Investigations of the Local Structure and the EPR Parameters for the Tetragonal Ni^+ Center in SrF_2

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Abstract

The local structure and the spin Hamiltonian parameters g factors $g_{//}$ and $g\perp$ and the hyperfine structure constants $A_{//}$ and $A\perp$ of a tetragonal Ni^+ center in SrF_2 are investigated, using the high order perturbation formulas for a $3d^9$ ion in tetragonally elongated octahedra. According to these studies, the impurity Ni^+ is found to locate at the distance of about 0.36 Å from the nearest fluorine plane. The obtained spin Hamiltonian parameters agree well with the experimental data.

Keywords: Electron paramagnetic resonance, Spin hamiltonians, Ni^+, SrF_2

1. Introduction

Ni-doped fluorite-type crystals have been extensively investigated because of the paramagnetic defects arising from X-ray irradiation (Casas-Gonzales J., 1980; Studzinski P., 1984; Alonso P. J., 1983; Alonso P. J., 1983).These impurity centers usually exhibit tetragonal symmetry, as observed by Electron Paramagnetic Resonance(EPR) and Electron Nuclear Double Resonance(ENDOR) techniques (Casas-Gonzales J., 1980; Studzinski P., 1984; Alonso P. J., 1983; Alonso P. J., 1983). For example, the spin Hamiltonian parameters g factors $g_{//}$ and $g\perp$ and the hyperfine structure constants $A_{//}$ and $A\perp$ for the tetragonal Ni^+ center in SrF_2 produced by X-ray irradiation were measured (Alonso P. J., 1983).The off-center displacement and the anisotropic g factors for the tetragonal Ni^+ center in SrF_2 were investigated by using the simple formulas of the g factors for a $3d^9$ ion in tetragonally elongated octahedra (Alonso P. J., 1983). It was found that the impurity Ni^+ may not occupy exactly the host Sr^{2+} site but suffer so large displacement along [100] (or C_4) axis that it is only 0.365Å away from the nearest fluorine plane (Alonso P. J., 1983). 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^+ doped LiF and NaF(Hayes W, 1964). In addition, the hyperfine structure constants were not interpreted, either. In order to explain the g factors and the hyperfine constants for the tetragonal center in SrF_2:Ni^+ and to investigate the local structure of the impurity Ni^+ 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.

2. Theory and Calculations

In pure strontium fluoride, Sr^{2+} is coordinated to eight fluorine ions forming an ideal cube, When irradiated by X-ray, Ni-doped SrF_2 can exhibit Ni^+ center of tetragonal symmetry by Ni^+ occupying the host Sr^{2+} site with additional off-center shift along one of [100] axis (Alonso P. J., 1983). This may be due to the smaller size and the less charge of the impurity Ni^+ than those of the host Sr^{2+}, which is likely to make the Ni^+ unstable on the host Sr^{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. 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 ^2E irreducible representation may be separated into two orbital singlets $^2B_1(|x^2-y^2>)$ and $^2A_1(|z^2>)$, with the former lying lowest, while the upper $^2T_2$ representation would split into an orbital singlet $^2B_2(|xy>)$ and a doublet $^2E(|xz>, |yz>)$(Abragam A, 1970). It is noted that in the treatments of the previous work (Alonso P. J., 1983), 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 W H, 2005).

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

$$+k\zeta_d^3(4/E_1-1/E_2)/E_2^2-2k\zeta_d^3(2/E_1E_2-1/E_2^2)/E_1+g_e\zeta_d^3(1/E_1E_2^2-1/2E_2^3)$$

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

$$+k\zeta_d^3(2/E_1-1/E_2)\times(1/E_2+2/E_1)/2E_2-g_e\zeta_d^3(1/E_1^2-1/E_1E_2+1/E_2^2)/2E_2$$

$$A_{//}= P(-\kappa-4/7)+P(8k\zeta_d/E_1+6k\zeta_d/7E_2-3k\zeta_d^2/7E_2^2-40k\zeta_d^2/7E_1E_2$$

$$+\kappa\zeta_d^2/E_2^2)$$

$$A_{\perp}= P(-\kappa+2/7)+P[11k\zeta_d/7E_2+9k\zeta_d^2/14E_2^2-4k\zeta_d^2/7E_1^2+11k\zeta_d^2/7E_1E_2$$
$$+\kappa\zeta_d^2(2/E_1^2+1/2E_2^2)] \quad (1)$$

where g_e(g_e=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., $\zeta_d \approx k\,\zeta_d^0$ 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:

