Optik 125 (2014) 5820–5824

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Theoretical studies of the g factors and local structure for the rhombic Fe^+ center in NaF

Chang-Chun Ding*, Shao-Yi Wu, Yong-Kun Cheng, Min-Quan Kuang

School of Physical Electronics, University of Electronic Science and Technology of China, Chengdu 610054, PR China

ARTICLE INFO

Article history:
Received 19 October 2013
Accepted 30 May 2014

Keywords:
Local geometry
Electron paramagnetic resonance (EPR)
Defect structures
Fe^+
NaF

ABSTRACT

The anisotropic *g* factors and local structure for the rhombic Fe^+ center in NaF are theoretically studied using the perturbation formulas of the *g* factors for a rhombically distorted octahedral $3d^7$ cluster. The impurity Fe^+ is found not to occupy exactly the host Na^+ site in NaF but to experience the off-center displacement of about 0.28 Å along [1 1 0] axis due to size mismatch substitution. The calculated *g* factors based on the above impurity displacement show reasonable agreement with the experimental data. The local structure of the Fe^+ center is discussed.

1. Introduction

NaF containing iron shows interesting electrochemical [1,2], thermodynamical [3], corrosive [4] and metal affinity adsorbent [5] properties and can be treated as a model system to investigate the structures and behaviours (e.g., off-center displacements) of Fe impurities. Among various iron ions, monovalent Fe^+ ($3d^7$) is relatively scarce and seldom studied. The above structures and properties can be conveniently probed by means of electron paramagnetic resonance (EPR) technique. NaF containing iron under X ray irradiation has been experimentally studied with EPR technique, and the anisotropic *g* factors were measured for the rhombic Fe^+ center at 4.2 K [6]. Until now, the above EPR experimental results have not been theoretically interpreted, and information about the local structure of this Fe^+ center has not been acquired yet.

In view that microscopic mechanisms of the EPR spectra for Fe^+ in NaF can be helpful to the understandings of electronic states and physical properties of this system, further theoretical investigations on the *g* factors and impurity local structure would provide useful information of impurity behaviours in fluorides and are of scientific and practical significance. In this work, the EPR spectra and defect structure are theoretically studied for the rhombic Fe^+ center in NaF from the perturbation formulas of *g* factors for a rhombically distorted $3d^7$ cluster, and the suitable impurity off-center displacement is taken into account due to size mismatch.

2. Calculations

NaF:Fe under X ray irradiation can yield monovalent Fe^+ on the Na^+ site, arising from doped substitutional Fe^{2+} (in the form of FeF_2) capturing one electron during irradiation [6]. Although charge compensation is unnecessary, the smaller impurity Fe^+ than host Na^+ would make the former unstable at the host cation site and thus suffer an off-center displacement due to size mismatch. This may lower the local point symmetry from original cubic (O_h). According to the experimental anisotropic *g* factors ($g_x \neq g_y \neq g_z$) for this Fe^+ center [6], the local symmetry should be rhombic (C_{2v}). And the local structure of this impurity center can be described as the off-center displacement ΔZ along [1 1 0] (or *Z*) axis of the crystal.

The EPR spectra for a Fe^+ ($3d^7$) ion under an octahedral site can be characterized by an effective spin $S' = 1/2$ due to the splitting of the ground ^4F configuration into six Kramers doublets by the spin–orbit and low (rhombic) symmetrical crystal-field interactions [7,8]. The

---

* Corresponding author. Tel.: +86 2883202586; fax: +86 2883202009.
E-mail address: ccding626@163.com (C.-C. Ding).

http://dx.doi.org/10.1016/j.ijleo.2014.07.032
0030-4026/

observed EPR signals are attributed to the lowest lying doublet, corresponding to the anisotropic g factors. The second-order perturbation formulas of g factors for $3d^7$ (Fe^+) ions in rhombic octahedra can be expressed as [9]:

$$
\begin{aligned}
g_x &= \frac{\left\{4\left[\left(\frac{\alpha}{\alpha'}\right)^2+\frac{2k\alpha}{(x+2)}\left(\frac{\alpha'}{\alpha''}\right)+\frac{12}{x(x+2)}\right]+\left(\frac{\alpha}{\alpha'}\right)^2\upsilon_{4X}+\frac{8\upsilon_5}{(x+2)^2}+\frac{12\upsilon_6}{x(x+2)}-\frac{\alpha}{(\alpha'\alpha'')^{1/2}}\frac{4\upsilon_{7X}}{(x+2)}\right\}}{Z}\\
g_y &= \frac{\left\{4\left[\left(\frac{\alpha}{\alpha''}\right)^2+\frac{2k\alpha}{(x+2)}\left(\frac{\alpha''}{\alpha'}\right)+\frac{12}{x(x+2)}\right]+\left(\frac{\alpha}{\alpha''}\right)^2\upsilon_{4Y}+\frac{8\upsilon_5}{(x+2)^2}+\frac{12\upsilon_6}{x(x+2)}-\frac{\alpha}{(\alpha'\alpha'')^{1/2}}\frac{4\upsilon_{7Y}}{(x+2)}\right\}}{Z},\\
g_z &= \frac{2+\left\{4(k\alpha+2)\left[\frac{3}{x^2}-\frac{4}{(x+2)^2}\right]+\left[\frac{9}{x^2}-\frac{4}{(x+2)^2}\right](\upsilon_{1X}+\upsilon_{1Y})-\frac{\alpha(\upsilon_{3X}+\upsilon_{3Y})}{(\alpha'\alpha'')^{1/2}}\left(\frac{3}{x}-\frac{4}{x+2}\right)\right\}}{Z}
\end{aligned}
\tag{1}
$$

where $Z=(\alpha/\alpha'\alpha'')+(6/x^2)+(8/(x+2)^2)$. α (or α' and α'') are the effective Lande factors parallel to Z (or X and Y) axes, respectively. The quantity x can be determined from the energy splittings Δ ($=E\{^4B_1[^4T_1(F)]\}-E\{^4B_3[^4T_1(F)]\}$) and δ ($=E\{^4B_2[^4T_1(F)]\}-E\{^4B_3[^4T_1(F)]\}$) of $^4T_1$ ground state in rhombic crystal-fields by the expression [9]

$$
\Delta=\frac{\zeta\alpha'\alpha''}{3}\left[\frac{3}{\alpha x}+\frac{4\zeta}{\alpha\zeta(x+2)+6\delta}\right]-\frac{\zeta\alpha}{6}(x+3). \tag{2}
$$

