EPR Investigation of the Structure of a Rhombic Co^{2+} Center in an NaF Crystal

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The local structure of the rhombic Co^{2+} center in NaF crystal is investigated by using the perturbation formulas of electron paramagnetic resonance (EPR) **g** factors $g_i\,(i = x,y,z)$ and hyperfine constants A_i for a $3d^7$ (Co^{2+}) ion in rhombic octahedral symmetry based on a cluster approach. In these formulas, the contributions from the admixture among different states, covalency effect as well as rhombic crystal field are included. By studying the EPR data of the rhombic Co^{2+} center, one can reasonably obtain the local structural (or rhombic distortion) parameters $\Delta R_c (\approx 0.268$ Å) for the central Co^{2+} and $\Delta R_p (\approx 0.181$ Å) for the two F^- ions along [100] and [010] axes closest to the Na^+ vacancy V_{Na}. The reasonableness of the results is also discussed.

Key words: Local Geometry; Electron Paramagnetic Resonance (EPR); Crystal- and Ligand Field Theory; NaF; Co^{2+}.

1. Introduction

The anisotropic **g** factors $g_i\,(i = x,y,z)$ and hyperfine constants A_i of Co^{2+} ions in NaF have decades ago been measured by the electron paramagnetic resonance (EPR) method [1], but until now the experimental results are not satisfactorily explained.

One can estimate the local structure of $3d^n$ impurity ions in crystals from their EPR data. Thus for $3d^7$ ions in rhombic octahedral symmetry, Tinkham [2] introduced first-order and Robbroeck et al. [3] second-order perturbation formulas of g_i. However the admixture among the ground and excited orbital states was neglected and the calculation of the contributions from the covalency effect and the rhombic crystal field was oversimplified. Based on the theory of Abragam and Pryce [4], and in consideration of the admixture among different states, Osaki and Uryu [5] gave implicit formulas of g_i. In their formulas, however, only the admixture between the excited triplet $^4T_2(F)$ and the ground state $^4T_1(F)$ is considered, and the covalency effect and the fourth-order rhombic potential part are neglected. Also several adjustable parameters are introduced. So the above formulas are not suitable to make quantitative investigations of the EPR parameters or the local structure of rhombic Co^{2+} centers. In order to overcome the above weaknesses, in [6], we have presented a cluster approach to the calculation of g_i for the $3d^7$ (Co^{2+}) ion in rhombic octahedra. In these formulas, the contributions from the admixture among different states, covalency effect and rhombic crystal field are considered and the parameters related to these effects can be estimated from optical spectra and structural data of the system under study. Based on these formulas, in the present work the local structure of the rhombic Co^{2+} center in NaF is obtained and the results are discussed.

2. Calculations

According to the cluster approach for a $3d^n$ ion in an octahedral complex, the LCAO molecular-orbitals should be taken as the one-electron basis functions, i. e. [7, 8],

$$|\gamma\rangle = N_\gamma^{1/2}(|d_\gamma\rangle - \lambda_\gamma|p_\gamma\rangle), \qquad (1)$$

where $\gamma = t_{2g}$ and e_g denote the irreducible representations of the O_h group. $|d\rangle$ is the d-orbital of the $3d^n$ ion and $|p\rangle$ the p-orbital of ligand ions. The normalization factors N_γ and mixing coefficients λ_γ can be obtained from the approximate relationship [7, 8]

$$f_\gamma = N_\gamma^2[1+\lambda_\gamma^2 S_{\mathrm{dp}}^2(\gamma) - 2\lambda_\gamma S_{\mathrm{dp}}(\gamma)] \tag{2}$$

and the normalization condition

$$N_\gamma(1-2\lambda_\gamma S_{\mathrm{dp}}(\gamma)+\lambda_\gamma^2) = 1, \tag{3}$$

where $f_\gamma[\approx (B/B_0+C/C_0)/2]$ is the ratio of the Racah parameters for the 3d^n ion in a crystal to those in the free state. $S_{\mathrm{dp}}(\gamma)$ are the group overlap integrals. Thus, the spin-orbit coupling coefficients ζ and ζ', the orbital reduction factors k and k', and the dipole hyperfine structure constants P and P' for the 3d^n cluster in the crystal can be expressed as

