Studies of the Local Phase-transition Behaviour for Ni^+-II Centers in $RbCaF_3$ Crystal from EPR Data

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By fitting the calculated EPR $g_i (i = x, y, z)$ factors to the observed values, the local release factor k_l which is introduced to characterize the release (or elongation) effect of impurity-ligand bonds along the rotational axis in the cubic-to-tetragonal phase transition of ABX_3 perovskites, is obtained for the Ni^+-II center in $RbCaF_3$ crystal. The result shows that, similar to the local rotational angle (or order parameter) ϕ, the local release factor is unlike that of the host crystal. It suggests that in the doped crystal the impurity can affect the local phase transition behaviour in the vicinity of impurity ions.

Key words: Local Phase Transition Behaviour; E. P. R.; Crystal-field Theory; Ni^+ ion; $RbCaF_3$.

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1. Introduction

The action of X-ray irradiation on insulation materials doped with nickel can give rise to the formation of the 'unstable' Ni^+ center. For example, three types of tetragonal Ni^+ centers were found in X-ray irradiated cubic $RbCaF_3$:Ni crystals from EPR experiments [1, 2]. The models for these centers consist of a Ni^+ ion surrounded by a Jahn-Teller tetragonally elongated fluorine octahedron (Ni^+-I center), and the same model, but with one and two nearest-neighbour fluorine vacancies (V_{F^-}), for Ni^+-II and Ni^+-III centers [1, 2]. Cubic $RbCaF_c$ crystals undergo a structural phase transition to a tetragonal phase at ≈ 195 K [3]. The phase transition consists of a rotation of fluorine octahedra around one of C_4 axis and the release (or elongation) of metal-ligand bonds [3]. The rotational angle ϕ is the order parameter of this transition, and the release of metal-ligand bonds can be written as [4, 5]

$$R_\perp \approx \frac{R_\perp^c}{\cos\phi} \approx R_\perp^c \left(1 + \frac{1}{2}\phi^2\right),$$
$$R_\parallel \approx R_\parallel^c \,(1 + k\,\phi^2)\,, \tag{1}$$

where $R_\perp$ and $R_\parallel$ are the metal-ligand distances perpendicular to and parallel to the rotational axis. The superscript "c" denotes the value in cubic phase. k is the release factor which is introduced to characterize the release effect of $R_\parallel$. Thus, the phase transition behaviour is often characterized by the parameters ϕ and k. Under the phase transition, the EPR spectra of the above Ni^+ centers in $RbCaF_3$ crystal should change, and so one can study the phase transition behaviour by using these Ni^+ centers as probes. However, since the charge and size of the probe Ni^+ differ from those of the replaced host ion Ca^{2+}, the probe affects the surrounding ions in such a way that the local phase transition behaviour in the vicinity of the probe may be unlike that in the pure crystal. For the Ni^+-II center, if the rotation axis is perpendicular to the Ni^+-V_{F^-} direction in $RbCaF_3$:Ni^+ (and so the symmetry of the Ni^+-II center is changed from tetragonal to rhombic under the phase transition), a local rotation angle $\phi \approx 2.4°$ at ≈ 77 K was obtained from the tilting of the g-tensor of the Ni^+-II center [1] (note that no information about the local angle ϕ was obtained from EPR measurements [1] for other Ni^+ centers and for the Ni^+-II center if the rotational axis was parallel with the Ni^+-V_{F^-} direction). This value is inconsistent with that (≈ 7° [3]) in pure $RbCaF_3$ crystal. The release factor k for pure $RbCaF_3$ crystal is 0.44 [5], however the local release factor k_l has not been known. In the present paper, we study the local release factor k_l by analyzing the EPR $g_i (i = x, y, z)$ factors under the phase transition. The result is discussed.