υ_{ij} can be written as [9]

$$
\begin{aligned}
\upsilon_{1X}&=\frac{k'\zeta'}{3}\left[\frac{15f_{1X}^2}{2E_{1X}}+\frac{2q_{1X}^2}{E_{2X}}\right], &\quad \upsilon_{1Y}&=\frac{k'\zeta'}{3}\left[\frac{15f_{1Y}^2}{2E_{1Y}}+\frac{2q_{1Y}^2}{E_{2Y}}\right],\\
\upsilon_{3X}&=\frac{k'\zeta'}{3}\left[\frac{15f_{1X}f_{2X}}{2E_{1X}}-\frac{2q_{1X}q_{2X}}{E_{2X}}\right], &\quad \upsilon_{3Y}&=\frac{k'\zeta'}{3}\left[\frac{15f_{1Y}f_{2Y}}{2E_{1Y}}-\frac{2q_{1Y}q_{2Y}}{E_{2Y}}\right],\\
\upsilon_{4X}&=\frac{k'\zeta'}{3}\left[\frac{15f_{2X}^2}{E_{1Y}}-\frac{4q_{2X}^2}{E_{2Y}}\right], &\quad \upsilon_{4Y}&=\frac{k'\zeta'}{3}\left[\frac{15f_{2Y}^2}{E_{1X}}-\frac{4q_{2Y}^2}{E_{2X}}\right],\\
\upsilon_5&=\frac{4k'\zeta'q_3^2}{3E_{2Z}}, &\quad \upsilon_6&=\frac{k'\zeta'}{3}\left[\frac{15f_3^2}{2E_{1Z}}+\frac{2q_3^2}{E_{2Z}}+\frac{2(\rho_X+\rho_Y)^2}{E_2}\right],\\
\upsilon_{7X}&=\upsilon_{3X}/2, &\quad \upsilon_{7Y}&=\upsilon_{3Y}/2,
\end{aligned}
\tag{3}
$$

where $E_{1X}, E_{1Y}, E_{1Z}, E_{2X}, E_{2Y}, E_{2Z}$ and E_3 are, respectively, the energy differences between the ground $^4B_3$ [$^4T_1(F)$] and the excited $^4B_3[^4T_2(F)]$, $^4B_2[^4T_2(F)]$, $^4B_1[^4T_2(F)]$, $^4B_3[^4T_1(P)]$, $^4B_2[^4T_1(P)]$, $^4B_1[^4T_1(P)]$ and $^4A[^4A_2(F)]$ states. These energy denominators and the splittings Δ and δ can be calculated from the d–d transition energy matrices for a $3d^7$ ion in rhombic symmetry. Note that the quantities f_i, q_i, α^i and W_{ij} in the above formulas are related to the admixture among the ground and excited states in rhombic symmetry and can be found in Ref. [9] (for saving pages, these expressions are ignored here). The rhombic field parameters D_s, D_ξ, D_t and D_η occur in these expressions and the d–d transition energy matrices, and the anisotropic g factors are related to the rhombic field parameters and hence to the local structure (e.g., the impurity off-center displacement) of the studied system.

From the cluster approach, the spin–orbit coupling coefficients ζ and ζ' and the orbital reduction factors k and k' in Eqs. (1)–(3) can be expressed as [10]:

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

Here ζ_d^0 and ζ_p^0 are the spin–orbit coupling coefficients of the free $3d^7$ and ligand ions, respectively. A denotes the integral $R\langle ns|\partial/\partial y|np_y\rangle$, with the reference impurity–ligand distance R. λ_γ and N_γ ($\gamma=e$ and t stand for the irreducible representations E_g and T_{2g} of group O_h) are, respectively, the orbital admixture coefficients and the normalization factors. They can be determined from the approximate relationships [10]

$$
\begin{aligned}
N^2&=N_t^2[1+\lambda_t^2S_{dpt}^2-2\lambda_tS_{dpt}],\\
N^2&=N_e^2[1+\lambda_e^2S_{dpe}^2+\lambda_s^2S_{ds}^2-2\lambda_eS_{dpe}-2\lambda_sS_{ds}],
\end{aligned}
\tag{5}
$$

And the normalization conditions [10]

$$
\begin{aligned}
N_t(1-2\lambda_tS_{dpt}+\lambda_t^2)&=1,\\
N_e(1-2\lambda_eS_{dpe}-2\lambda_sS_{ds}+\lambda_e^2+\lambda_s^2)&=1.
\end{aligned}
\tag{6}
$$

Here N is the average covalency factor. $S_{dp\gamma}$ and S_{ds} are the group overlap integrals. In general, the orbital admixture coefficients increase with the increase of the corresponding group overlap integrals, and one can reasonably apply the proportional relationship $\lambda_e/S_{dpe}\approx\lambda_s/S_{ds}$ between the orbital admixture coefficients and the related group overlap integrals within the same E_g representation.