Investigations on the local structure and the EPR parameters for the tetragonal Ni^+ center in CaF_2

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ABSTRACT

In this work, the local structure and the electron paramagnetic resonance (EPR) parameters g factors $g_{//}$ and $g\perp$ and the hyperfine structure constants $A_{//}$ and $A\perp$ of a tetragonal Ni^+ center (i.e.,$[NiF_4]^{3-}$cluster) in CaF_2 are theoretically investigated, using the high order perturbation formulas of these parameters for a $3d^9$ ion in tetragonal symmetry (elongated octahedron), in these formulas, the contributions to the spin Hamiltonian parameters from the s-and p-orbitals as well as the spin-orbit coupling coefficient of the ligands are taken into account. On the basis of the studies, the impurity Ni^+ is found to locate at the distance of about 0.355 Å from the nearest fluorine plane. The calculated EPR parameters based on the above local structure in this work are in agreement with the experimental data.

Key words: Electron paramagnetic resonance, crystal-field, spin hamiltonians, CaF_2, Ni^+.
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INTRODUCTION

Fluorite-type crystals doped with transition-metal impurities have been extensively theoretical and experimental studied for the paramagnetic defects created by x-ray irradiation. [1-3]. These impurity centers usually exhibit tetragonal symmetry, as observed by Electron Paramagnetic Resonance(EPR) and Electron Nuclear Double Resonance(ENDOR) techniques[1-2]. For example, the EPR spectrum of tetragonal Ni^+ in CaF_2 was measured decades ago and its spin-Hamiltonian(SH) parameters (g factors $g_{//}$ and $g\perp$ and hyperfine structure constants $A_{//}$ and $A\perp$) were given[2]. From the SH parameters, it is suggested that the Ni^+ ion may not occupy exactly the host cation site but have a large displacement along the [100] (or C_4) axis , as a result,

there is about 0.37 Å away from the nearest fluorine plane[2]. Till date, however, the above results have not been satisfactorily interpreted. In the treatments of the anisotropic g factors based on the simple perturbation formulas for a $3d^9$ ion in tetragonally elongated octahedral [2], the third-order perturbation terms were not completely involved and the higher order ones were ignored, and the contributions from the ligand orbitals and spin-orbit coupling interactions were also ignored (although these contributions may not   be important). Meanwhile, the energy separations 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^+ doped LiF and NaF[4]. In addition, the hyperfine structure constants were not interpreted, either. In order to interpret the EPR parameters and the local structure of the tetragonal Ni^+ center in CaF_2 to a better extent, in this work, high order perturbation formulas of these parameters are applied and the energy separations are quantitatively determined from the local structure of this center.

Theory and Calculations

In pure fluorite, Ca^{2+} is surrounded by eight oxygen ions forming an ideal cube, After irradiated by X-ray, Ni-doped CaF_2 can exhibit Ni^+ center of tetragonal symmetry by Ni^+ occupying the host Ca^{2+} site with additional off-center shift along one of [100] axis[2]. 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 the fluorine plane in the cube and the near square planar $[NiF_4]^{3-}$ cluster (i.e., the Ni^+ has a small distance ΔZ from the plane) is formed (this situation was also found in other Ni^+-doped fluorite-type crystals[1,5]). 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 Ni^+ ($3d^9$) ion in tetragonally elongated octahedra, the lower orbit doublet ^2E_g of the original cubic case would split into two orbital singlets $^2A_{1g}(|z^2>)$ and $^2B_{1g}(|x^2-y^2>)$, with the latter lying lowest, while the original   upper orbit triplet $^2T_2$ would be seperated into an orbital singlet $^2B_2(|xz>)$ and a doublet $^2E(|xz>, |yz>)$[6]. It is noted that in the treatments of the previous work [2], the notations $^2B_1$ and $^2B_2$ are interchanged, due to a rotation of the frame of axes. The perturbation formulas of the EPR parameters of the $^2B_1$ ground state for a $3d^9$ ion in tetragonal symmetry can be expressed as follows[7,8]

$g_{//}= g_e+8k'\zeta'/E_1+k\zeta'^2/E_2{}^2+4k'\zeta'\zeta/E_1E_2+g_e\zeta'^2(1/E_1{}^2-1/2E_2{}^2)$

$-k\zeta\zeta'^2(4/E_1-1/E_2)/E_2{}^2-2k'\zeta'\zeta(2/E_1E_2-1/E_2{}^2)/ E_1-g_e\zeta\zeta'^2(1/E_1E_2{}^2-1/2E_2{}^3)$