$$\zeta = N_{\mathrm{t}}(\zeta_{\mathrm{d}}^0+\lambda_{\mathrm{t}}^2\zeta_{\mathrm{p}}^0/2),\ \zeta' = (N_{\mathrm{t}}N_{\mathrm{e}})^{1/2}(\zeta_{\mathrm{d}}^0-\lambda_{\mathrm{t}}\lambda_{\mathrm{e}}\zeta_{\mathrm{p}}^0/2),$$

$$k = N_{\mathrm{t}}(1+\lambda_{\mathrm{t}}^2/2),\ k' = (N_{\mathrm{t}}N_{\mathrm{e}})^{1/2}(1-\lambda_{\mathrm{t}}\lambda_{\mathrm{e}}/2), \tag{4}$$

$$P = N_{\mathrm{t}}P_0, \quad P' = (N_{\mathrm{t}}N_{\mathrm{e}})^{1/2}P_0,$$

where ζ_{d}^0 and ζ_{p}^0 are the spin-orbit coupling coefficients of free 3d^n and ligand ions, respectively. P_0 is the dipolar hyperfine structure constant of the free 3d^n ion.

The EPR spectrum for a Co^{2+} ion in an octahedral site can be characterized by an effective spin $S' = 1/2$, due to the splitting of the ^{4}F ground term into six Kramers doublets by the spin-orbit interaction and low symmetry crystal fields [4, 5]. The EPR signals arise from the lowest lying doublet and yield the anisotropic g factors g_i and hyperfine constants A_i. The second-order perturbation formulas of g_i and A_i for 3d^7 (Co^{2+}) ions in rhombic octahedra can be expressed as [6]:

$$g_X = \left\{4\left[\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{2k\alpha}{(x+2)}\left(\frac{\alpha'}{\alpha''}\right) + \frac{12}{x(x+2)}\right] + \left(\frac{\alpha}{\alpha'}\right)^2 v_{4X} + \frac{8v_5}{(x+2)^2} + \frac{12v_6}{x(x+2)} - \frac{\alpha}{(\alpha'\alpha'')^{1/2}}\frac{4v_{7X}}{(x+2)}\right\}/Z,$$

$$g_Y = \left\{4\left[\left(\frac{\alpha}{\alpha''}\right)^2 + \frac{2k\alpha}{(x+2)}\left(\frac{\alpha''}{\alpha'}\right) + \frac{12}{x(x+2)}\right] + \left(\frac{\alpha}{\alpha''}\right)^2 v_{4Y} + \frac{8v_5}{(x+2)^2} + \frac{12v_6}{x(x+2)} - \frac{\alpha}{(\alpha'\alpha'')^{1/2}}\frac{4v_{7Y}}{(x+2)}\right\}/Z,$$

$$g_Z = 2 + \left\{4(k\alpha+2)\left[\frac{3}{x^2} - \frac{4}{(x+2)^2}\right] + \left[\frac{9}{x^2} - \frac{4}{(x+2)^2}\right](v_{1X}+v_{1Y}) - \frac{\alpha(v_{3X}+v_{3Y})}{(\alpha'\alpha'')^{1/2}}\left(\frac{3}{x} - \frac{4}{x+2}\right)\right\}/Z, \tag{5}$$

$$A_X = P\left\{(-\kappa/2)\left[\left(\frac{\alpha^2}{\alpha'\alpha''}\right) + \frac{12}{x(x+2)}\right] + \frac{8k\alpha}{x+2} - \left(\frac{\alpha^2}{\alpha'\alpha''}\right)W_Z - \frac{32W_{XY}}{(x+2)^2} - \frac{12W_X}{x(x+2)} + \frac{4\alpha W_{XZ}}{(x+2)(\alpha'\alpha'')^{1/2}}\right\}/Z$$
$$+ P'\left\{\left(\frac{\alpha}{\alpha'}\right)^2 v_{4X} + \frac{8v_5}{(x+2)^2} + \frac{12v_6}{x(x+2)} - \frac{4\alpha v_{7X}}{(x+2)(\alpha'\alpha'')^{1/2}}\right\}/Z,$$

