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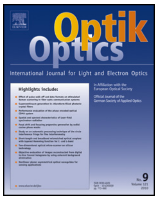

Theoretical studies of the spin Hamiltonian parameters for the tetragonal Cu^{2+} centres in NaF and $CsCdF_3$

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ABSTRACT

The spin Hamiltonian parameters (*g* factors and hyperfine structure constants) for Cu^{2+} in NaF and $CsCdF_3$ are theoretically studied using the high order perturbation formulas of these parameters for a $3d^9$ ion in a tetragonally elongated octahedron. The Cu^{2+} centres are found to suffer the relative elongation ratios of about 5.5% and 3.1% for Cu^{2+} in NaF and $CsCdF_3$, respectively, along the C_4 axis due to the Jahn–Teller effect. The theoretical results of the spin Hamiltonian parameters show good agreement with the experimental data. The larger *g* anisotropy for Cu^{2+} in NaF than $CsCdF_3$ is attributed to the larger relative tetragonal elongation ratio arising from the longer distance and hence the weaker bonding (or lower force constant) in the former. The significant discrepancies in the hyperfine structure constants for the two systems are analysed in view of their different core polarization constants and the reduction factors H related to the local structures.

1. Introduction

NaF and $CsCdF_3$ crystals doped with copper arouse extensive interest of researchers due to the interesting optical absorption [1,2], ionic transportation [3,4], thermoluminscence [5] and dielectric properties [6]. On the other hand, Cu^{2+} ($3d^9$) in crystals can also be regarded as a model system because of the relatively simpler energy level structure with only one ground state and one excited state when situated into ideal octahedral crystal-fields [7,8]. Usually, transition-metal impurities (e.g., Cu^{2+}) play an important role in the properties of these materials with dopants arising from their useful and abundant energy levels and transitions, which strongly depend upon local structures around the impurities in the hosts. Suitably, NaF and $CsCdF_3$ (or other ABF_3 type fluoroperovskites) usually act as typical host materials for the investigations of impurity behaviours because octahedral Na^+ or Cd^{2+} sites of ideal cubic symmetry can be spacious enough to accommodate various transition-metal ions. The local structure properties and behaviours of transition-metal impurities in crystals can be conveniently studied by means of electron paramagnetic resonance (EPR) technique, and the experimental results are described by the spin Hamiltonian parameters (e.g., zero-field splitting, anisotropic *g* factors and hyperfine structure constants). For example, EPR experiments were carried out for Cu^{2+} doped NaF and $CsCdF_3$, and the *g* factors $g_{||}$ and $g_\perp$ and the hyperfine structure constants $A_{||}$ and $A_\perp$ were also measured for the tetragonal Cu^{2+} centres at 77 K [9,10].

Until now, however, the above EPR results have not been satisfactorily interpreted, although the EPR signals were assigned to the tetragonally elongated Cu^{2+} centres in the previous works [9,10]. And information about local structures around impurity Cu^{2+} has not been obtained yet. Since the information of defect structures would be helpful to understand the properties of these materials, theoretical investigations of the EPR spectra and the defect structures for Cu^{2+} in NaF and $CsCdF_3$ are of scientific and practical significance. In this work, the spin Hamiltonian parameters and the local structures are quantitatively studied for the above tetragonal Cu^{2+} centres by utilizing the perturbation formulas of these parameters for a tetragonally elongated octahedral $3d^9$ cluster. The ligand orbital and spin–orbit coupling contributions are taken into account from the cluster approach in view of covalency, and the suitable lattice distortions due to the Jahn–Teller effect are quantitatively involved from the superposition model.

2. Calculations

When an impurity Cu^{2+} ion enters the lattices of NaF and $CsCdF_3$, it may prefer to occupy substitutionally the host octahedral Na^+ and Cd^{2+} sites, and conserve original cubic (O_h) point symmetry. As a Jahn–Teller ion, Cu^{2+}($3d^9$) would suffer the Jahn–Teller effect via the vibration interactions, e.g., stretching the two Cu^{2+}—F^- bonds

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along [0 0 1] (or C_4) axis by a relative tetragonal elongation ratio τ, which reduces local symmetry from original cubic to tetragonal (D_{4h}) [11–13]. As a result, the twofold orbital degeneracy of the cubic ^2E_g ground state is lifted, and this irreducible representation is split into two singlets $^2B_{1g}$ (ε) and $^2A_{1g}$ (θ), with the former lying lowest [7,8]. On the other hand, the cubic excited orbital triplet $^2T_{2g}$ can be separated into an orbital singlet $^2B_{2g}$ (ζ) and a doublet ^2E_g(ξ, η) [7,8].

