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Theoretical investigations of the spin Hamiltonian parameters for the tetragonal $[Rh(CN)_4Cl_2]^{4-}$ complex in KCl

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ABSTRACT

The spin Hamiltonian parameters (g factors, hyperfine structure constants and superhyperfine parameters) for the tetragonal $[Rh(CN)_4Cl_2]^{4-}$ complex in KCl are theoretically investigated from the perturbation formulas of these parameters for a $4d^7$ ion in a tetragonally elongated octahedron. This center can be assigned to the substitutional Rh^{2+} on host K^+ site reduced from Rh^{3+} by capturing one electron during the electron irradiation, associated with the two axial ligands CN^- replaced by two Cl^-. The crystal-fields of the two axial Cl^- are weaker than those of the four planar CN^-, yielding the tetragonal elongation distortion. This system belongs to the case of low spin ($S = 1/2$) under strong crystal-fields, different from that of high spin ($S = 3/2$) under weak and intermediate crystal-fields (e.g., $3d^7$ ions such as Fe^+ and Co^{2+} in conventional chlorides). The calculated spin Hamiltonian parameters show good agreement with the experimental data. The above $[Rh(CN)_4Cl_2]^{4-}$ complex due to the different axial and perpendicular ligands is unlike the tetragonally elongated $[RhCl_6]^{4-}$ complex due to the Jahn–Teller effect in the similar NaCl:Rh^{2+} crystals.

1. Introduction

KCl single crystals containing rhodium have attracted interest of researchers due to the important electrochemical [1,2], catalytic [3], crystal-field [4] and magnetic resonance [5–7] properties. Normally, the above properties can be sensitively correlated to local structures of the dopants which are conveniently investigated with the aid of electron paramagnetic resonance (EPR). For example, EPR measurements were performed on $[Rh(CN)_6]^{3-}$ doped KCl single crystals submitted to 2 MeV electron irradiation at 77 K [7]. And the spin Hamiltonian parameters (g factors and hyperfine structure constants) for the paramagnetic impurity Rh^{2+} (reduced from the original Rh^{3+} in form of $[Rh(CN)_6]^{3-}$ complex by capturing an electron during electron irradiation) and superhyperfine parameters for the ligand ^{35}Cl were measured for a tetragonal $[Rh(CN)_4Cl_2]^{4-}$ complex [7]. Nevertheless, the above experimental results have not been satisfactorily interpreted until now, except that the g and A factors were tentatively analyzed based on the simple second perturbation formulas using various adjustable parameters [7].

Usually, theoretical studies on spin Hamiltonian parameters can be helpful to reveal the microscopic mechanisms of the EPR spectra and the electronic states useful to understand properties this material with Rh dopants. It is noted that the studied $[Rh(CN)_4Cl_2]^{4-}$ complex belongs to the case of strong crystal-fields with low spin ($S = 1/2$) and $g \sim 2$ [8], quite dissimilar to the conventional case of weak and intermediate fields with high spin ($S = 3/2$) and $g \sim 4.3$ for $3d^7$ (e.g., Co^{2+}) ions in chlorides (e.g., AgCl) [9,10]. Therefore, further theoretical studies of the spin Hamiltonian parameters for the tetragonal $[Rh(CN)_4Cl_2]^{4-}$ complex are of scientific significance. In this work, the spin Hamiltonian parameters of this unique $[Rh(CN)_4Cl_2]^{4-}$ complex in KCl are theoretically investigated from the perturbation formulas of these parameters for a $4d^7$ ion in tetragonally elongated octahedra. The local structure of this complex is quantitatively involved in the calculations with the related tetragonal field parameters determined from the superposition model.

