



Trends in
**Applied Sciences
Research**

ISSN 1819-3579



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Theoretical Studies of the Local Structure and the Spin Hamiltonian Parameters for Ni^{2+} in CaF_2

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Abstract: The local structure and the spin Hamiltonian parameters g factors g_{\parallel} and g_{\perp} and the hyperfine structure constants A_{\parallel} and A_{\perp} for the tetragonal Ni^{2+} center (i.e., $[\text{NiF}_4]^{3-}$ cluster) in CaF_2 are theoretically studied from the high order perturbation formulas of these parameters for a $3d^8$ ion in tetragonal symmetry (elongated octahedron). Based on the studies, the impurity Ni^{2+} is found to locate at the distance of about 0.35Å from the nearest fluorine plane. The theoretical spin Hamiltonian parameters show good agreement with the experimental data.

Key words: Electron paramagnetic resonance, crystal-fields, spin hamiltonians, Ni^{2+} , CaF_2

Introduction

Ni-doped fluorite-type crystals have been extensively investigated because of the paramagnetic defects arising from X-ray irradiation (Studzinski *et al.*, 1984; Alonso *et al.*, 1983; Casas-González *et al.*, 1980). These impurity centers usually exhibit tetragonal symmetry, as observed by Electron Paramagnetic Resonance (EPR) and Electron Nuclear Double Resonance (ENDOR) techniques (Alonso *et al.*, 1980, 1983; Studzinski *et al.*, 1984). For example, the spin Hamiltonian parameters g factors g_{\parallel} and g_{\perp} and the hyperfine structure constants A_{\parallel} and A_{\perp} for the tetragonal Ni^{2+} center in CaF_2 produced by X-ray irradiation were measured (Casas-González *et al.*, 1980). The off-center displacement and the anisotropic g factors for the tetragonal Ni^{2+} center in CaF_2 were investigated by using the simple perturbation formulas of the g factors for a $3d^8$ ion in tetragonally elongated octahedra (Casas-González *et al.*, 1980). It was found that the impurity Ni^{2+} may not occupy exactly the host Ca^{2+} site but suffer so large displacement along $[100]$ (or C_4) axis that it is only 0.37Å away from the nearest fluorine plane (Casas-González *et al.*, 1980). In their theoretical treatment, however, the third-order perturbation terms were not completely involved and the fourth-order ones were neglected as well. Meanwhile, the energy denominators in the formulas of the g factors were not correlated with the local structure around the impurity center, but taken from the values of Ni^{2+} doped LiF and NaF (Hayes and Wilkens, 1964). In addition, the hyperfine structure constants were not interpreted, either. In order to explain the g factors and the hyperfine structure constants for the tetragonal center in $\text{CaF}_2:\text{Ni}^{2+}$ and to investigate the local structure of the impurity Ni^{2+} more exactly, high order perturbation formulas of these parameters are applied and the related energy differences are quantitatively determined from the local structure of this center. The results are discussed.

Theory and Calculations

In pure fluorite, Ca^{2+} is coordinated to eight oxygen ions forming an ideal cube. When irradiated by X-ray, Ni-doped CaF_2 can exhibit Ni^{2+} center of tetragonal symmetry by Ni^{2+} occupying the host

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Ca^{2+} site with additional off-center shift along one of $[100]$ axis (Casas-González *et al.*, 1980). This may be due to the smaller size and the less charge of the impurity Ni^{+} than those of the host Ca^{2+} , which is likely to make the Ni^{+} unstable on the host Ca^{2+} site and tend to suffer a significant axial displacement. As a result, the impurity Ni^{+} would be much close to one of the fluorine plane in the cube and the near square planar $[\text{NiF}_4]^{3-}$ cluster (i.e., the Ni^{+} has a small distance ΔZ from the plane) is formed. The other four ligands are much farther from the impurity and their influence may be ignored for simplicity. This tetragonal center can be regarded as an elongated octahedron, with its local structure characterized by the distance ΔZ .

For a $\text{Ni}^{+}(3d^9)$ ion in tetragonally elongated octahedra, the lower 2E irreducible representation may be separated into two orbital singlets ${}^2B_1(|x^2-y^2\rangle)$ and ${}^2A_1(|z^2\rangle)$, with the former lying lowest, while the upper 2T_2 representation would split into an orbital singlet ${}^2B_2(|xy\rangle)$ and a doublet ${}^2E(|xz\rangle, |yz\rangle)$ (Abragam and Bleaney, 1970). It is noted that in the treatments of the previous work (Casas-González *et al.*, 1980), the notations 2B_1 and 2B_2 are interchanged, due to a rotation of the frame of axes. The perturbation formulas of the spin Hamiltonian parameters of the 2B_1 ground state for a $3d^9$ ion in tetragonal symmetry can be expressed as follows (Wei *et al.*, 2005):

