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Theoretical Investigations of the EPR Parameters for Ir^{4+} in $KNbO_3$

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Abstract: The EPR parameters anisotropic g factors $g_{//}$ and $g_{\perp}$ and the hyperfine structure constants $A_{//}$ and $A_{\perp}$ for the Ir^{4+} center in rhombohedral $KNbO_3$ are theoretically investigated from the perturbation formulas of these parameters for a $5d^5$ ion in trigonally distorted octahedra. It is found that the impurity-ligand bonding angle β related to the [111] (or C_3) axis in the Ir^{4+} impurity center is about $0.47°$ larger than the host value β_H ($\approx 54.62°$) due to Jahn-Teller effect and charge or size mismatching substitution of Nb^{5+} by Ir^{4+}. This leads to the slightly compressed ligand octahedron in the impurity center. The theoretical results based on the above angular distortion in this work show good agreement with the experimental data.

Key words: Electron paramagnetic resonance, crystal-fields and spin hamiltonian, Ir^{4+}, $KNbO_3$

INTRODUCTION

Potassium niobate ($KNbO_3$) is one of the most studied members in the important class of perovskite structure ferroelectrics, which have numerous technological applications (Gunter and Huignard, 1998; Donnerberg, 1999). For example, this material is widely used for laser frequency doubling and nonlinear optical devices (Kotomin *et al.*, 2002; Xue and Zhang, 1998). For $KNbO_3$, there are cubic, tetragonal, orthorhombic and rhombohedral phases with the phase transition temperatures of 701K, 488K and 210K, respectively (Xue and Zhang, 1998). In particular, $KNbO_3$ exhibits unique photorefractivity of promising applications when doped with some transition-metal ions (e.g., Fe) (Gunter and Huignard, 1998; Donnerberg, 1999). Later on, studies on $KNbO_3$ with various dopants (e.g., Fe^{3+}, Co^{2+} and Ir^{4+}) were carried out by means of electron paramagnetic resonance (EPR) technique and the anisotropic g factors $g_{//}$ and $g_{\perp}$ and the hyperfine structure constants $A_{//}$ and $A_{\perp}$ were also measured (Possenriede *et al.*, 1989). Since the EPR results may be helpful to understand properties of doped $KNbO_3$, theoretical analyses on these experimental findings (for the tetragonal Fe^{3+} and Co^{2+} centers) were performed (Possenriede *et al.*, 1989; Abragam and Bleaney, 1970; Geschwind and Remeika, 1962). For the trigonal Ir^{4+} ($5d^5$) center in rhombohedral $KNbO_3$ observed at 20K (Possenriede *et al.*, 1989), however, satisfactory explanations have not been made until now. Although the authors obtained the orbital reduction factor k (≈ 0.75) by fitting the average experimental g factors (Possenriede *et al.*, 1989), the low symmetrical distortion (or local structure) around the impurity Ir^{4+} accounting for the g anisotropy Δg ($= g_{\perp}-g_{//}$) was not analyzed. In addition, the hyperfine structure constants were not explained, either.

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Considering that the EPR behaviours for Ir^{4+} ($5d^5$) are dissimilar to those for the first transition-metal ($3d^n$) ions and that information about local structure and g anisotropy would be useful to understand the impurity (particularly $4d^n$ and $5d^n$ ions) properties in $KNbO_3$, further theoretical studies on the trigonal Ir^{4+} center are of significance. In this work, the local structure and the EPR parameters for the Ir^{4+} center in $KNbO_3$ are theoretically investigated from the perturbation formulas of these parameters for a $5d^5$ ion in trigonally distorted octahedra by considering suitable local lattice (angular) distortion.

CALCULATIONS

For an Ir^{4+} in rhombohedral $KNbO_3$, it can occupy the octahedral Nb^{5+} site due to their similar charge and ionic radii and conserve the original trigonal symmetry (Possenriede *et al.*, 1989). Usually, the impurity-ligand angle β related to [111] (or C_3) axis may be unlike the host angle β_H [$\approx$ 54.62° (Possenriede *et al.*, 1989)] due to the difference in charge and ionic radius for the impurity and host ions.