$$A_Y = P\left\{(-\kappa/2)\left[\left(\frac{\alpha^2}{\alpha'\alpha''}\right) + \frac{12}{x(x+2)}\right] + \frac{8k\alpha}{x+2} - \left(\frac{\alpha^2}{\alpha'\alpha''}\right)W_Z - \frac{32W_{XY}}{(x+2)^2} - \frac{12W_Y}{x(x+2)} + \frac{4\alpha W_{YZ}}{(x+2)(\alpha'\alpha'')^{1/2}}\right\}/Z$$
$$+ P'\left\{\left(\frac{\alpha}{\alpha'}\right)^2 v_{4Y} + \frac{8v_5}{(x+2)^2} + \frac{12v_6}{x(x+2)} - \frac{4\alpha v_{7Y}}{(x+2)(\alpha'\alpha'')^{1/2}}\right\}/Z,$$

$$A_Z = P\left\{(-\kappa/2)\left[2+8\left(\frac{3}{x^2} - \frac{4}{x(x+2)^2}\right)\right] + 4k\alpha\left(\frac{3}{x^2} - \frac{4}{(x+2)^2}\right) + (W_X+W_Y)\left(\frac{9}{x^2} - \frac{4}{(x+2)^2}\right) + \frac{\alpha^2 W_Z}{\alpha'\alpha''}\right\}/Z$$
$$- P\frac{2\alpha(W_{XZ}+W_{YZ})\left(\frac{3}{x} - \frac{4}{x+2}\right)}{Z(\alpha'\alpha'')^{1/2}} + P'\left\{(v_{1X}+v_{1Y})\left(\frac{9}{x^2} - \frac{4}{(x+2)^2}\right) - \frac{\alpha(v_{3X}+v_{3Y})\left(\frac{3}{x} - \frac{4}{x+2}\right)}{(\alpha'\alpha'')^{1/2}}\right\}/Z,$$

where $$Z = \left(\frac{\alpha}{\alpha'\alpha''}\right) + \frac{6}{x^2} + \frac{8}{(x+2)^2}. \tag{6}$$

κ is the core polarization constant. x can be determined from the energy splittings Δ (= $E\{^4\mathrm{B}_1[^4\mathrm{T}_1(\mathrm{F})]\} - E\{^4\mathrm{B}_3[^4\mathrm{T}_1(\mathrm{F})]\}$) and δ (= $E\{^4\mathrm{B}_2[^4\mathrm{T}_1(\mathrm{F})]\} - E\{^4\mathrm{B}_3[^4\mathrm{T}_1(\mathrm{F})]\}$) of the ^{4}T$_1$ ground state in the rhombic crystal field by the expression

$$\Delta = \frac{\zeta\alpha'\alpha''}{3}\left[\frac{3}{\alpha x} + \frac{4\zeta}{\alpha\zeta(x+2)+6\delta}\right] - \frac{\zeta\alpha}{6}(x+3). \tag{7}$$

v_{ij} can be written as [6]

$$\begin{aligned}
v_{1X} &= \frac{k'\zeta'}{3}\left[\frac{15 f_{1X}^2}{2E_{1X}} + \frac{2q_{1X}^2}{E_{2X}}\right],\\
v_{1Y} &= \frac{k'\zeta'}{3}\left[\frac{15 f_{1Y}^2}{2E_{1Y}} + \frac{2q_{1Y}^2}{E_{2Y}}\right],\\
v_{3X} &= \frac{k'\zeta'}{3}\left[\frac{15 f_{1X} f_{2X}}{2E_{1X}} - \frac{2q_{1X} q_{2X}}{E_{2X}}\right],\\
v_{3Y} &= \frac{k'\zeta'}{3}\left[\frac{15 f_{1Y} f_{2Y}}{2E_{1Y}} - \frac{2q_{1Y} q_{2Y}}{E_{2Y}}\right],\\
v_{4X} &= \frac{k'\zeta'}{3}\left[\frac{15 f_{2X}^2}{E_{1Y}} + \frac{4q_{2X}^2}{E_{2Y}}\right],\\
v_{4Y} &= \frac{k'\zeta'}{3}\left[\frac{15 f_{2Y}^2}{E_{1X}} + \frac{4q_{2Y}^2}{E_{2X}}\right],\\
v_5 &= \frac{4k'\zeta' q_3^2}{3E_{2Z}},\\
v_6 &= \frac{k'\zeta'}{3}\left[\frac{15 f_3^2}{2E_{1Z}} + \frac{2q_3^2}{E_{2Z}} + \frac{2(\rho_X+\rho_Y)^2}{E_3}\right],\\
v_{7X} &= v_{3X}/2, \quad v_{7Y} = v_{3Y}/2,
\end{aligned} \tag{8}$$