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2. Calculated Method

According to the crystal-field theory, we derive the high-(fourth-) order perturbation formulas of g_i for a 3 d^9 ion in orthorhombic symmetry. They are

$$
\begin{aligned}
g_x = {} & g_e + 2k_0\zeta/E_2 - 4k_0\zeta^2/E_1E_3 + k_0\zeta^2(2/E_1 - 1/E_3)/E_2 + g_e\zeta^2[2/E_1^2 - (1/E_2^2 - 1/E_3^3)/2] \\
& + k_0\zeta^3(1/E_2 - 1/E_3)(1/E_3 - 1/E_2)/(2E_1) + k_0\zeta^3(2/E_1 - 1/E_2)(2/E_1 + 1/E_2)/(2E_3) \\
& - k_0\zeta^3(1/E_2 - 1/E_3)/(2E_2E_4) - (g_e\zeta^3/4)[(1/E_3 - 2/E_1)/E_2^2 + (2/E_3 - 1/E_2)/E_3^2 \\
& + 2(1/E_2 - 1/E_3)/E_1^2 + 2(1/E_2^2 - 1/E_3^2)/E_1, \\
g_y = {} & g_e + 2k_0\zeta/E_3 - 4k_0\zeta^2/E_1E_2 + k_0\zeta^2(2/E_1 - 1/E_2)/E_3 + g_e\zeta^2[2/E_1^2 - (1/E_3^2 - 1/E_2^2)/2] \\
& + k_0\zeta^3(1/E_2 + 1/E_3)(1/E_2 - 1/E_3)/(2E_1) + k_0\zeta^3(2/E_1 - 1/E_3)(2/E_1 + 1/E_3)/(2E_2) \\
& - k_0\zeta^3(1/E_3 - 1/E_2)/(2E_3E_4) - (g_e\zeta^3/4)[(1/E_2 - 2/E_1)/E_3^2 + (2/E_2 - 1/E_3)/E_2^2 \\
& + 2(1/E_2 + 1/E_3)/E_1^2 + 2(1/E_3^2 - 1/E_2^2)/E_1, \\
g_z = {} & g_e + 8k_0\zeta/E_1 + k_0\zeta^2/E_2E_3 + 2k_0\zeta^2(1/E_1E_2 + 1/E_1E_3) - g_e\zeta^2[1/E_1^2 - (1/E_2^2 + 1/E_3^2)/4] \\
& + k_0\zeta^3[8/E_1 - (1/E_2 + 1/E_3)]/(2E_2E_3) - 2k_0\zeta^3(1/E_1E_2 + 1/E_1E_3 - 1/E_2E_2]/E_1 \\
& + (g_e\zeta^3/4)[2(1/E_2^2 + 1/E_3^2)/E_1 - (1/E_2 + 1/E_3)/E_2E_3],
\end{aligned}
\tag{2}
$$

where $g_e = 2.0023$, k_0 $(= \zeta/\zeta_0)$ is the orbital reduction factor, ζ the spin-orbit coupling coefficient of a 3d^9 ion in crystal, ζ_0 the corresponding coefficient of a free ion (for Ni$^+$, $\zeta_0 \approx 603$ cm^{-1} [6]), and

$$
\begin{aligned}
E_1 &= 10D_q, \\
E_2 &= 10D_q - 3D_s + 5D_t - 3D_\xi + 4D_\eta, \\
E_3 &= 10D_q - 3D_s + 5D_t + 3D_\xi - 4D_\eta, \\
E_4 &= -4D_s - 5D_t,
\end{aligned}
\tag{3}
$$

where D_s, D_t, D_ξ, and D_η are the low-symmetry field parameters in orthorhombic symmetry.

From the superposition model [7], we have

$$
\begin{aligned}
D_s &\approx (2/7)\bar{A}_2(R_0)[(R_0/R_z)^{t_2} - (R_0/R_x)^{t_2} - (R_0/R_y)^{t_2}], \\
D_t &\approx (8/21)\bar{A}_4(R_0)[(R_0/R_z)^{t_4} - (R_0/R_x)^{t_4} - (R_0/R_y)^{t_4}], \\
D_\xi &\approx (2/7)\bar{A}_2(R_0)[(R_0/R_x)^{t_2} - (R_0/R_y)^{t_2}], \\
D_\eta &\approx (10/21)\bar{A}_4(R_0)[(R_0/R_x)^{t_4} - (R_0/R_y)^{t_4}],
\end{aligned}
\tag{4}
$$

where the power-law exponents are $t_2 \approx 3$ and $t_4 \approx 5$ because of the ionic nature of the bonds [7, 8]. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters with the reference distance $R_0(\approx \bar{R})$. For a 3d^n ion in octahedra, $\bar{A}_4(R_0) \approx (3/4)D_q$ [7, 8]. We take $D_q \approx 600$ cm^{-1} for $(\mathrm{NiF_6})^{5-}$ octahedra, obtained from self-consistent charge extended Hückel (SCCEH) calculation [2]. The ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0) \approx 9 \sim 12$ for 3d^n ions in many crystals [8–10], and we take $\bar{A}_2(R_0) \approx 9\,\bar{A}_4(R_0)$. R_x, R_y and R_z are, respectively, the metal-ligand distances along x, y and z axes. According to (1). we have