Unlike Fe^{3+} and Mn^{2+} ($3d^5$) ions, Ir^{4+}($5d^5$) in octahedra belongs to the case of strong crystal field. The five 5d electrons occupy the t_{2g} orbitals (corresponding to one t_{2g} hole), associated with the ground state $^2T_{2g}$ of low spin (S = ½) (Abragam and Bleaney, 1970; Geschwind and Remeika, 1962). When the ligand octahedron is trigonally distorted, the $^2T_{2g}$ state may split into one orbital singlet $^2A_{1g}$ and one doublet ^2E_g, the later or former lying lowest for elongation ($\beta < \beta_0 \approx$ 54.74°, the value of cubic symmetry) or compression ($\beta > \beta_0$) along the C_3 axis. The energy separation between $^2A_{1g}$ and ^2E_g is often defined as the trigonal field parameter V (Abragam and Bleaney, 1970; Geschwind and Remeika, 1962; O'Reilly and Offenbacher, 1971). In addition, inclusion of the spin-orbit coupling interactions may result in splitting of the above states into three Kramers doublets. The perturbation formulas of the anisotropic g factors and the hyperfine structure constants were derived for $4d^5$ ions in trigonal fields, by involving the contributions from the orbital reduction (or covalency effect) and spin-orbit coupling interactions (Abragam and Bleaney, 1970; Geschwind and Remeika, 1962). Further, in consideration of the anisotropies (different orbitals behaviours for the π and σ components) of these contributions, improved investigations were carried out based on the molecular orbital calculations (O'Reilly and Offenbacher, 1971). Thus, the formulas of the EPR parameters for trigonal $5d^5$ clusters can be expressed as:

$$g_{//} = 2 \mid (1+k_\pi) \cos^2\alpha - \sin^2\alpha \mid,$$
$$g_\perp = 2 \mid k_\sigma \sin2\alpha/\sqrt{2} + \sin^2\alpha \mid,$$
$$A_{//} = P \kappa \cos2\alpha + 2 N_\pi P [-2 N_\pi/7 - 6 \cos^2\alpha + 3\sin2\alpha/(7\sqrt{2})]$$
$$A_\perp = P \kappa \sin^2\alpha - 2 N_\pi^2 P [\sin^2\alpha/7 + 11 \sin2\alpha/(14\sqrt{2})] \tag{1}$$

with

$$\alpha = \frac{1}{2} \tan^{-1} \frac{\sqrt{2}\zeta_\sigma}{\frac{1}{2}\zeta_\pi - V} \tag{2}$$

where N_π and N_σ are the normalization factors of the $t^\pm$ (or ^2E_g) and t^0 (or $^2A_{1g}$) components. $P = g_s g_n \beta \beta_n$ is the dipolar hyperfine structure parameter of Ir^{4+}. κ is the core polarization constant. The trigonal field parameter V can be calculated from the local structure of the impurity center, by using the generalized crystal-field model (Zhao and Lei, 1997):

$$V = 9 (3\cos^2\beta-1) eq <r^2>/(7R^3) + 5 (35\cos^4\beta-30\cos^2\beta + 3) eq <r^4>/(21R^5)$$
$$+ 5\sqrt{2} \sin^3 \beta \cos \beta eq <r^4>/(3R^5), \tag{3}$$

where q (= 2e) is the effective charge of the oxygen ligand in view of an equivalent t_{2g} hole in the central Ir^{4+}. R and β are the metal-ligand bonding length and the bonding angle related to the C_3 axis. Thus, the local structure (or trigonal distortion) of the impurity center is connected with the trigonal field parameter V and hence with the EPR parameters, particularly the anisotropy Δg (= $g_\perp$-$g_{//}$). $<r^n>$ (n = 2, 4) are the expectation values of the 5d radial wavefunction of Ir^{4+} in crystals, which can be expressed in terms of the corresponding free-ion values (Abragam and Bleaney, 1970) and the average covalency factor N in consideration of the covalency (or admixture) between the central metal and the ligand orbitals (Zhao and Lei, 1997):

$$<r^2> \approx 2.43\ N^2\ a.u., \quad <r^4> \approx 9.38\ N^2\ a.u.. \tag{4}$$

The orbital reduction factors k_π and k_σ as well as the spin-orbit coupling coefficients ζ_π and ζ_σ in the above formulas are determined from the cluster approach similar to the treatments in recent work (Dong and Chen, 2006):

$$k_\pi = N_\pi\ (1 + \lambda_\pi^2/2), \qquad k_\sigma = (N_\pi N_\sigma)^{\frac{1}{2}}\ [1 - \lambda_\pi\ (\lambda_\sigma + \lambda_s A)/2],$$
$$\zeta_\pi = N_\pi\ (\zeta_d^0 + \lambda_\pi^2\ \zeta_p^0/2), \qquad \zeta_\sigma = (N_\pi N_\sigma)^{\frac{1}{2}}(\zeta_d^0 - \lambda_\pi\ \lambda_\sigma \zeta_p^0/2), \tag{5}$$

