The Studies of Geometrical Microstructure of Tetragonal Co^{2+}-V_O Centers in $KNbO_3$ and $KTaO_3$ Crystals from EPR Data

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From the perturbation formulas for the EPR g factors $g_{||}$ and $g_{\perp}$ of a $3d^7$ ion in tetragonal octahedral crystal field based on a cluster approach, the geometrical microstructures of tetragonal Co^{2+}-V_O centers in $KNbO_3$ and $KTaO_3$ crystals are obtained by fitting the calculated $g_{||}$ and $g_{\perp}$ to the observed values. It is found that the Co^{2+} ion in Co^{2+}-V_O centers is displaced away from the oxygen vacancy V_O by 0.3 Å in $KNbO_3$ and by 0.29 Å in $KTaO_3$. These results are comparable with those of Fe^{3+}-V_O centers in ABO_3 perovskite-type crystals obtained from both the shell-model simulations and the embedded-cluster calculations, and from theoretical studies of EPR data. The experimental values of $g_{||}$ and $g_{\perp}$ for the tetragonal Co^{2+}-V_O centers in both crystals are also explained reasonably.

Key words: Electron Paramagnetic Resonance (EPR); Crystal- and Ligand-Field Theory; Defect Structure; Co^{2+}; $KNbO_3$; $KTaO_3$.

1. Introduction

Oxide perovskites ABO_3 are important ferroelectric, electro-optical and photorefractive crystals. Many studies were made on transition-metal ($3d^n$) ions in these crystals. These studies show that divalent and trivalent states of substitutional $3d^n$ ions at B sites can be charge compensated by a nearest-neighbour oxygen vacancy V_O, and so tetragonal M^{n+}-V_O centers are formed [1 - 2]. The microstructure of these M^{n+}-V_O centers has attracted the attention of many investigators. For example, by analyzing the EPR zero-field splittings b_2^0 for Mn^{2+}-V_O centers in $SrTaO_3$ and Fe^{3+}-V_O centers in $SrTiO_3$, $KTaO_3$ and $PbTiO_3$ from the simple superposition model where the intrinsic parameter $\bar{b}_2(r)$ remains stable by the inverse power law, Siegal and Muller [3] suggested that the $3d^5$ ion moves by a distance ΔR towards the vacancy V_O. Since the effective charge of the anion vacancy is positive, they [3] believed that Coulomb interaction does not play an important role for these defect centers. On the other hand, for the Fe^{3+}-V_O center in $KNbO_3$ the shell-model simulations and the embedded-cluster calculations made by Donnerberg [4] consistently show that the Fe^{3+} impurity ion is displaced in the opposite direction to that of the vacancy V_O. The result contrasts to the interpretations based on the above simple superposition model (note: the zero-field splitting b_2^0 for the Fe^{3+}-V_O center in $KNbO_3$ is close to those in $SrTiO_3$, $KTaO_3$ and $PbTiO_3$ [3, 4]). Donnersberg [4] therefore thought that the intrinsic parameter in the superposition model should based on a Lennard-Jones-type function $\bar{b}_2(r) = -A(r_0/r)^n + B(r_0/r)^m$ instead of the simple inverse power law $\bar{b}_2(r) = \bar{b}_2(R_0(r_0/r)^{t_2})$ for the studies of b_2^0 in the axial defect aggregates of $3d^5$ ions in ABO_3 crystals. We also studied the microstructure of Fe^{3+}-V_O centers in ABO_3 oxide perovskites by analyzing their EPR data from the high-order perturbation formulas of zero-field splitting on the basis of the spin-orbit coupling mechanism [5]. The displacement direction or relaxation pattern is consistent with that in [4]. In order to further confirm the relaxation pattern obtained in [4] and [5], the microstructure of other tetragonal M^{n+}-V_O paramagnetic centers in ABO_3 crystals should be studied. In this paper, we study the microstructure of tetragonal Co^{2+}-V_O centers in $KNbO_3$ and $KTaO_3$ crystals by calculating the factors $g_{||}$ and $g_{\perp}$ from the perturbation formulas based on the cluster approach.