$$
\begin{aligned}
& R_x \approx R_{\mathrm{eq}}^{\mathrm{c}}(1 + k\phi^2), \quad R_y \approx R_{\mathrm{eq}}^{\mathrm{c}}\left(1 + \frac{1}{2}\phi^2\right), \\
& R_z \approx R_{\mathrm{ax}}^{\mathrm{c}}\left(1 + \frac{1}{2}\phi^2\right).
\end{aligned}
\tag{5}
$$

In the cubic phase of $\mathrm{RbCaF_3}$ ($T \approx 230$ K), $\phi \approx 0$, $R_{\mathrm{eq}}^{\mathrm{c}} \approx 2.179$ Å obtained by analyzing the isotropic part of the superhyperfine interaction parameter [2], and $R_{\mathrm{ax}}^{\mathrm{c}} \approx 2.33$ Å as shown in [11] for Ni$^+$-II centers in fluoroperovskites, thus $R_x = R_y$, $D_\xi = D_\eta = 0$, and the Ni$^+$-II center has tetragonal symmetry. Using these parameters in the above formulas and assuming $k_0 \approx 0.935$, we obtain

$$
g_x = g_y \approx 2.116, \quad g_z \approx 2.710. \tag{6}
$$

The results are consistent with those observed: $g_x \approx (g_y \approx 2.115)$ and g_z (≈ 2.688) [1, 2] for a tetragonal Ni$^+$-II center in cubic $\mathrm{RbCaF_3}$ ($T \approx 230$ K).

In the tetragonal phase of $\mathrm{RbCaF_3}$ ($T \approx 77$ K), $\phi \approx 2.4°$, $R_x \neq R_y$, so the Ni$^+$II center has orthorhombic symmetry. Using the parameters mentioned above and the host release factor $k_h \approx 0.44$ [5] in the above formulas, we have calculated g_i for the orthorhombic Ni$^+$-II center. The results (see Table 1), particularly, $g_x > g_y$, disagree with the observed values (see Table 1). So, the local release factor k_l in the Ni$^+$-II center may be different from the host one. By fitting the calculated g_i to the observed values, we obtain

$$
k_l \approx 2. \tag{7}
$$

Table 1. g-tensor for a rhombic Ni^+-center in the tetragonal phase of $RbCaF_3$ at 77 K.

	Cal a)	Cal b)	Experiment [1]
g_x	2.114	2.111	2.111
g_y	2.113	2.118	2.121
g_z	2.704	2.704	2.672

a) Calculated by using the host release factor $k_h \approx 0.44$.
b) Calculated by using the local release factor $k_l \approx 2$.

Comparisons between the calculated and observed g_i are shown in Table 1.

3. Discussions

From the above studies one can find that, similar to the local rotational angle ϕ, the local release factor is unlike the host one. So the local phase behaviour in the vicinity of an Ni^+ impurity is indeed different from that of the host crystal and also from impurity to impurity [4, 5, 12]. Noteworthily, for the local factor $k_l > 0.5$ we have $R_x > R_y$ and so $g_x < g_y$, whereas for the host $k_h > 0.5$, $R_x < R_y$ and so $g_x > g_y$. The result of $k_l > 0.5 > k_h$ (and so that the relative magnitude between the metal-ligand distance parallel with and perpendicular to the rotational axis in impurity centers differs from that in host crystal) was also found for other paramagnetic impurities, such as Ni^{2+}, Fe^{3+}, and Gd^{3+} in $RbCaF_3$ crystals from EPR studies [4, 5, 12]. So, the above local release factor k_l can be understood.

The EPR parameters at various temperatures come from both the static contribution related to the geometry of paramagnetic centers and the vibrational contribution due to electron-phonon interaction [13–14]. In the above studies, the vibrational contribution is not considered. Although the static contribution is dominant [15, 16], neglecting the vibrational contribution may result in the calculation errors in g_i and k_l. Even so, the errors cannot change the result of $k_l > 0.5 > k_h$ because $g_x < g_y$. So, the difference of the local factor k_l from the host factor k_h obtained above can be regarded as reasonable.

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