where A denotes the integral $R\left\langle ns\ |\ \frac{\partial}{\partial y}\ |\ np_y \right\rangle$. ζ_d^0 and ζ_p^0 are the spin-orbit coupling coefficients of the free $5d^5$ and the ligand ions, respectively. λ_γ ($\gamma = \pi$, σ and s) are the admixture coefficients for the various components of the orbitals. They and the normalization factors can be determined from the empirical relationship

$$N^2 = N_\pi^2\ [1 + \lambda_\pi^2\ S_\pi^2 - 2\ \lambda_\pi\ S_\pi],$$
$$N^2 = N_\sigma^2\ [1 + \lambda_\sigma^2\ S_\sigma^2 + \lambda_s^2\ S_s^2 - 2\lambda_\sigma\ S_\sigma - 2\ \lambda_s\ S_s], \tag{6}$$

and the normalization conditions

$$N_\pi\ (1 - 2\lambda_\pi\ S_\pi + \lambda_\pi^2) = 1,$$
$$N_\sigma\ (1 - 2\lambda_\sigma\ S_\sigma - 2\lambda_s\ S_s + \lambda_\sigma^2 + \lambda_s^2) = 1. \tag{7}$$

Here S_γ are the group overlap integrals between central ion and the ligand orbitals. In general, the admixture coefficients increase with the increase of the group overlap integrals and one can approximately apply the proportional relationship between the admixture coefficients and the related group overlap integrals, i.e., $\lambda_\sigma/S_\sigma \approx \lambda_s/S_s$ within the same σ component. Obviously, when taking $S_\gamma = \lambda_\gamma = 0$ and A = 0, the above formulas return to those in the absence of the ligand contributions (Abragam and Bleaney, 1970; Geschwind and Remeika, 1962).

For the studied Ir^{4+} center in $KNbO_3$, from the Nb^{5+}-O^{2-} distance R [$\approx$ 2.01 Å (Possenriede *et al.*, 1989)] and the Slater-type SCF functions (Clementi and Raimondi, 1963), the integrals $S_\pi \approx 0.0176$, $S_\sigma \approx 0.0544$, $S_s \approx 0.0436$ and A $\approx$ 1.3089 are calculated.

As mentioned before, the impurity-ligand bonding angle β may be slightly different from the host β_H due to the charge and size mismatching substitution of Nb^{5+} by Ir^{4+}. For convenience, one can express the local angle in terms of the angular distortion $\Delta\beta$ as $\beta = \beta_H + \Delta\beta$. Thus, only the average covalency factor N and the local angle β (or angular distortion $\Delta\beta$) are unknown in the formulas of the g factors. Substituting these values into Eq. 1-3 and fitting the calculated g factors to the observed values, we have

$$N \approx 0.815, \qquad \Delta\beta \approx 0.47°. \tag{8}$$

Table 1: The EPR parameters for the trigonal Ir^{4+} center in $KNbO_3$

Parameters	Cal. [a]	Cal. [b]	Cal. [c]	Cal. [d]	Expt. [e]
$g_{//}$	1.667	2.010	1.486	1.651	1.651
$g_\perp$	1.667	1.504	1.880	1.666	1.666
$A_{//}$ (10^{-4} cm^{-1})	-	-20.0	-20.0	-20.0	-22.0
$A_\perp$ (10^{-4} cm^{-1})	-	-17.0	-16.0	-17.0	-

[a]Calculations based on the simple cubic formula $g = (g_s + 4k)/3$, with the spin-only value $g_s = 2.0023$ and the fitted orbital reduction factor $k \approx 0.75$, in the previous work (Possenriede *et al.*, 1989). [b]Calculations based on the formulas Eq. 1-3 in this work and the structure parameters of the host Nb^{5+} site (i.e., $\Delta\beta = 0$). [c]Calculations based on the angular distortion $\Delta\beta$ in Eq. 8 and neglecting of the ligand orbital and spin-orbit coupling contributions in this work. [d]Calculations based on both the angular distortion $\Delta\beta$ in Eq. 8 and the ligand orbital and spin-orbit coupling contributions in this work. [e]Possenriede *et al.* (1989).

