

# Studies on the G Factors and Superhyperfine Parameters of the Tetragonal $[\text{Fe}(\text{CN})_4\cdot(\text{CN})\text{Cl}]^{5-}$ Group in NaCl

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**Abstract.** The  $g$  factors and superhyperfine parameters of the tetragonal  $[\text{Fe}(\text{CN})_4\cdot(\text{CN})\text{Cl}]^{5-}$  group in NaCl are theoretically investigated from the perturbation formulas of these parameters for a tetragonally elongated octahedral low spin ( $S=1/2$ )  $3d^7$  cluster. This center is ascribed to the substitutional  $\text{Fe}^{+}$  on host  $\text{Na}^{+}$  site associated with one of the axial ligands  $\text{CN}^{-}$  replaced by  $\text{Cl}^{-}$ . Since the crystal-fields arising from the axial  $\text{Cl}^{-}$  and  $\text{CN}^{-}$  ions are weaker than those of the four planar  $\text{CN}^{-}$ , the impurity center is characterized as the tetragonally elongated octahedron. The calculated  $g$  factors and superhyperfine parameters show reasonable agreement with the measured values. The results are discussed.

## 1. Introduction

NaCl including iron cyanide has attracted wide interest due to the promising applications in integrated circuit industry [1], electrodeposition [2], biosensors [3] and biosorbents [4,5]. Normally, the above applications are sensitively correlated to local structures of the dopants which can be conveniently investigated with the aid of electron paramagnetic resonance (EPR) technique. EPR measurements were carried out for  $[\text{Fe}(\text{CN})_6]^{4-}$  doped NaCl subject to  $x$ - or  $\gamma$  irradiation at low temperature [6], and the  $g$  factors and ligand  $^{35}\text{Cl}^{-}$  superhyperfine parameters were measured for a tetragonal  $[\text{Fe}(\text{CN})_4\cdot(\text{CN})\text{Cl}]^{5-}$  group [6]. However, the above experimental results have not been satisfactorily interpreted until now. Usually, theoretical studies on  $g$  factors and superhyperfine parameters would be helpful to reveal the microscopic mechanisms of the EPR spectra and local behaviors of impurity iron in NaCl useful to understand properties this material with iron dopants. The studied  $[\text{Fe}(\text{CN})_4\cdot(\text{CN})\text{Cl}]^{5-}$  group 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 intermediate crystal-fields with high spin ( $S=3/2$ ) and  $g \sim 4.3$  for  $3d^7$  (e.g.,  $\text{Fe}^{+}$ ,  $\text{Co}^{2+}$ ) ions in chlorides [7,8]. Thus, further theoretical studies of the EPR spectra

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for the tetragonal  $[\text{Fe}(\text{CN})_4(\text{CN})\text{Cl}]^{5-}$  group are of scientific significance. In this work, the  $g$  factors and superhyperfine parameters of this  $[\text{Fe}(\text{CN})_4(\text{CN})\text{Cl}]^{5-}$  group in NaCl are theoretically investigated from the perturbation formulas of these parameters for a low spin ( $S=1/2$ )  $3d^7$  ion in tetragonally elongated octahedra, by connecting the local structure with the EPR analysis.