$$\begin{aligned} g_{\parallel} &= g_s + 8k\zeta_d/E_1 + k\zeta_d^2/E_2^2 + 4k\zeta_d^2/E_1E_2 - g_s\zeta_d^2(1/E_1^2 - 1/2E_2^2) + k\zeta_d^3(4/E_1 - 1/E_2)/E_2^2 \\ &\quad - 2k\zeta_d^3(2/E_1E_2 - 1/E_2^2)/E_1 + g_s\zeta_d^3(1/E_1E_2^2 - 1/2E_2^3), \\ g_{\perp} &= g_s + 2k\zeta_d/E_2 - 4k\zeta_d^2/E_1E_2 + k\zeta_d^2(2/E_1 - 1/E_2)/E_2 + 2g_s\zeta_d^2/E_1^2 \\ &\quad + k\zeta_d^3(2/E_1 - 1/E_2)(1/E_2 + 2/E_1)/2E_2 - g_s\zeta_d^3(1/E_1^2 - 1/E_1E_2 + 1/E_2^2)/2E_2, \\ A_{\parallel} &= P [(-\kappa - 4/7) + (8k\zeta_d/E_1 + 6k\zeta_d^2/7E_2 - 3k\zeta_d^2/7E_2^2 - 40k\zeta_d^2/7E_1E_2 + \kappa\zeta_d^2/E_2^2)], \\ A_{\perp} &= P [(-\kappa + 2/7) + 11k\zeta_d/7E_2 + 9k\zeta_d^2/14E_2^2 - 4k\zeta_d^2/7E_1^2 + 11k\zeta_d^2/7E_1E_2 \\ &\quad + \kappa\zeta_d^2(2/E_1^2 + 1/2E_2^2)], \end{aligned} \quad (1)$$

where $g_s(\approx 2.0023)$ is the spin-only value. k is the orbital reduction factor. κ is the core polarization constant. ζ_d and P are, respectively, the spin-orbit coupling coefficient and the dipolar hyperfine structure parameter of the $3d^9$ ion in crystals. They can be written in terms of the corresponding free-ion values, i.e., $\zeta_d \approx \zeta_d^0$ and $P \approx kP_0$. E_1 and E_2 are the energy separations between the excited ${}^2B_{2g}$ and 2E_g and the ground ${}^2B_{1g}$ states (Wei *et al.*, 2005):

$$E_1 = 10Dq, E_2 = 10Dq - 3D_s + 5D_t \quad (2)$$

Here Dq is the cubic field parameter and D_s and D_t the tetragonal field parameters. From the superposition model and the geometrical relationship of the $[\text{NiF}_4]^{3-}$ cluster, the tetragonal field parameters can be expressed as

$$\begin{aligned} D_s &= (4/7)\bar{A}_2(R_0) (3\cos^2\alpha - 1) (R_0/R')^{t_2}, \\ D_t &= (4/21)\bar{A}_4(R_0) (35\cos^4\alpha - 30\cos^2\alpha + 3) (R_0/R')^{t_4}, \end{aligned} \quad (3)$$

where t_2 and t_4 are the power-law exponents, we take $t_2 \approx 3$ and $t_4 \approx 5$ here. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters. The reference bonding length is taken as the metal-ligand distance for the face-center site, i.e., $R_0 \approx 1.932 \text{ \AA}$ (Weast, 1989). R' denotes the $\text{Ni}^{+}\text{-F}^{-}$ bonding length due to the distance ΔZ between the impurity and the fluorine plane. For $3d^n$ octahedral clusters, $\bar{A}_4(R_0) \approx (3/4)Dq$ and the ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0) \approx 9 \sim 12$ are regarded as valid in many crystals (Yu *et al.*, 1994; Edgar, 1976) and $\bar{A}_2(R_0) \approx 12 \bar{A}_4(R_0)$ is adopted here. From Self-consistent Charge Extended Hückel (SCCEH) calculations (Aramburu *et al.*, 1992), the cubic field parameter Dq ($\approx 600 \text{ cm}^{-1}$) was obtained for the octahedral $[\text{NiF}_6]^{5-}$ cluster. Thus, the value $Dq \approx 400 \text{ cm}^{-1}$ can be approximately estimated for the studied $[\text{NiF}_4]^{3-}$ cluster here.

Table 1: The spin Hamiltonian parameters for the tetragonal Ni²⁺ center in CaF₂

	$g_{ }$	g_{\perp}	$A_{ }$ (10^{-4} cm ⁻¹)	A_{\perp} (10^{-4} cm ⁻¹)
Cal. ^a	2.707	2.081	-	-
Cal. ^b	2.567	2.104	82.0	35.9
Expt. ^c	2.569 (5)	2.089 (5)	81.3 (3)	36.5 (3)

^aCalculations based on the simple perturbation formulas (Casas-González, 1980) and the energy denominators for LiF and NaF:Ni²⁺ (Hayes and Wilkens, 1964) in the previous work. ^bCalculations based on the high order perturbation formulas and the local structure (i.e., the distance ΔZ of Eq. 4) in this study ^cCasas-González, 1980

In the studied system, ζ_d^0 are about 629 cm⁻¹ for the free Ni²⁺ ion (Griffith, 1964). The orbital reduction factor k (≈ 0.68) is adopted here. Substituting these parameters into the formulas of the g factors and fitting the theoretical values to the experimental data, we have

$$\Delta Z \approx 0.35 \text{ \AA} \quad (4)$$

The corresponding calculated values are shown in Table 1. The energy levels in Eq. 1 are also obtained from Eq. 2 and 3, i.e., $E_1 \approx 4000$ cm⁻¹ and $E_2 \approx 8138$ cm⁻¹.