where E_{1X}, E_{1Y}, E_{1Z}, E_{2X}, E_{2Y}, E_{2Z}, and E_3 are, respectively, the energy differences between the ground state ${}^4\mathrm{B}_3[{}^4\mathrm{T}_1(\mathrm{F})]$ and the excited states ${}^4\mathrm{B}_3[{}^4\mathrm{T}_2(\mathrm{F})]$, ${}^4\mathrm{B}_2[{}^4\mathrm{T}_2(\mathrm{F})]$, ${}^4\mathrm{B}_1[{}^4\mathrm{T}_2(\mathrm{F})]$, ${}^4\mathrm{B}_3[{}^4\mathrm{T}_1(\mathrm{P})]$, ${}^4\mathrm{B}_2[{}^4\mathrm{T}_1(\mathrm{P})]$, ${}^4\mathrm{B}_1[{}^4\mathrm{T}_1(\mathrm{P})]$, and ${}^4\mathrm{A}[{}^4\mathrm{A}_2(\mathrm{F})]$. They and the splittings Δ, δ can be calculated from the d-d transition energy matrices of $3\mathrm{d}^7$ ions in rhombic symmetry.

The parameters 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 [6] (for saving pages, they are not written 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, so the anisotropic g factors g_i and hyperfine structure constants A_i are related to the rhombic field parameters and hence to the rhombic distortion of the studied systems.

3. Application to the Rhombic Co^{2+} Center in NaF

The rhombic center in $\mathrm{NaF{:}Co}^{2+}$ crystal may be characterized as a substitutional Co^{2+} ion associated with one nearest Na^+ vacancy V_Na along the [110] axis due to charge compensation, as reported for similar rhombic centers induced by some $3\mathrm{d}^n$ ions in cubic crystals, *e. g.*, V^{2+} in LiCl and NaCl [9, 10] and Cr^{3+} in MgO [11, 12]. Since the effective charge of V_Na is negative, the central Co^{2+} ion may be attracted towards V_Na by one amount ΔR_c, and the two F^- ions closest to V_Na along the [100] and [010] axes are expected to shift away from V_Na by another amount ΔR_p (see Fig. 1) due to the electrostatic interactions (note: since the distances from other four F^- ions to V_Na are larger, their displacements may be much smaller and are ignored here). Thus, the local structure of this rhombic center can be described by the rhombic distortion parameters ΔR_c and ΔR_p.

According to the superposition model [13] and the geometrical relation of the rhombic Co^{2+} center in the $\mathrm{NaF{:}Co}^{2+}$ crystal (see Fig. 1), we can determine the rhombic field parameters as follows:

$$\begin{aligned}
D_\mathrm{s} &= -\frac{2}{7}\bar{A}_2(R_0)\left[\left(\frac{R_0}{R_1}\right)^{t_2} + \left(\frac{R_0}{R_2}\right)^{t_2} - (3\cos^2\Theta - 1)\left(\frac{R_0}{R_3}\right)^{t_2}\right],\\
D_\xi &= -\frac{2}{7}\bar{A}_2(R_0)\left[\cos 2\Phi_1\left(\frac{R_0}{R_1}\right)^{t_2} - \cos 2\Phi_2\left(\frac{R_0}{R_2}\right)^{t_2} + \sin^2\Theta\left(\frac{R_0}{R_3}\right)^{t_2}\right],\\
D_\mathrm{t} &= \frac{2}{21}\bar{A}_4(R_0)\left[(7\cos 4\Phi_1 + 3)\left(\frac{R_0}{R_1}\right)^{t_4} + (7\cos 4\Phi_2 + 3)\left(\frac{R_0}{R_2}\right)^{t_4}\right]\\
&\quad + \frac{2}{21}\bar{A}_4(R_0)(7\sin^4\Theta + 35\cos^4\Theta - 30\cos^2\Theta + 3)\left(\frac{R_0}{R_3}\right)^{t_4},\\
D_\eta &= -\frac{10}{21}\bar{A}_4(R_0)\left[\cos 2\Phi_1\left(\frac{R_0}{R_1}\right)^{t_4} - \cos 2\Phi_2\left(\frac{R_0}{R_2}\right)^{t_4} + \sin^2\Theta(7\cos^2\Theta - 1)\left(\frac{R_0}{R_3}\right)^{t_4}\right]
\end{aligned} \tag{9}$$