## 2. Calculations

Dimagnetic  $\text{Fe}^{2+}$  (in form of  $[\text{Fe}(\text{CN})_6]^{4+}$ ) doped into the lattice of NaCl can occupy the substitutional  $\text{Na}^+$  site and construct the octahedral  $[\text{Fe}(\text{CN})_6]^{4+}$  group. Upon  $x$ - and  $\gamma$ -irradiation at low temperature, some diamagnetic  $\text{Fe}^{2+}$  can be reduced into paramagnetic  $\text{Fe}^+(3d^7)$  by capturing one electron with one axial  $\text{CN}^-$  replaced by  $\text{Cl}^-$  and form the tetragonal  $[\text{Fe}(\text{CN})_4(\text{CN})\text{Cl}]^{5-}$  group. Since the crystal-fields arising from the axial  $\text{Cl}^-$  and  $\text{CN}^-$  ions are weaker than those arising from the four planar  $\text{CN}^-$  ions, this group exhibits a tetragonally elongated octahedron. Unlike the conventional case of intermediate crystal-fields with high spin ( $S=3/2$ ) and higher  $g$  values ( $\sim 4.3$ ) for  $\text{Fe}^+$  or  $\text{Co}^{2+}$  in chlorides [7,8], the studied  $[\text{Fe}(\text{CN})_4(\text{CN})\text{Cl}]^{5-}$  group belongs to the case of strong crystal-fields with low spin ( $S=1/2$ ) and lower  $g$  values ( $\sim 2$ ) [6]. For a tetragonally elongated octahedral low spin  $3d^7$  cluster, the original cubic ground state  ${}^2E_g$  may split into two orbital singlets  $\theta$  ( ${}^2A_{1g}$ ) and  $\varepsilon$  ( ${}^2B_{1g}$ ), the former lying lowest [11-13].

In order to investigate the EPR spectra of this tetragonal  $\text{Fe}^+$  center, the perturbation formulas of  $g$  factors and superhyperfine parameters for a tetragonally elongated octahedral low spin  $3d^7$  group are adopted here. In view of significant covalency of the system, the ligand orbital and spin-orbit coupling contributions are taken into account, and the ligand unpaired spin densities are quantitatively determined from the cluster approach in a consistent way. Thus, we have [9]:

$$g_{//} = g_s + 2k' \zeta'^2 / E_{1//}^2 - 4k \zeta (1/E_{2//} - 1/E_{5//}),$$

$$g_{\perp} = g_s + 2k' \zeta'^2 / E_{1\perp}^2 + 3k \zeta / E_{\perp} - k' \zeta' (1/E_{2\perp} - 1/E_{5\perp}),$$

$$A' = A_s + 2A_{\sigma} + 2(1 - \lambda_c^2) [1 + 12 \langle r^2 \rangle / (7R^2) + 30 \langle r^4 \rangle / (7R^4)] A_D,$$

$$B' = A_s - A_{\sigma} - (1 - \lambda_c^2) [1 + 12 \langle r^2 \rangle / (7R^2) + 30 \langle r^4 \rangle / (7R^4)] A_D, \quad (1)$$

with

$$1/E_{\perp} = 1/E_{3\perp} + 1/E_{4\perp} + 0.38 (1/E_{3\perp} - 1/E_{4\perp}). \quad (2)$$

Here the denominators  $E_i$  ( $i=1-5$ ) are the energy separations between the excited  ${}^4T_{1g}[t_2^5 e^2({}^3A_2)]$ ,  ${}^2T_{1g}[t_2^5 e^2({}^3A_2)]$ ,  ${}^2T_{1g}[t_2^5 e^2({}^1E)]$ ,  ${}^2T_{2g}[t_2^5 e^2({}^1E)]$  and  ${}^2T_{2g}[t_2^5 e^2({}^1A_1)]$  and the ground  ${}^2A_{1g}$  states under tetragonal crystal-fields. The subscripts  $\alpha$  ( $=//$  and  $\perp$ ) denote the two components of the tetragonal splittings for the above energy separations. They are expressed from the energy matrices for a  $3d^7$  ion under tetragonal symmetry in terms of the cubic and tetragonal field parameters  $Dq$ ,  $Ds$  and  $Dt$  and Racah parameters  $B$  and  $C$  [9]:

$$E_{1//} = 10 Dq - 4 B - 4 C,$$

$$E_{1\perp} = 10 Dq - 4 B - 4 C - 3 Ds + 5 Dt,$$

$$E_{2//} = 10 Dq + 2 B - C,$$

$$E_{2\perp} = 10 Dq + 2 B - C + 3Ds - 5Dt,$$

$$E_{3\perp} = 10 Dq + 6 B - C - 3 Ds + 5 Dt,$$

$$E_{4\perp} = 10 Dq + 14 B + C - 3 Ds + 5 Dt,$$

$$E_{5//} = 10 Dq + 6 B - C,$$

$$E_{5\perp} = 10Dq + 6B - C + 3Ds - 5Dt \quad (3)$$

$\zeta$  and  $\zeta'$  are the spin-orbit coupling coefficients, and  $k$  and  $k'$  are the orbital reduction factors. Based on the cluster approach, these quantities can be expressed as [9]:

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

Here the subscripts t and e denote the cubic irreducible representations  $\gamma = T_{2g}$  and  $E_g$ .  $\zeta_d^0$  and  $\zeta_p^0$  are the spin-orbit coupling coefficients of the free  $3d^7$  and ligand ions, respectively.  $N_\gamma$  and  $\lambda_\gamma$  (or  $\lambda_s$ ) are, respectively, the normalization factors and the orbital admixture coefficients.  $A$  stands for the integral  $R \langle ns | \partial / \partial y | np_y \rangle$ , with the reference distance  $R$ . The molecular orbital coefficients  $N_\gamma$  and  $\lambda_\gamma$  (or  $\lambda_s$ ) are usually obtained from the normalization conditions and the approximate relationships [9] in terms of the group overlap integrals and covalency factor  $N$ . Here, the proportionality relationship  $\rho \lambda_e / S_{dpe} \approx \lambda_s / S_{ds}$  between the orbital admixture coefficients and the related group overlap integrals is adopted, with the proportionality factor  $\rho$  taken as an adjustable parameter.

In the formulas of 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  $Fe^+ - 3d$  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  $Fe^+ 3d^7$  radial wave function. The isotropic and anisotropic parts of superhyperfine parameters can be expanded as [10]:

$$A_s = f_s A_s^0, \quad A_p = f_p A_p^0, \quad A_D = g\beta g_n \beta_n / R^3. \quad (5)$$

Here  $f_s$  ( $\approx N_e \lambda_s^2 / 3$ ) and  $f_p$  ( $\approx N_e \lambda_e^2 / 3$ ) are the unpaired spin densities for the ligand 3s and  $3p\sigma$  orbitals related to the corresponding molecular orbital coefficients from the cluster approach [9].  $A_s^0 = (8\pi/3) g_s \mu_B g_n \mu_n |\phi(0)|^2$  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.  $\mu_B$  and  $\mu_n$  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  $[(g_{\parallel} + 2g_{\perp})/3]$  of those in Eq. (1).

The tetragonal field parameters are determined from the local structure of the  $[Fe(CN)_4 \cdot (CN)Cl]^{5-}$  group using the superposition model [11]:

$$Ds = 2 [\bar{A}_2(CN) - \bar{A}_2(Cl)] / 7,$$

$$Dt = 8 [\bar{A}_4(CN) - \bar{A}_4(Cl)] / 21. \quad (6)$$

Here  $\bar{A}_2(L)$  and  $\bar{A}_4(L)$  are the intrinsic parameters for the distinct ligands  $L$  ( $= CN^-$  and  $Cl^-$ ). For  $3d^n$  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 [8] and are suitably adopted here. In the above expressions, the tetragonal field parameters relevant to the local structure are quantitatively correlated to the  $g$  factors, especially the  $g$  anisotropy  $\Delta g$  ( $= g_{\perp} - g_{\parallel}$ ).