2. Calculation

For a $Co^{2+}(3d^7)$ ion in tetragonal octahedral symmetry, the perturbation formulas for $g_{\|}$ and $g_{\perp}$, based on the cluster approach, where the contributions of the configuration interaction and the covalency effect are considered, are [6]

$$g_{\|} = 2 + \frac{4(k\alpha+2)\left[\frac{3}{x^2} - \frac{4}{(x+2)^2}\right] + 2\left[\frac{9}{x^2} - \frac{4}{(x+2)^2}\right]\nu_1 - 2\frac{\alpha}{\alpha'}\left[\frac{3}{x} - \frac{4}{x+2}\right]\nu_3}{\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2}}, \tag{1}$$

$$g_{\perp} = \frac{4\left[\left(\frac{\alpha}{\alpha'}\right)^2 \frac{2k\alpha}{x+2} + \frac{12}{x(x+2)}\right] + \left(\frac{\alpha}{\alpha'}\right)^2 \nu_4 + \frac{8}{(x+2)^2}\nu_5 + \frac{12}{x(x+2)}\nu_6 + \frac{\alpha}{\alpha'}\frac{4}{x+2}\nu_7}{\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2}},$$

where x is determined from the energy separation Δ $\left[= E(^4A_2) - E(^4E)\right]$ of the ground orbital $^4T_1$ state in the tetragonal field by using the expression

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

and

$$\nu_1 = \frac{k'\zeta'}{3}\left[\frac{15 f_1^2}{2E_{1X}} + \frac{2q_1^2}{E_{2X}}\right],$$

$$\nu_3 = \frac{k'\zeta'}{3}\left[\frac{15 f_1 f_2}{2E_{1X}} - \frac{2q_1 q_2}{E_{2X}}\right],$$

$$\nu_4 = \frac{k'\zeta'}{3}\left[\frac{15 f_2^2}{E_{1X}} + \frac{4q_2^2}{E_{2X}}\right], \quad \nu_5 = \frac{4k'\zeta' q_3^2}{3E_{2Z}},$$

$$\nu_6 = \frac{k'\zeta'}{3}\left[\frac{15 f_3^2}{2E_{1Z}} + \frac{2q_3^2}{E_{2Z}} + \frac{8\rho^2}{E_3}\right], \quad \nu_7 = \frac{\nu_3}{2}, \tag{3}$$

where the energy denominators $E_{1X}, E_{1Z}, E_{2X}, E_{2Z}$, and E_3, and also the separation Δ can be calculated from the d-d transition energy matrices of the $3d^7$ ion in tetragonal symmetry. ζ and ζ' are the spin-orbit coupling coefficients and k and k' the orbital reduction factors. From the cluster approach, they can be written as [6, 7]

$$\zeta = N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0/2), \ \zeta' = (N_t N_e)^{1/2}(\zeta_d^0 - \lambda_t\lambda_e\zeta_p^0/2),$$

$$k = N_t(1 + \lambda_t/2), \ k' = (N_t N_e)^{1/2}(1 - \lambda_t\lambda_e/2), \tag{4}$$

where ζ_d^0 and ζ_p^0 are, respectively, the spin-orbit coupling coefficients of the d electrons of a free $3d^7$ ion and that of the p electrons of a free ligand ion. N_γ and λ_γ ($\gamma = t_{2g}$ or e_g) are the normalization factor and the orbital mixing coefficient. They can be obtained from a semiempirical LCAO method [6, 7]. From this method we have the normalization condition

$$N_\gamma(1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2) = 1 \tag{5}$$

and the approximate relation

$$f_\gamma = N_\gamma^2\left[1 + \lambda_\gamma^2 S_{dp}^2(\gamma) - 2\lambda_\gamma S_{dp}(\gamma)\right], \tag{6}$$

where $S_{dp}(\gamma)$ is the group overlap integral. f_γ [$\approx (B/B_0 + C/C_0)/2$] is the ratio of the Racah parameters for a $3d^n$ ion in a crystal (which can be obtained from the optical spectra of the studied system) to those for a free ion.