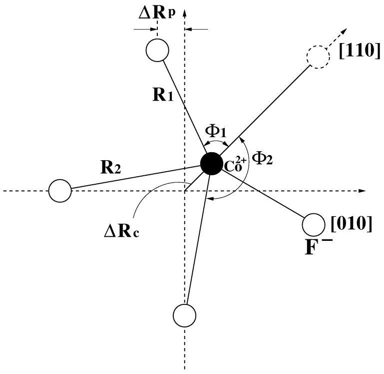

Fig. 1. Local structure of the Rhombic Co^{2+}-V$_{\mathrm{Na}}$ center in the NaF: Co^{2+} crystal.

with

$$R_1=\left[\left(R_0-\Delta R_{\mathrm{c}}/\sqrt{2}\right)^2+\left(\Delta R_{\mathrm{p}}+\Delta R_{\mathrm{c}}/\sqrt{2}\right)^2\right]^{1/2},$$

$$\Phi_1=\pi/4+\mathrm{tg}^{-1}\left[\left(\sqrt{2}\Delta R_{\mathrm{p}}+\Delta R_{\mathrm{c}}\right)/\left(\sqrt{2}R_0-\Delta R_{\mathrm{c}}\right)\right],$$

$$R_2=\left[\Delta R_{\mathrm{c}}^2/2+\left(R_0+\Delta R_{\mathrm{c}}/\sqrt{2}\right)^2\right]^{1/2},$$

$$\Phi_2=\pi-\mathrm{tg}^{-1}\left[R_0/\left(R_0+\sqrt{2}\Delta R_{\mathrm{c}}\right)\right],$$

$$R_3=\left(\Delta R_{\mathrm{c}}^2+R_0^2\right)^{1/2},\quad \Theta=\mathrm{tg}^{-1}(\Delta R_{\mathrm{c}}/R_0),\qquad(10)$$

where $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters with the reference distance (or impurity-ligand distance) R_0. For 3d^n ions in octahedral clusters, $\bar{A}_4(R_0)\approx(3/4)Dq$ and $\bar{A}_2(R_0)\approx(9\sim 12)\bar{A}_4(R_0)$ [14–16], and we take $\bar{A}_2(R_0)\approx 9\bar{A}_4(R_0)$ here. The power-law exponents are taken as $t_2\approx 3$ and $t_4\approx 5$ due to the ionic nature of the bonds [13, 14]. Since the ionic radius $r_i\approx 0.72$ Å [17]) of the impurity Co^{2+} differs from the radius $r_h(\approx 0.97$ Å [17]) of the replaced host Na$^+$ ion, one can reasonably estimate the distance R_0 from the empirical formula [18, 19]

$$R_0\approx R_{\mathrm{H}}+(r_i-r_h)/2,\qquad(11)$$

where $R_{\mathrm{H}}(\approx 2.317$ Å [17]) is the cation-anion distance in the host NaF crystal. So, we obtain $R_0\approx 2.192$ Å for the NaF:Co^{2+} crystal. Thus the integrals $S_{\mathrm{dp}}(\gamma)$ can be calculated from the Slater-type SCF functions [20–21] and R_0 in NaF: Co^{2+}, i. e., $S_{\mathrm{dp}}(\mathrm{t_{2g}})\approx 0.0041$ and $S_{\mathrm{dp}}(\mathrm{e_g})\approx 0.0168$.

From the optical spectra of the NaF:Co^{2+} crystal [22], we have

$$Dq\approx -830\ \mathrm{cm}^{-1},\ B\approx 990\ \mathrm{cm}^{-1},\ C\approx 3980\ \mathrm{cm}^{-1}.\qquad(12)$$