Although NaF and $CsCdF_3$ hosts may show dominant iconicity, the studied $[CuF_6]^{4-}$ clusters can exhibit some covalency and impurity-ligand orbital admixtures. Thus, the ligand orbital and spin–orbit coupling contributions may be taken into account from the cluster approach. In order to study the EPR spectra and local structures for Cu^{2+} in NaF and $CsCdF_3$, the high (fourth-) order perturbation formulas [14] of g factors and hyperfine structure constants for a tetragonally elongated octahedral $3d^9$ cluster based on the cluster approach are adopted here. Thus, we have:

$$\begin{aligned}
g_{||} = \;& g_s + 8k'\zeta'/E_1 + k\zeta'^2/{E_2}^2 + 4\,k'\zeta\zeta'/(E_1E_2) + g_s\zeta'^2[1/E_1^2 - 1/(2E_2^2)] - k\zeta\zeta'^2(4/E_1 - 1/E_2)/E_2^2 \\
& - 2k'\zeta\zeta'^2[2/(E_1E_2) - 1/E_2^2]/E_1 - g_s\zeta\zeta'^2[1/(E_1E_2^2) - 1/(2E_2^2)], \\
g_{\perp} = \;& g_s + 2k'\zeta'/E_2 - 4k\zeta'^2/(E_1E_2) + k'\zeta\zeta'(2/E_1 - 1/E_2)/E_2 + 2g_s\zeta'^2/E_1^2 + \zeta\zeta'(k\zeta' - k'\zeta)/(E_1E_2^2) \\
& - \zeta\zeta'(1/E_2 - 2/E_1)(2k\zeta'/E_1 + k'\zeta/E_2)/(2E_2) - g_s\zeta\zeta'^2\,[1/E_1^2 - 1/(E_1E_2) + 1/E_2^2]/(2E_2), \\
A_{||} = \;& P\,\{(-\kappa - 4H/7) + [8k'\zeta'/E_1 + 6k\zeta'/(7E_2) - 3k\zeta'^2/(7E_2^2) - 40k'\zeta\zeta'/(7E_1E_2) + \kappa\zeta'^2/E_2^2]\}, \\
A_{\perp} = \;& P\{(-\kappa + 2H/7) + [11k'\zeta'/(7E_2) + 9k'\zeta\zeta'/(14{E_2}^2) - 4\zeta'^2/(7E_1^2) \\
& + 11\,k'\zeta\zeta'/(7E_1E_2) + \kappa\zeta'^2[2/E_1^2 + 1/(2E_2^2)]\}.
\end{aligned} \tag{1}$$

Here g_s (≈2.0023) is the spin-only value. ζ and ζ' are the spin–orbit coupling coefficients, and k and k' are the orbital reduction factors. P and κ are, respectively, the dipolar hyperfine structure parameter and the core polarization constant. H is the reduction factor due to the central ion orbital admixtures in crystals arising from the low symmetrical (tetragonal elongation) distortion. E_1 and E_2 are the energy separations of the excited $^2B_{2g}$ and ^2E_g states related to the ground $^2B_{1g}$ state [14]. They are usually determined from the energy matrices for a $3d^9$ ion in tetragonal symmetry in terms of the cubic field parameter Dq and the tetragonal field parameters Ds and Dt [14]:

$$\begin{aligned}
E_1 &\approx 10\,\mathrm{Dq}, \\
E_2 &\approx 10\,\mathrm{Dq} - 3\,\mathrm{Ds} + 5\,\mathrm{Dt}.
\end{aligned} \tag{2}$$