Utilizing the reference metal-ligand distance  $R$  ( $\approx 2.81 \text{ \AA}$  [12]) for NaCl, the group overlap integrals  $S_{dpt} \approx 0.0042$ ,  $S_{dpe} \approx 0.0165$ ,  $S_{ds} \approx 0.0076$  and  $A \approx 1.4196$  are calculated from the Slater-type self-consistent field functions [13,14]. From the optical spectral studies

for  $\text{Fe}^+$  in chlorides and nitrides [15], the spectral parameters  $Dq(\text{CN}^-) \approx 1780 \text{ cm}^{-1}$ ,  $Dq(\text{Cl}^-) \approx 800 \text{ cm}^{-1}$  and  $N \approx 0.725$  are acquired for the studied  $[\text{Fe}(\text{CN})_4(\text{CN})\text{Cl}]^{5-}$  group. The total cubic field parameter is expressed as:  $Dq \approx [5Dq(\text{CN}) + Dq(\text{Cl})]/6$ . The molecular orbital coefficients can be determined from the cluster approach [9] if the proportionality factor  $\rho$  is known. In view i) that the 3s orbital is usually more compact than the 3p one for the same ligand  $\text{Cl}^-$  and ii) that the reference distance  $R$  is long for the studied group, the admixture of  $\text{Fe}^+ - 3d$  with  $\text{Cl}^- - 3s$  orbitals may be much less than that with  $\text{Cl}^- - 3p$  orbitals. Thus, the proportionality factor should be significantly lower than unity, and one can take  $\rho \approx 0.43$  here. Then the related molecular orbital coefficients  $N_t \approx 0.728$ ,  $N_e \approx 0.742$ ,  $\lambda_t \approx 0.618$ ,  $\lambda_e \approx 0.486$  and  $\lambda_s \approx 0.169$  are obtained. Using the free-ion values  $\zeta_d^0 \approx 356 \text{ cm}^{-1}$  [16] for  $\text{Fe}^+$  and  $\zeta_p^0 \approx 587 \text{ cm}^{-1}$  [17] for  $\text{Cl}^-$ , the spin-orbit coupling coefficients  $\zeta \approx 341 \text{ cm}^{-1}$ ,  $\zeta' \approx 168 \text{ cm}^{-1}$  and the orbital reduction factors  $k \approx 0.868$  and  $k' \approx 0.575$  are also acquired from Eq. (4). It is noted that the spin-orbit coupling contributions of ligand  $\text{CN}^-$  are neglected here due to the much smaller  $\zeta_p^0 \approx 75 \text{ cm}^{-1}$  for nitrogen [18]. As regards superhyperfine parameters, the expectation values are  $\langle r^2 \rangle \approx 1.774 \text{ a.u.}$  and  $\langle r^4 \rangle \approx 8.385 \text{ a.u.}$ , respectively, for  $\text{Fe}^+ 3d^7$  radial function [7]. In the energy denominators, the Racah parameters B and C can be determined from the free-ion parameters  $B_0 \approx 869 \text{ cm}^{-1}$  and  $C_0 \approx 3638 \text{ cm}^{-1}$  of  $\text{Fe}^+$  [16]. The nuclear parameters are  $A_s^0 \approx 1570 \times 10^{-4}$  and  $A_p^0 \approx 46.8 \times 10^{-4} \text{ cm}^{-1}$  for  $^{35}\text{Cl}^-$  [19]. Substituting the relevant quantities into Eq. (1), the theoretical g factors and superhyperfine parameters (Calc. <sup>c</sup>) are calculated and listed in Table 1. In order to analyze importance of covalency (or the ligand contributions), the calculated g factors (Calc. <sup>b</sup>) based on omission of the ligand contributions (i.e., taking  $k = k' = N$  and  $\zeta = \zeta' = N\zeta_d^0$ ) are also collected in Table 1. Meanwhile, the g factors (Calc. <sup>a</sup>) based on the simple second-order g formulas using various adjustable parameters and the superhyperfine parameters based on the fitted  $f_s \approx 0.6\%$  and  $f_p \approx 3.2\%$  in the previous studies [6] are also given in Table 1.

**TABLE 1** THE G FACTORS AND SUPERHYPERFINE PARAMETERS (IN  $10^{-4} \text{ CM}^{-1}$ ) FOR THE TETRAGONAL  $[\text{Fe}(\text{CN})_4(\text{CN})\text{Cl}]^{5-}$  GROUP IN NaCl.