In the formulas of the hyperfine structure constants, the free-ion value $P_0 \approx -140 \times 10^{-4}$ cm⁻¹ for Ni²⁺ can be obtained from those for isoelectronic 3d⁸ ions (McGarvey, 1967) by extrapolation. By fitting the calculated hyperfine structure constants to the observed values, the core polarization constant is determined:

$$\kappa \approx 0.62 \quad (5)$$

The corresponding hyperfine structure constants are also shown in Table 1. For comparisons, the theoretical results of the g factors based on the simple perturbation formulas and the energy separations ($E_1 \approx 4900$ cm⁻¹ and $E_2 \approx 8000$ cm⁻¹) taken from Ni²⁺ doped LiF and NaF (Hayes and Wilkens, 1964) are collected in Table 1.

Discussion

From Table 1, it can be found that the theoretical spin Hamiltonian parameters based on the high order perturbation formulas and the distance ΔZ ($\approx 0.35 \text{ \AA}$) in this work are in good agreement with the observed values. The calculated results of present studies are also better than those in the previous work (Casas-González *et al.*, 1980).

The distance ($\approx 0.35 \text{ \AA}$) of the impurity Ni²⁺ from the fluorine plane based on the analyses of the spin Hamiltonian parameters in this work is consistent with that ($\approx 0.37 \text{ \AA}$) based on the simple perturbation formulas of the g factors (Casas-González *et al.*, 1980). The above result is also supported by the recent density functional theory (DFT) studies on the same system, which yields the distance of about 0.33 \AA (Aramburu *et al.*, 2002). Therefore, the local structure of the impurity Ni²⁺ center in CaF₂ obtained in this study can be regarded as reasonable. In fact, when the host Ca²⁺ is replaced by the smaller and less charged Ni²⁺, the impurity may be unstable at the host Ca²⁺ site and then suffer a large off-center displacement due to the size and/or charge mismatching substitution. As a result, the Ni²⁺ is very close to one fluorine plane and this center can be conveniently described as [NiF₄]³⁻ cluster.

The theoretical g factors obtained in this study are slightly better than those in the previous studies (Casas-González *et al.*, 1980). This means that the high order perturbation formulas of the spin Hamiltonian parameters can be regarded as more valid than the simple ones. Meanwhile, the energy denominators ($E_1 \approx 4000$ cm⁻¹ and $E_2 \approx 8138$ cm⁻¹) obtained from the local structure of the impurity center in present studies are somewhat different from those ($E_1 \approx 4900$ cm⁻¹ and $E_2 \approx 8000$ cm⁻¹) for Ni²⁺ in LiF and NaF (Hayes and Wilkens, 1964). Further, the calculated hyperfine structure constants are in good agreement with the experimental data. Therefore, the spin Hamiltonian parameters and the related parameters used here can be regarded as reasonable.

There are some errors in the above calculations. First, approximation of the theoretical model can lead to some errors in the final results. Second, the displacements of the four nearest and four next nearest F⁻ ions are not considered in the analyses. In fact, these fluorine ions may shift slightly towards the center of the cube due to the large off-center displacement of the impurity Ni²⁺. For the sake of simplicity and reduction of number of the adjustable parameters, the errors arising from neglecting of the above ligand displacements may be taken as absorbed in the distance ΔZ and the orbital reduction factor k in the calculations. Therefore, the ΔZ ($\approx 0.35\text{\AA}$) obtained in this study can be tentatively regarded as the effective distance between the impurity and its nearest ligand plane. Finally, the contributions from the ligand orbitals and spin-orbit coupling coefficient are also ignored here. Fortunately, these contributions are expected to be unimportant and negligible due to the small magnitude of the spin-orbit coupling interaction for the ligand F⁻ compared with that of the impurity Ni²⁺.

Conclusions

The local structure and the spin Hamiltonian parameters for the tetragonal Ni²⁺ center in CaF₂:Ni²⁺ are theoretically investigated from the high order perturbation formulas of these parameters in this study. It is found that the impurity Ni²⁺ locates at the distance of about 0.35Å from the nearest fluorine plane, i.e., the [NiF₄]²⁻ cluster is expected.

Acknowledgment

This study was supported by the Youth Foundation of Science and Technology of UESTC under grant No. JX04022. The authors are grateful to Mr. Ze-Xin Feng for his helpful computations.

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