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

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 $[NiF_4]^{3-}$ cluster, the tetragonal field parameters can be expressed as:

$$D_s=\frac{4}{7}\bar{A}_2(R_0)(3\cos^2\alpha-1)(\frac{R_0}{R'})^{t2}$$

$$D_t=\frac{4}{21}\bar{A}_4(R_0)(35\cos^4\alpha-30\cos^2\alpha+3)(\frac{R_0}{R'})^{t4} \quad (3)$$

Where t_2 and t_4 are the power-law exponents, we take $t_2\approx3$ and $t_4\approx5$ 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., $R_0\approx2.0515$Å (Weast R C., 1989). R' denotes the Ni^+-F^- bonding length due to the distance ΔZ between the impurity and the fluorine plane. For $3d^n$ octahedral clusters, $\bar{A}_4(R_0)\approx3D_q/4$ and $\bar{A}_2(R_0)\approx9\sim12\bar{A}_4(R_0)$ are regarded as valid in many crystals (Yu W L, 1994) and $\bar{A}_2(R_0)\approx11.5\bar{A}_4(R_0)$ is adopted here. From Self-consistent Charge Extended Huckel (SCCEH) calculations (Aramburu J A, 1992), 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.

In the studied system, ζ_d^0 are about 629 cm^{-1} for the free Ni^+ ion (Griffith J.S., 1964). The orbital reduction factor k (≈0.697) is adopted here. Substituting these parameters into the formulas of the g factors and fitting the theoretical values to the experimental data, we have

$$\Delta Z \approx 0.36 Å$$

The corresponding calculated values are shown in Table 1. The energy levels in Eq. 1 are also obtain from Eq. 2 and 3, i.e., $E_1 \approx 4000\ cm^{-1}$ and $E_2 \approx 9700\ cm^{-1}$.

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 (Wu Shao yi, 2008). By fitting the calculated hyperfine structure constants to the observed values, the core polarization constant is determined:

$$\kappa \approx 0.62$$

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

3. 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 (≈0.36Å) in this work are in good agreement with the observed values. So the spin Hamiltonian parameters and the related parameters adopted here can be regarded as reasonable. The distance(≈0.36Å) of the impurity Ni^+ from the fluorine plane based on the analysis of the spin Hamiltonian parameters in this work is consistent with that (0.365Å) based on the simple perturbation formulas of the *g* factors (Alonso P. J., 1983). The Ni^+ ion situated in an off-center position displaced along one of the <100> directions of the crystal was found in other fluorite-type crystals (Casas-Gonzales J., 1980; Studzinski P., 1984; Alonso P. J., 1983), for example, Aramburu and Fernandez had calculated the off-center displacement of Ni^+-doped in CaF_2 by using the density functional theory (DFT), which yields the distance about 0.33Å(Aramburu J. A, 2003). Therefore, the local structure of the impurity Ni^+ center in SrF_2 obtained in this study can be regard as reasonable. In fact, when the host Sr^{2+} is replaced by the smaller and less charged Ni^+, the impurity may be unstable at the host Sr^{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 its center can be conveniently described as $[NiF_4]^{3-}$cluster.

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 Ni^+. 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(≈0.36Å) obtained in this study can be tentatively regarded as the effective distance between the impuriy 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 Ni^+.

4. Conclusions

The local structure and the spin Hamiltonian parameters for the tetragonal Ni^+ center in SrF_2: Ni^+ are theoretically investigated from the high order perturbation formulas of these parameters in this work. It is found that the impurity Ni^+ locates at the distance of about 0.36Å from the nearest fluorine plane, i.e., the $[NiF_4]^{3-}$ cluster is expected.

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Table 1. The spin Hamiltonian parameters for the tetragonal Ni^+ center in SrF_2

	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}(10^{-4}cm^{-1})$	$A_{\perp}(10^{-4}cm^{-1})$
Cal[a]	2.596	2.089	--	--
Cal[b]	2.593	2.099	78.3	36.0
Expt[4]	2.597	2.092	78.3(8)	35.0(2)

[a]Calculations based on the simple perturbation formulas in the previous work[4].

[b]Calculations based on the high order perturbation formulas and the local structure in this study