2. Calculations

When Rh^{3+} (in form of $[Rh(CN)_6]^{3-}$) enters the lattice of KCl, the substitutional $[Rh(CN)_6]^{4-}$ group may locate on the host K^+ site. During the electron irradiation process at 77 K, some diamagnetic Rh^{3+} can be reduced into paramagnetic Rh^{2+} by capturing one electron, with the two axial CN^- replaced by two Cl^-. Thus, the tetragonal $[Rh(CN)_4Cl_2]^{4-}$ complex is formed. Because the crystal-fields of the two axial Cl^- ions are weaker than those of the four planar CN^- groups, this complex actually shows a tetragonally elongated octahedron. Quite different from the case of weak and

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intermediate crystal-fields with high spin (S = 3/2) and higher g values (~4.3) for the isoelectronic Fe^{+} and Co^{2+} in conventional chlorides [9,10], the studied $[Rh(CN)_4Cl_2]^{4-}$ complex belongs to the case of strong crystal-fields with low spin (S = 1/2) and much lower g values (~2) [6,7]. The ground state is the orbital doublet $^2E_g(t_{2g}^6e_g)$ with an unpaired electron in E_g state. When the ligand octahedron is tetragonally elongated, the ground ^2E_g state would further split into two orbital singlets θ ($^2A_{1g}$) and ε ($^2B_{1g}$), the former lying lowest [11–13].

In order to investigate the spin Hamiltonian parameters of this Rh^{2+} center, the perturbation formulas [13] of g factors, hyperfine structure constants and superhyperfine parameters for a tetragonally elongated octahedral $4d^7$ complex are adopted here. In these formulas, the ligand orbital and spin–orbit coupling contributions are taken into account in view of significant covalency of the system, and the ligand unpaired spin densities are quantitatively determined from the uniform formulas from the cluster approach. Thus, we have [13]

$$g_{//} = g_s \cos 2\theta + 2k^2 \sin^2\theta,$$

$$g_{\perp} = g_s \cos^2\theta + \sqrt{6}k^2 \sin 2\theta,$$

$$A_{//} = P\left[-\kappa + \frac{4N}{7} - \frac{\sqrt{6}\sin 2\theta}{7} + \frac{8\sin^2\theta}{7}\right],$$

$$A_{\perp} = P\left[-\kappa - \frac{2N}{7} + \frac{15\sqrt{6}\sin^2\theta}{14} - \frac{4\sin^2\theta}{7}\right],$$

$$A' = A_s + 2A_p + 2(1-\lambda_e^2)\left[1 + \frac{12\langle r^2\rangle}{7R^2} + \frac{30\langle r^4\rangle}{7R^4}\right]A_D,$$

$$B' = A_s - A_p - (1-\lambda_e^2)\left[1 + \frac{12\langle r^2\rangle}{7R^2} + \frac{30\langle r^4\rangle}{7R^4}\right]A_D \quad (1)$$

with

$$\mathrm{tg}2\theta = \frac{[\sqrt{6}\zeta'/(\zeta/2 - \Delta E)]}{2} \quad (2)$$

Here g_s (=2.0023) is the pure spin value. The quantity ΔE (=10Dq − Ds − 10Dt) is the energy difference between the ground $^2A_{1g}$ and the excited ^2E_g states. Dq is the cubic field parameter, and Ds and Dt are the tetragonal field parameters.

In Eqs. (1) and (2), ζ and ζ' are the spin–orbit coupling coefficients, charactering the diagonal and off-diagonal matrix elements of the spin–orbit coupling operator. k and k' are the orbital reduction factors, arising from the anisotropic (diagonal and off-diagonal) interactions of the orbital angular momentum operator. Based on the cluster approach, the spin–orbit coupling coefficients and the orbital reduction factors can be expressed as [14]:

$$\zeta = N_t\left(\zeta_d^0 + \frac{\lambda_t^2\zeta_p^0}{2}\right), \quad \zeta' = (N_tN_e)^{1/2}\left(\zeta_d^0 - \frac{\lambda_t\lambda_e\zeta_p^0}{2}\right),$$
$$k = N_t\left(1 + \frac{\lambda_t^2}{2}\right), \quad k' = (N_tN_e)^{1/2}\left[1 - \lambda_t\frac{\lambda_e + \lambda_s A}{2}\right] \quad (3)$$

Here the subscripts t and e denote the cubic irreducible representations $\gamma = T_{2g}$ and E_g. ζ_d^0 and ζ_p^0 are the spin–orbit coupling coefficients of the free $4d^7$ and ligand ions, respectively. N_γ and λ_γ (or λ_s) are, respectively, the normalization factors and the orbital admixture coefficients. A stands for the integral $R\langle ns|\partial/\partial y|np_y\rangle$, where R is the metal–ligand distance of the studied system. The molecular orbital coefficients N_γ and λ_γ (or λ_s) are usually obtained from the normalization conditions [14]

$$N_t(1 - 2\lambda_t S_{dpt} + \lambda_t^2) = 1,$$
$$N_e(1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) = 1 \quad (4)$$

and the approximate relationships [14]

$$N^2 = N_t^2[1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}],$$
$$N^2 = N_e^2[1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}] \quad (5)$$