The parameters α, α', f_i and q_i in (1) - (3) are related to the configuration interaction due to the admixture among the ground and the excited states, and their expressions are given in [6]. It is noteworthy that the tetragonal field parameters D_s and D_t (which depend on the local structural data) occur in these expressions and d-d transition energy matrices. So, by studying the g factors from the above formulas, the microstructures of the Co^{2+} centers in crystal can be obtained.

For Co^{2+} in $KNbO_3$ and $KTaO_3$ crystals, to our knowledge no optical spectra were reported. However, we can reasonably estimate them from the optical spectra of similar crystals. Since molecular orbital calculations [8, 9] on different $3d^n$ ion complexes show that $Dq \propto R_0^{-5}$ is approximately valid, and since the Racah parameters B and C decrease slightly with decreasing bond length R_0 [10], from the optical

Table 1. Group overlap integrals, LCAO coefficients, orbital reduction factors and spin-orbit coupling coefficients for Co^{2+} in $KNbO_3$ and $KTaO_3$ crystals.

	$S_{dp}(t_{2g})$	$S_{dp}(e_g)$	N_t	N_e	λ_t	λ_e	k	k'	ζ	ζ'
$KNbO_3$	0.01462	0.04594	0.8995	0.9102	0.3491	0.3635	0.9544	0.8574	487	474
$KTaO_3$	0.01493	0.04670	0.8971	0.9080	0.3538	0.3683	0.9533	0.8438	486	473

spectra of MgO:Co^{2+} [11] and the bond lengths $R_0 \approx$ 2.105 Å, 2.00 Å and 1.994 Å for MgO, $KNbO_3$ and $KTaO_3$ [12], respectively, we estimate

$$Dq \approx -1214\,\mathrm{cm}^{-1}, B \approx 785\,\mathrm{cm}^{-1}, C \approx 3920\,\mathrm{cm}^{-1} \tag{7}$$

for $KNbO_3$:Co^{2+} and

$$Dq \approx -1232\,\mathrm{cm}^{-1}, B \approx 780\,\mathrm{cm}^{-1}, C \approx 3900\,\mathrm{cm}^{-1} \tag{8}$$

for $KTaO_3$:Co^{2+}. The integrals $S_{dp}(\gamma)$ (see Table 1) are calculated from the Slater-type SCF functions [13, 14] and the distance R_0. For a free Co^{2+} ion [15], $B_0 \approx 1115\,\mathrm{cm}^{-1}$, $C_0 \approx 4366\,\mathrm{cm}^{-1}$, $\zeta_d^0 \approx 533\,\mathrm{cm}^{-1}$, and for a free O^{2-} ion [16], $\zeta_p^0 \approx 136\,\mathrm{cm}^{-1}$. Thus the LCAO coefficients, the parameters k, k', ζ and ζ' can be calculated from (4) - (6). They are shown in Table 1.

In the tetragonal Co^{2+}-V_O center, considering the influence of the nearest-neighbour V_O in the C_4 axis, the Co^{2+} ion should be displaced along the C_4 axis by $\Delta R_{Co^{2+}}$ (note: the displacement towards the V_O is defined as a positive displacement direction). The four planar O^{2-} ions in the Co^{2+}-V_O center should be slightly shifted (mainly along the C_4 axis [4]). Thus, as in [4] for the similar tetragonal Fe^{3+}-V_O center in $KNbO_3$, we define the effective Co^{2+} ion displacement ΔR^{eff} ($\approx \Delta R_{Co^{2+}} - \Delta R_{O^{2-}}$) as the spatial separation projected along the C_4 axis between Co^{2+} and the four planar O^{2-} ions, and so we have

$$R_1 \approx R_0 + \Delta R^{\mathrm{eff}}, R_2 \approx [R_0^2 + (\Delta R^{\mathrm{eff}})^2]^{1/2},$$
$$\cos\theta \approx \Delta R^{\mathrm{eff}}/R_2, \tag{9}$$

where R_1 denotes the bond length for a Co^{2+}-O^{2-} bond along the C_4 axis and R_2 denotes the bond length for the other four Co^{2+}-O^{2-} bonds in the Co^{2+}-V_O center. θ is the angle between R_2 and the C_4 axis.