$g_\perp = g_e+2k'\zeta'/E_2-4k\zeta'^2/E_1E_2+k'\zeta'\zeta(2/E_1-1/E_2)/E_2+2g_e\zeta'^2/E_1{}^2$

$+\zeta\zeta'(k\zeta'-k'\zeta)/E_1E^2{}_2-\zeta\zeta'(1/E_1-2/E_2)(2k\zeta'/E_1+ k'\zeta/E_2)/2 E_2-g_e\zeta\zeta'^2(1/E_1{}^2 -1/E_1E_2 +1/E_2{}^2)/2E_2$

$A_{//}= P[-\kappa-4/7 +(g_{//}-g_e)+3(g_\perp-g_e)/7]$

$A_\perp=P[-\kappa+2/7+11(g_\perp-g_e)/14]$ (1)

where g_e (=2.0023) is the spin-only value. κ is the isotropic core polarization constant, P is the dipolar hyperfine structure parameter of the $3d^9$ ion in crystals. The energy denominators E_1 and

E_2 stand for the energy separations between the excited $^2B_{2g}$ and ^2E_g and the ground $^2B_{1g}$ states and can be obtained from the strong cubic field approach:

$$E_1 = E(^2B_2) - E(^2B_1) = 10Dq$$
$$E_2 = E(^2E) - E(^2B_1) = 10Dq - 3D_s + 5D_t \qquad (2)$$

Here D_q is the cubic field parameter, and D_s, D_t the tetragonal ones

Based on the cluster approach, the spin-orbit coupling coefficients ζ, ζ' and the orbital reduction factors k, k' in equation (1) may be written as[9,10]

$$\zeta = N_t(\zeta_d + \lambda_t^2 \zeta_p/2) \qquad\qquad \zeta' = (N_t N_e)^{1/2}(\zeta_d - \lambda_t \lambda_e \zeta_p/2)$$
$$k = N_t(1 + \lambda_t^2/2) \qquad\qquad k' = (N_t N_e)^{1/2}[1 - \lambda_t(\lambda_e + \lambda_s A)/2] \qquad (3)$$

where ζ_d and ζ_p are the spin-orbit coupling coefficients of the $3d^9$ and the ligand ions in free states, respectively. A denotes the integral $R\langle ns|\frac{\partial}{\partial y}|np_y\rangle$, where R is the impurity-ligand distance in the studied system. N_γ and λ_γ (or λ_s) are, respectively, the normalization factors and the orbital mixing coefficients for the cubic (O_h) irreducible representations γ (= e_g and t_{2g}). They are usually determined from the normalization conditions[9,10]

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

and the approximate relationships[9,10]

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

Here N is the average covalency factor, characteristic of the covalency effect of the studied system. $S_{dp\gamma}$ (and S_{ds}) are the group overlap integrals. In general, the mixing coefficients increase with increasing the group overlap integrals, and one can approximately adopt the proportional relationship between the mixing coefficients and the related group overlap integrals, i.e., $\lambda_e/S_{dpe} \approx \lambda_s/S_s$ within the same irreducible representation e_g [11].

From the superposition model [12] and the geometrical relationship of the $[NiF_4]^{3-}$ cluster, the tetragonal field parameters can be expressed as:

$$D_s = \frac{4}{7}\bar{A}_2(R_0)(3\cos^2\alpha - 1)(\frac{R_0}{R'})^{t2}$$
$$D_t = \frac{4}{21}\bar{A}_4(R_0)(35\cos^4\alpha - 30\cos^2\alpha + 3)(\frac{R_0}{R'})^{t4} \qquad (6)$$

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., $R_0 \approx 1.932$Å [13]. From the distance R_0 and the Slater-type SCF functions[14,15] the integrals $S_{dpt} = 0.0027$, $S_{dpe} = 0.0115$, $S_{ds} = 0.0059$ and $A = 1.4337$ are

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obtained. R' denotes the Ni^+-F^- bonding length due to the distance ΔZ between the impurity and the fluorine plane.   For $3d^n$ octahedral clusters, $\bar{A}_4(R_0) \approx 3D_q/4$ and $\bar{A}_2(R_0) \approx 9\ 12\bar{A}_4(R_0)$ are

regarded as valid in many crystals[16,17,18] and $\bar{A}_2(R_0) \approx 12\bar{A}_4(R_0)$ is adopted here. From Self-consistent Charge Extended Huckel (SCCEH) calculations[19], the cubic field parameter Dq=600cm^{-1} was obtained for the octahedral $[NiF_6]^{5-}$ cluster. Thus, the value Dq=400cm^{-1} can be approximately estimated for the studied $[NiF_4]^{3-}$ cluster here.