<sup>a</sup> Calculations of g factors based on the simple second-order g formulas and the superhyperfine

	$g_{\parallel}$	$g_{\perp}$	$A'$	$B'$
Calc. <sup>a</sup>	2.0023	2.159	12.4	7.9
Calc. <sup>b</sup>	2.021	2.264	-	-
Calc. <sup>c</sup>	2.009	2.086	15.6	8.5
Expt. [6]	2.001	2.075	13.8	9.4

parameters based on the fitted  $f_s \approx 0.6\%$  and  $f_p \approx 3.2\%$  in the previous studies [6].

<sup>b</sup> Calculations of g factors from the conventional crystal-field model formulas without the ligand contributions (i.e., taking  $k = k' = N$  and  $\zeta = \zeta' = N\zeta_d^0$ ).

<sup>c</sup> Calculations based on Eq. (1) containing the ligand contributions in this work.

### 3. Discussion

One can find from Table 1 that the theoretical g factors and superhyperfine parameters (Calc. <sup>c</sup>) are in reasonable agreement with the experimental data for  $[\text{Fe}(\text{CN})_4(\text{CN})\text{Cl}]^{5-}$  group in NaCl, and the EPR spectra of this system are suitably interpreted here.

The positive anisotropy  $\Delta g$  is attributed to the lowest  ${}^2A_{1g}$  state for a low spin  $3d^7$  ion under tetragonally elongated octahedra. The tetragonal elongation distortion arises mainly from the weaker crystal-fields of the axial  $\text{Cl}^-$  and  $\text{CN}^-$  ions than those of the four planar  $\text{CN}^-$  ions. Remarkably, this low spin  $[\text{Fe}(\text{CN})_4(\text{CN})\text{Cl}]^{5-}$  group with different axial and perpendicular ligands and low g value ( $\approx 2.0$  [6]) is quite unlike the isoelectronic high spin

( $S=3/2$ )  $[\text{FeF}_6]^{5-}$  group in NaF with the impurity off-center displacement and high  $g$  value ( $\approx 4.135$  [20]).

The  $g$  factors (Calc. <sup>c</sup>) containing the ligand orbital and spin-orbit coupling contributions are in better agreement with the experimental data than those (Calc. <sup>b</sup>) in the absence of these contributions and those (Calc. <sup>a</sup>) based on the simple second-order  $g$  formulas using various adjustable parameters of the previous work [6]. Because of significant covalency and ligand contributions, the anisotropy  $\Delta g$  and the average [ $(g_{\parallel} + 2g_{\perp})/3$ ] (Calc. <sup>b</sup>) without the ligand contributions are larger than the observed values. This point is further illustrated by the low covalency factor  $N$  ( $\approx 0.725 < 1$ ), the obvious orbital admixture coefficients ( $\approx 0.2 - 0.6$ ) and the relative deviations (anisotropies) of 51% and 103% for the orbital reduction factors and the spin-orbit coupling coefficients from the cluster approach calculations. The proportionality factor  $\rho$  ( $\approx 0.43 \ll 1$ ) reveals a significant (about 60%) decrease for the ratio  $\lambda_c/S_{ds}$  as compared to  $\lambda_c/S_{dpe}$ . In fact, the admixture of  $\text{Fe}^+ - 3d$  orbital with  $\text{Cl}^- - 3s$  orbital can be much less than that with  $\text{Cl}^- - 3p$  orbital, because the  $3s$  orbital is usually more compact than the  $3p$  one for the same ligand. The unpaired spin densities  $f_s \approx 0.7\%$  and  $f_p \approx 5.8\%$  obtained from the present cluster approach treatments are comparable with those ( $\approx 0.6\%$  and  $3.2\%$  [6]) by fitting the experimental superhyperfine parameters in the previous work [6] and those ( $\approx 1.1\%$  and  $8.6\%$  [21]) for the isoelectronic tetragonal  $\text{Rh}^{2+}(4d^7)$  center in AgCl and can be regarded as suitable.

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