\kappa \approx 0.3$ [32, 35], the expectation value for Cu^{2+} in tutton salts. The CT energy levels E_{CT1} and E_{CT2} are about $38000\ cm^{-1}$ and $35000\ cm^{-1}$ [36] for K_2PdCl_4, and $30500\ cm^{-1}$ and $27500\ cm^{-1}$ [18] for K_2PdBr_4, respectively. Substituting these values into (8), the theoretical EPR parameters (Cal.^{c}) are calculated and listed in Table 2. For comparisons, the results (Cal.^{a}) of the previous works [16] and those (Cal.^{b}) including only the CF contributions (i. e., all the CT terms vanish in (8)) are also collected in Table 2.

Table 1. The group overlap integrals (and also the integral A), the spin-orbit coupling coefficients (in cm^{-1}), the orbital reduction factors and the dipolar hyperfine structure parameters (in $10^{-4}\ cm^{-1}$) of CF and CT mechanisms for K_2PdX_4:Cu^{2+} (X = Cl and Br).

X	S_{dpt}	S_{dpe}	S_{ds}	A	ζ_{CF}	ζ_{CF}'	k_{CF}'
Cl	0.0132	0.0377	0.0255	1.418	672	507	0.856
Br	0.0115	0.0346	0.0231	1.524	984	135	0.826
X	k_{CF}'	P_{CF}	P_{CF}'	ζ_{CT}'	k_{CT}	P_{CT}	P_{CT}'
Cl	0.480	292	295	650	0.431	268	287
Br	0.388	267	270	932	0.440	292	310

Table 2. The g-shifts $\Delta g_i (= g_i - g_s$, where $i = \parallel$ or $\perp)$ and the hyperfine structure constants A_i (in $10^{-4}\ cm^{-1}$) for K_2PdX_4:Cu^{2+}.

Hosts		$\Delta g_\parallel$	$\Delta g_\perp$	$A_\parallel$	$A_\perp$
K_2PdCl_4	Cal.^{a}	0.2279	0.0454	−160.5	−35.0
	Cal.^{b}	0.1814	0.026	−193.4	−39.9
	Cal.^{c}	0.2321	0.044	−170.2	−34.2
	Expt. [13]	0.2303(2)	0.047(2)	−163.6(5)	−34.5(6)
K_2PdBr_4	Cal.^{a}	0.1411	0.0464	−175.4	−46.6
	Cal.^{b}	0.037	0.005	−251.1	−55.3
	Cal.^{c}	0.144	0.038	−196.8	−45.4
	Expt. [14]	0.141(3)	0.041(2)	−189.5	−45.8

[a] Calculations based on the complicated perturbation formulas and various adjustable MO coefficients in the previous work [18]. [b] Calculations based on only the CF contributions in this work. [c] Calculations based on both the CF and CT contributions in this work.

2.3. Validity and Applicability of Present Theoretical Treatments

In order to clarify the validity of the theoretical model and formulas established in this work, the advantages of adopting only one adjustable parameter

Table 3. The g-shifts Δg_i and the hyperfine structure constants A_i (in 10^{-4} cm^{-1}) in terms of the respective contributions for various tetragonally elongated octahedral Cu^{2+} centers.

		$RbCaF_3:Ni^+$	$SrCl_2:Cu^{2+}$	$MgO:Cu^{2+}$	$NaCl:Cu^{2+}$
$\Delta g_\parallel$	Cal.[a]	0.6153	0.1957	0.3418	0.3302
	Cal.[b]	0.6642	0.2368	0.3829	0.3731
	Expt. [37]	0.6607	0.2340(20)	0.3817	0.3707
$\Delta g_\perp$	Cal.[a]	0.1004	0.0270	0.0773	0.0548
	Cal.[b]	0.1128	0.0393	0.0942	0.0685
	Expt. [38]	0.1117	0.0381(20)	0.0937	0.0677
$A_\parallel$	Cal.[a]	−84.1	−177.3	−176.0	−116.2
	Cal.[b]	−79.4	−160.2	−163.1	−107.4
	Expt. [39]	−77.8(17)	−157.8(10)	–	−105.9
$A_\perp$	Cal.[a]	−35.9	−47.8	−43.7	−44.3
	Cal.[b]	−33.8	−42.6	−40.2	−40.1
	Expt. [40]	−31.2(17)	−40.0(60)	–	−38.9

[a] Calculations based on only the CF contributions in this work. [b] Calculations based on both the CF and CT contributions in this work.