Thus, using the formulas of the g factors (Eq. (1)), and fitting the calculated g factors to the experimental data, we have:

$$\Delta Z \approx 0.355 Å \qquad N \approx 0.774$$

The values $N_t \approx 0.7751$, $N_e \approx 0.7795$, $\lambda_t \approx 0.5413$, $\lambda_e \approx 0.4854$ and $\lambda_s \approx 0.2477$ are calculated from equations (4) and (5). Then the parameters $\zeta \approx 494$ cm^{-1}, $\zeta' \approx 448$ cm^{-1}, $k \approx 0.889$ and $k' \approx 0.601$ can be determined from equation (3) and the free-ion values $\zeta_d \approx 605$ cm^{-1} for Ni^+ [7] and $\zeta_p \approx$ 220 cm^{-1} for F^- [7].The energy levels in Eq. 1 are also obtain from Eq. 2 and 6, $E_1 \approx 4000$ cm^{-1} and

$E_2 \approx 8108$ cm^{-1}. The corresponding calculated values are shown in Table 1.

In the formulas of the hyperfine structure constants, the free-ion value P_0=-140×10^{-4} cm^{-1} for Ni^+

can be obtained from those for isoelectronic $3d^9$ ions by extrapolation[20]. By fitting the calculated hyperfine structure constants to the observed values, the core polarization constant is determined:

$$\kappa \approx 0.623$$

The corresponding hyperfine structure constants are also shown in Table 1.

Table1:The EPR parameters for the tetragonal Ni^+ center in CaF_2

	$g_{//}$	$g_\perp$	$A_{//}(10^{-4} cm^{-1})$	$A_\perp(10^{-4}cm^{-1})$
Cal[a]	2.707	2.081	--	--
Cal[b]	2.567	2.105	82.0	35.9
Cal[c]	2.569	2.104	81.8	36.0
Expt[2]	2.569	2.089	81.3(3)	36.5(3)

[a]*Calculations based on the simple perturbation formulas in the previous work[2].*

[b]*Calculations based on the high order perturbation formulas and the local structure but neglecting the ligand orbital contributions (i.e., taking $\zeta = \zeta' = N \zeta_d$ and $k = k' = N$) in this work.*

[c]*Calculations based on the high order perturbation formulas and including both the local structure and the ligand orbital contributions in this work.*

DISCUSSION

From Table 1, one can find that the calculated EPR parameters based on the high order perturbation formulas including the ligand orbital contributions and the distance ΔZ in this work are in good agreement with the experimental data. This means that the formulas and the related parameters adopted in this work can be regarded as suitable.

(1)The distance(≈ 0.355Å) of the impurity Ni^+ from the fluorine plane based on the analyses of the EPR parameters in this work is consistent with that (0.37Å) based on the simple perturbation formulas of the g factors[2]. The above result is also supported by the density functional theory (DFT) studies on the same system, which yields the distance of about 0.33Å[21]. Therefore, the local structure of the impurity Ni^+ center in CaF_2 obtained in this study can be regard as reasonable. In fact, when the host Ca^{2+} is replaced by the smaller and less charged Ni^+, the impurity may be unstable at the host Ca^{2+} site and then suffer a large off-center displacement due to the size and/or charge mismatching substitution. As a result, the Ni^+ is very close to one fluorine plane and this center can be conveniently described as $[NiF_4]^{3-}$cluster.

(2)The theoretical g factors obtained in this study are slightly better than those in the previous studies[2]. 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 $E_2 \approx 8108$ 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 $E_2 \approx$ 8000cm^{-1}) for Ni^+ in LiF and NaF[4]. Further, the calculated hyperfine structure constants are in good agreement with the experimental data. Therefore, the EPR parameters and the related parameters used here can be regarded as reasonable.

(3) From Table 1, it can be found that the calculated results based on the high order perturbation formulas including the ligand orbital contributions are much better than that neglecting those contributions. This means that the contributions from the SO coupling and the orbitals of the ligands should be included in the explanations of EPR parameters, although these contributions are not important.

CONCLUSION

In this paper, the local structure and the EPR parameters for the tetragonal Ni^+ center in CaF_2: Ni^+ are theoretically studied from the high order perturbation formulas of these parameters including both the local structure and ligand contributions. It is found that the impurity Ni^+ locates at the distance of about 0.355Å from the nearest fluorine plane, i.e. , the $[NiF_4]^{3-}$ cluster is expected.

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