The spin–orbit coupling coefficients (ζ and ζ') and the orbital reduction factors (k and k') denote the anisotropic contributions (i.e., diagonal and off-diagonal matrix elements) of the spin–orbit coupling and orbital angular momentum operators within the irreducible representations γ (=e and t standing for E_g and T_{2g}) of group O_h. The above contributions are related to the anisotropic expansions of 3d electronic clouds and the impurity 3d and ligand 2p (or 2s) orbital admixtures in crystals, which can be described from the cluster approach under the scheme of the improved crystal-field model containing ligand orbital and spin–orbit coupling interactions [15]. The above influences of ligand contributions can be characterized by the normalization factors N_γ and the orbital admixture coefficients λ_γ. They are determined from the approximate relationships [15]

$$\begin{aligned}
N^2 &= N_t^2[1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}], \\
N^2 &= N_e^2[1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}]
\end{aligned} \tag{3}$$

and the normalization conditions [15]

$$\begin{aligned}
N_t(1 - 2\lambda_t S_{dpt} + \lambda_t^2) &= 1, \\
N_e(1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) &= 1.
\end{aligned} \tag{4}$$

Here N is the covalency factor, indicating covalency of the systems. $S_{dp\gamma}$ (and S_{ds}) are the group overlap integrals. Then the spin–orbit coupling coefficients and the orbital reduction factors are obtained from the cluster approach [15]:

$$\begin{aligned}
&\zeta = N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0/2), \qquad \zeta' = (N_tN_e)^{1/2}(\zeta_d^0 - \lambda_t\lambda_e\zeta_p^0/2), \\
&k = N_t(1 + \lambda_t^2/2), \qquad k' = (N_tN_e)^{1/2}[1 - \lambda_t(\lambda_e + \lambda_s A)/2],
\end{aligned} \tag{5}$$

where ζ_d^0 and ζ_p^0 are, respectively, the spin–orbit coupling coefficients of the free $3d^9$ and ligand ions. A is the integral $R\left\langle ns|\frac{\partial}{\partial y}|np_y\right\rangle$, where R denotes the reference impurity-ligand distance of the studied systems.

In general, the orbital admixture coefficients increase with increasing the group overlap integrals, and one can approximately adopt the proportionality relationship $\lambda_e/S_{dpe} \approx \lambda_s/S_{ds}$ between the orbital admixture coefficients and the related group overlap integrals within the same irreducible representation E_g.

As mentioned before, the $[CuF_6]^{4-}$ clusters may suffer the Jahn–Teller elongation distortions, and the bond lengths parallel with and perpendicular to the C_4 axis can be expressed in terms of the reference distance R and the relative tetragonal elongation ratio τ as:

$$R_{||} \approx R(1 + 2\tau), \qquad R_{\perp} \approx R(1 - \tau) \tag{6}$$

Thus, the tetragonal field parameters are determined from the local geometry and the superposition model [16]:

$$\begin{aligned}
\mathrm{Ds} &\approx (4/7)\bar{A}_2(R)[(1-\tau)^{-t_2} - (1+2\tau)^{-t_2}] \\
\mathrm{Dt} &\approx (16/21)\bar{A}_4(R)[(1-\tau)^{-t_4} - (1+2\tau)^{-t_4}]
\end{aligned} \tag{7}$$

Here $t_2 \approx 3$ and $t_4 \approx 5$ [16] are the power-law exponents. $\bar{A}_2(R)$ and $\bar{A}_2(R)$ are the intrinsic parameters, with the reference distance R. For octahedral $3d^n$ clusters, the relationships $\bar{A}_4(R) \approx (3/4)\,\mathrm{Dq}$ and $\bar{A}_2(R) \approx 12\bar{A}_4(R)$ [17–19] have been proved valid in many crystals and are reasonably applied here. Then the local structures (low symmetrical distortions due to the Jahn–Teller effect) are connected with the tetragonal field parameters and hence with the spin Hamiltonian parameters, particularly the g anisotropy Δg ($=g_{||} - g_{\perp}$), of the systems.

In general, the reference impurity-ligand distances R in the impurity centres can be dissimilar to the host cation–anion distances R_H (≈2.317 and 2.232 Å [20,21]) in NaF and $CsCdF_3$ due to size mismatch. The investigations based on experimental superhyperfine constant and extended X-ray absorption fine structure (EXAFS) measurements reveal that the empirical relationship $R \approx R_H + (r_i - r_h)/2$ [21] is approximately valid for an impurity ion in crystals. Using the ionic radius r_i (≈0.72 Å [20]) for the impurity Cu^{2+} and the radii r_h (≈0.97 Å and 0.97 [20]) for the host octahedral Na^+ and Cd^{2+}, one can obtain $R \approx 2.192$ and 2.107 Å for Cu^{2+} in NaF and $CsCdF_3$ here. From the reference distances R, the group overlap