(i. e., the average covalency factor N) over the previous work [18] may be analyzed here. Firstly, reduction in the number of adjustable parameters in present work is achieved by establishing the relationships among the related MO coefficients (e. g., N_γ^x and λ_γ^x) based on the cluster approach (see (5) – (7)). Secondly, the tetragonal field parameters are determined from the local structures of the systems based on the superposition model, and their influence on the EPR parameters is also explicitly indicated in the CF energy denominators E_1 and E_2. On the contrary, various MO coefficients (e. g., α_0, α_1, α_2, and μ) were taken as adjustable parameters, and the tetragonal distortions (local structures) of the impurity centers were not included in the previous treatments [18].

The general applicability of the above formulas can be further checked by analyzing some other tetragonally elongated $3d^9$ centers. The following systems are studied: similar square planar $[NiF_4]^{3-}$ cluster (center III) in $RbCaF_3:Ni^+$ and $[CuCl_4]^{2-}$ cluster in $SrCl_2:Cu^{2+}$, and normal elongated octahedral $[CuO_6]^{10-}$ and $[CuCl_6]^{4-}$ clusters (induced by the Jahn-Teller effect) in $MgO:Cu^{2+}$ and $NaCl:Cu^{2+}$. The calculated results in terms of merely CF (Cal. [a]) and both CF and CT contributions (Cal. [b]) are compared with the experimental data [37 – 40] in Table 3.

3. Discussion

Table 2 reveals that the theoretical results (Cal. [c]) of the EPR parameters based on both the CF and CT contributions in this work show reasonable agreement with the observed values, and are also comparable with those (Cal. [a]) of the previous studies [18]. This means that the present investigations based on only one adjustable parameter seem applicable to the studies of EPR spectra for $3d^9$ ions in elongated octahedra with significant covalency and CT contributions.

1) The contributions to the g-shifts $\Delta g_i (= g_i - g_s$, where $i = \parallel$ or $\perp)$ from the CT mechanism are the same in sign and about 28% (for $i = \parallel$) and 69% (for $i = \perp$) larger in magnitude than those from the corresponding CF ones for K_2PdCl_4. For the ligand Br, the above contributions rapidly increase to almost 4 and 8 times those of the respective CF terms. This can be ascribed to the much larger ζ_p^0 (≈ 2460 cm^{-1} [34]) and lower CT energy levels for $[CuBr_4]^{2-}$ cluster than that for $[CuCl_4]^{2-}$ cluster [18, 36]. The importance of the CT contributions for the hyperfine structure constants is less significant than that for the g factors due to the large isotropic part characterized by the core polarization constant. Interestingly, the ratios of the CT contributions related to the corresponding CF ones obtained in this work are comparable with those in the previous studies [18] based on various adjustable parameters (e. g., four independent MO coefficients) and can be regarded as reasonable.

2) The large anisotropies ($g_\parallel - g_\perp$ and $A_\parallel - A_\perp$) of the EPR parameters depend mainly upon the tetragonal distortions of the square planar $[CuX_4]^{2-}$ clusters. This structure can be regarded as a limit for an elongated octahedron (i. e., two axial ligands are removed to infinite), which may result in significant tetragonal distortions and hence the large anisotropies of the EPR parameters for the studied systems. Thus, the local structures of the impurity centers are connected with the studies of the EPR spectra.

3) From Table 3, one can find that the calculated results based on the theoretical model and formulas (including both the CF and CT contributions) in this work also show reasonable agreement with the experimental data for various tetragonally elongated octahedral $3d^9$ clusters [37 – 40]. The contributions from the CT mechanism are less important for $RbCaF_3:Ni^+$ and $MgO:Cu^{2+}$ due to the weaker covalency and ligand spin-orbit coupling interactions. In addition, for similar Cu^{2+}-Cl^- combinations in $SrCl_2:Cu^{2+}$ (or $NaCl:Cu^{2+}$), the influence of the CT mechanism is less significant than that in the above $K_2PdCl_4:Cu^{2+}$. Since the impurity-ligand distance $R(\approx 2.467$ Å or 2.81 Å) for $SrCl_2:Cu^{2+}$ or $NaCl:Cu^{2+}$ is much larger than that (≈ 2.265 Å) for $K_2PdCl_4:Cu^{2+}$, the weaker covalency

(or less intense impurity-ligand orbital admixtures) and hence relatively smaller CT contributions can be expected in the former. Therefore, the above formulas in this work are applicable not only to square planar $3d^9$ centers but also to normal tetragonally elongated octahedral ones.

4. Conclusion

The EPR parameters for K_2PdX_4:Cu^{2+} are theoretically investigated from the perturbation formals of these parameters for a tetragonally elongated octahedral $3d^9$ cluster including both the CF and CT contributions. By applying the cluster approach, the related MO coefficients are determined in a uniform way, and the tetragonal field parameters are obtained from the superposition model and the local structures of the systems. Finally, the experimental EPR parameters are reasonably interpreted from only one adjustable parameter.

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