Table 2. EPR g factors for Co^{2+}-V_O in $KNbO_3$ and $KTaO_3$ crystals.

	$g_{\|}$		$g_{\perp}$	
	Calc.	Exp. [21]	Calc.	Exp. [21]
$KNbO_3$	2.067	2.056(5)	5.002	5.020(10)
$KTaO_3$	2.038	2.061(2)	4.957	4.933(8)

From the superposition model for the crystal-field parameters [17], we obtain

$$D_s = \frac{4}{7}\bar{A}_2(R_0)\Big[(3\cos^2\theta - 1)(R_0/R_2)^{t_2} + \frac{1}{2}(R_0/R_1)^{t_2}\Big], \tag{10}$$

$$D_t = \frac{8}{21}\bar{A}_2(R_0)\Big[\frac{1}{2}(35\cos^4 - 30\cos^2 + 3 - 7\sin^4\theta) \cdot (R_0/R_2)^{t_4} + (R_0/R_1)^{t_4}\Big],$$

where t_2 and t_4 are the power law exponents. We take $t_2 \approx 3$ and $t_5 \approx 5$ here because of the ionic nature of the bonds [6, 17]. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ (R_0) are the intrinsic parameters. For $3d^n$ octahedral clusters we have $\bar{A}_4(R_0) \approx \frac{3}{4}Dq$ [17, 18]. The ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0)$ is in the range of 9 ~ 12 for $3d^n$ ions in many crystals [6, 19, 20]. We take $\bar{A}_2(R_0)/\bar{A}_4(R_0) \approx 12$ here. Thus, substituting these parameters, the optical spectrum parameters in (7) and (8) and the parameters in Table 1 into the above formulas, we can for the Co^{2+}-V_O center in $KNbO_3$

$$\Delta R^{\mathrm{eff}} \approx -0.30\,\text{Å}, \tag{11}$$

and for Co^{2+}-V_O center in $KTaO_3$

$$\Delta R^{\mathrm{eff}} \approx -0.29\,\text{Å}, \tag{12}$$

by fitting the calculated $g_{\|}$ and $g_{\perp}$ to the observed values [21]. Comparisons of $g_{\|}$ and $g_{\perp}$ between calculation and experiment are shown in Table 2.

3. Discussion

From the above studies, one can find that, to explain reasonably the g factors $g_{\|}$ and $g_{\perp}$ for Co^{2+}-V_O centers in $KNbO_3$ and $KTaO_3$ crystals, the Co^{2+} ion should be displaced away from the V_O. The displacements ΔR^{eff} in magnitude and direction are comparable with those of Fe^{3+}-V_O centers in ABO_3 perovskite crystals obtained from both the shell-model simulations and the embedded-cluster calculations [4], and from the theoretical studies of EPR data [5], but the displacement direction is opposite to that of Fe^{3+}-V_O centers obtained from the simple superposition model based on the inverse power law for $3d^5$ ions in some ABO_3 crystals [3]. Noteworthily, doubt exists as to the validity of the simple superposition model if $3d^5$ impurity centers are not slightly distorted from cubic [4, 18]. Donnerberg [4] pointed out that if the ligand coordination spheres significantly deviate from the original octahedral configuration, e. g., the Fe^{3+}-V_O center in an ABO_3 crystal, a Lennard-Jones-type radial function rather than the inverse power law radial function ought to be used. So, we think that the relaxation pattern obtained in the present paper for the Co^{2+}-V_O center and in the previous papers [4, 5] for Fe^{3+}-V_O centers in ABO_3 crystals is reasonable. This relaxation pattern is expected to be valid for other tetragonal M^{n+}-V_O centers in ABO_3 crystals and so Coulomb interaction may be of importance for these systems. Of course, this opinion should be further confirmed for other similar systems.

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