In the above formulas, N is the average covalency factor, characteristic of covalency of the system. $S_{dp\gamma}$ (and S_{ds}) are the group overlap integrals between the impurity and ligand orbitals. Normally, the orbital admixture coefficients decrease with decreasing the group overlap integrals, and one can approximately utilize the proportional relationship $\rho\lambda_e/S_{dpe} \approx \lambda_s/S_{ds}$ between the orbital admixture coefficients and the related group overlap integrals within the same irreducible representation E_g. Here the proportionality factor ρ is taken as an adjustable parameter.

In superhyperfine parameters, A_s stands for the isotropic contributions from the ligand 3s orbitals. A_p and A_D denote the anisotropic contributions from the admixture between Rh^{2+}–4d and Cl^-–3p orbitals and the dipole–dipole interactions between central ion electrons and ligand nucleus, respectively. $\langle r^n\rangle$ (n = 2, 4) are the expectation values of the square and quartic of Rh^{2+} $4d^7$ radial wave function. The isotropic and anisotropic parts of the superhyperfine parameters can be expanded as [15]:

$$A_s = f_sA_s^0, \quad A_p = f_pA_p^0, \quad A_D = \frac{g\beta g_n\beta_n}{R^3}. \quad (6)$$

Here $A_s^0 = (8\pi/3)g_s\mu_B g_n\mu_n|\phi(0)|^2$ and $A_p^0 = g_s\mu_B g_n\mu_n\langle r^{-3}\rangle_{3p}$ are the related nuclear parameters of ligand $^{35}Cl^-$. g_n is the nuclear g value. μ_B and μ_n are the electron Bohr magneton and nuclear magneton. $\phi(0)$ is the wave function of chlorine 3s orbital at the nucleus. $\langle r^{-3}\rangle_{3p}$ is the expectation value of the inverse cube of Cl^-–3p radial wave function. For the dipole–dipole interaction term, the g factor is conveniently taken as the average [=$(g_{//} + 2g_\perp)/3$] of those in Eq. (1).

The unpaired spin densities f_s and f_p for the ligand 3s and 3pσ orbitals are determined from the relevant molecular orbital coefficients based on the cluster approach:

$$f_s \approx \frac{N_e\lambda_s^2}{3}, \quad f_p \approx \frac{N_e\lambda_e^2}{3} \quad (7)$$

In the calculations of the spin Hamiltonian parameters, the tetragonal field parameters are connected with the local structure of the $[Rh(CN)_4Cl_2]^{4-}$ complex from the superposition model [16]:

$$Ds = -4\frac{[\bar{A}_2(Cl) - \bar{A}_2(CN)]}{7},$$
$$Dt = 16\frac{[\bar{A}_4(Cl) - \bar{A}_4(CN)]}{21} \quad (8)$$

Here $\bar{A}_2(L)$ and $\bar{A}_4(L)$ are the intrinsic parameters for the various ligands L (=CN^- and Cl^-). For transition-metal ions in octahedra, the relationships $\bar{A}_4(L) \approx (3/4)Dq(L)$ and $\bar{A}_2(L) \approx 10.8\bar{A}_4(L)$ were proved valid in many crystals [16–18] and are suitably adopted here. In the above expressions, the tetragonal field parameters relevant to the local structure are quantitatively correlated to the spin Hamiltonian parameters, especially the g anisotropy Δg (=$g_\perp - g_{//}$).

Utilizing the metal–ligand distance R (≈3.1466 Å [19]) for KCl, the group overlap integrals $S_{dpt} \approx 0.0023$, $S_{dpe} \approx 0.0103$, $S_{ds} \approx 0.0042$ and $A \approx 1.5896$ are calculated from the Slater-type self-consistent field (SCF) wave functions [20,21]. From the optical spectra for Rh^{2+} in chlorides and nitrides [22–24], the spectral parameters Dq (CN^-) ≈ 2800 cm^{-1}, Dq (Cl^-) ≈ 1675 cm^{-1}