By using the values $B_0\approx 1115$ cm^{-1} and $C_0\approx 4366$ cm^{-1} for the free Co^{2+} ion [23], we have $f_\gamma\approx 0.900$, and so $N_{\mathrm{t}}\approx 0.949$, $N_{\mathrm{e}}\approx 0.953$, $\lambda_{\mathrm{t}}\approx 0.235$, and $\lambda_{\mathrm{e}}\approx 0.241$ from (2) and (3). Substituting $\zeta_{\mathrm{d}}^0\approx 533$ cm^{-1} [23] and $P_0\approx 254\times 10^{-4}$ cm^{-1} [24] for the free Co^{2+} ion and $\zeta_{\mathrm{p}}^0\approx 220$ cm^{-1} for a free F$^-$ ion [25] into (4), we have

$$\zeta\approx 512\ \mathrm{cm}^{-1},\ \zeta'\approx 501\ \mathrm{cm}^{-1},$$
$$k\approx 0.976,\ k'\approx 0.924,\qquad(13)$$
$$P\approx 241\times 10^{-4}\ \mathrm{cm}^{-1},\ P'\approx 242\times 10^{-4}\ \mathrm{cm}^{-1}.$$

Thus there are only the two unknown parameters ΔR_{c} and ΔR_{p} in the formulas of the EPR g factors. By fitting the calculated g_i to the observed values, we obtain

$$\Delta R_{\mathrm{c}}\approx 0.268\ \text{Å},\quad \Delta R_{\mathrm{p}}\approx 0.181\ \text{Å}.\qquad(14)$$

Comparisons between the calculated and observed g_i are shown in Table 1 (note: in the above calculations, the axes are chosen as $X\|[1\bar{1}0]$, $Y\|[110]$ and $Z\|[001]$, whereas the EPR experiment coordination axes are $X'\|[001]$, $Y'\|[1\bar{1}0]$ and $Z'\|[110]$. So, a rotation of the axes of the calculation coordination is needed in order that the theoretical values can be compared with the experimental results [1]. Thus, we have $g_{X'}=g_Z$, $g_{Y'}=g_X$, $g_{Z'}=g_Y$, $A_{X'}=A_Z$, $A_{Y'}=A_X$, $A'_Z=A_Y$).

Substituting the above parameters, including the rhombic distortion parameters ΔR_{c} and ΔR_{p}, into (6) and taking the core polarization constant $\kappa\approx 0.284$ (which is consistent with the value $0.25\sim 0.3$ for the Cu^{2+} ion in Tutton salts [26] and 0.325 (10) for the Co^{2+} ion [27]), the hyperfine structure constants A_i can be obtained. They also agree with the observed values (see Table 1).

4. Discussions

1) Since $\Delta R_{\mathrm{c}}>0$ and $\Delta R_{\mathrm{p}}>0$, the directions of the displacements of Co^{2+} and F$^-$ accord with the expectation based on the electrostatic interaction (see Fig. 1), showing that the estimated local structural parameters

are suitable in physics. In fact, this point is also supported by the calculations on similar rhombic impurity centers (such as V^{2+} in LiCl and NaCl [28] and Cr^{3+} in MgO [5]) based on their EPR data. It is noted that there may be some errors in the above calculated displacements ΔR_c and ΔR_p arising from the approximations of the theoretical model and the neglection of the displacements of other four F$^-$ ions. Even so, one finds that by considering a suitable local lattice relaxation for the impurity Co^{2+} in the NaF crystal, the EPR parameters can be reasonably explained.

2) Interestingly, the above theoretical results of the EPR parameters for the rhombic Co^{2+} center can be reduced to those for the cubic case when taking $\Delta R_\mathrm{c} = \Delta R_\mathrm{p} = 0$. Thus, we have $g_X = g_Y = g_Z \approx 4.412$ and $A_X = A_Y = A_Z \approx 167 \times 10^{-4}$ cm^{-1}. The results are also in agreement with the isotropic EPR parameters (i. e., g $\approx$ 4.391 and $A \approx 110 \times 10^{-4}$ cm^{-1} [22] and g $\approx$ 4.5 [1]) for the cubic Co^{2+} center induced by irradiation.

3) The experimental value of A_X is not given due to overlap of the spectral line in the EPR measurements [1]. So, the theoretical value ($\approx 207 \times 10^{-4}$ cm^{-1}) of A_X obtained in this work remains to be further checked with experiments.

In conclusion, it appears that from the above formulas based on the cluster approach, the local structure of the rhombic Co^{2+} center in NaF can be obtained by studying its EPR parameters. This method can also be applied to other rhombic Co^{2+} octahedral clusters in crystals.

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