Thus the molecular orbital coefficients $N_\pi \approx 0.822$, $N_\sigma \approx 0.844$, $\lambda_\pi \approx 0.484$, $\lambda_\sigma \approx 0.394$ and $\lambda_s \approx 0.316$ can be calculated from Eq. 6 and 7. By using the free-ion values $\zeta_d^0 \approx 2400$ cm^{-1} for Ir^{4+} (Raizman and Suss, 1980) and $\zeta_p^0 \approx 603$ cm^{-1} for O^{2-} (O'Reilly and Offenbacher, 1971), the parameters $\zeta_\pi \approx 2030$ cm^{-1}, $\zeta_\sigma \approx 1951$ cm^{-1}, $k_\pi \approx 0.918$ and $k_\sigma \approx 0.670$ are obtained from Eq. 5. The corresponding g factors are shown in Table 1. Substituting the dipolar hyperfine structure parameter $P \approx 33 \times 10^{-4}$ cm^{-1} (Schirmer *et al.*, 1984) for Ir^{4+} into the formulas of the hyperfine structure constants and fitting the calculated results to experiment, one can acquire the core polarization constant

$$\kappa \approx 0.80 \qquad\qquad (9)$$

The corresponding theoretical results are also shown in Table 1. For comparison, the calculated results based on the fitted orbital reduction factor k (≈ 0.75) and the simple cubic formula $g = (g_s + 4k)/3$, with the spin-only value $g_s = 2.0023$ in the previous work (Possenriede *et al.*, 1989) are also given in Table 1. In addition, the EPR parameters based on Eq. 1-3 but in the absence of the angular distortion (i.e., $\Delta\beta = 0$) and those based on the formulas Eq. 1-3 and the angular distortion in Eq. 8 but in the absence of the ligand orbital and spin-orbit coupling contributions (i.e., $\zeta_\pi = \zeta_\sigma = N \zeta_d^0$, $k_\pi = k_\sigma = N$) in this work are collected in Table 1, too.

DISCUSSION

From Table 1, one can find that the theoretical g factors and $A_{//}$ (Cal. [d]) based on the angular distortion $\Delta\beta$ in Eq. 8 of this work are in good agreement with the observed values. Meanwhile, the calculation results by considering the $\Delta\beta$ and the ligand contributions (Cal. [d]) are also better than those of the previous treatments (Possenriede *et al.*, 1989) based on cubic case (Cal. [a]) and those in the absence of the angular distortion (Cal. [b]) or ligand orbital and spin-orbit coupling contributions (Cal. [c]).

- The calculated g factors based on the host angle β_H [$\approx 54.62°$ (Possenriede *et al.*, 1989)] are in poor agreement with the observed values, particularly, the anisotropy Δg is opposite in sign and one order in magnitude larger than the experimental value. This means that the property (elongation or compression of the ligand octahedron along the C_3 axis) and the magnitude of the trigonal distortion based on the structure parameters of the host Nb^{5+} site are not suitable for the studied $[IrO_6]^{-8}$ cluster. Therefore, the oxygen octahedron is expected to suffer certain compression and to change from elongation ($\beta_H < \beta_0$) in the host to compression ($\beta \approx 55.09° > \beta_0$) in the impurity center. Thus, the positive angular distortion $\Delta\beta$ and the compression of the ligand octahedron for the Ir^{4+} center related to the host Nb^{5+} site in $KNbO_3$ can be understood. It is noted that the above conclusion for the positive $\Delta\beta$ in $KNbO_3$:Ir^{4+} here is opposite to that in the similar rhombohedral $KNbO_3$:$Fe^{3+}(3d^5)$, where $\Delta\beta$ ($\approx -0.17°$) was obtained by superposition model analyses (Possenriede *et al.*, 1989). In fact, since the impurity Fe^{3+} has less

charge (+3e) and smaller ionic radius [$\approx$ 0.64Å (Weast, 1989)] than those [+5e and 0.69Å (Weast, 1989)] of the host Nb^{5+}, the electrostatic interactions between the impurity and the ligand triangles may become weaker. As a result, the ligand triangles tend to displace away from the impurity by an amount and decrease the bonding angles related to the C_3 axis in the Fe^{3+} center. For the studied Ir^{4+} center in this work, the charge (+4e) and ionic radius [$\approx$ 0.68Å (Weast, 1989)] are close to but slightly smaller than those of the replaced cation. The impurity-ligand interactions would also be weaker than those in the host and a smaller angle (or negative $\Delta\beta$) would be expected. On the other hand, however, the $5d^5$ cluster with $^2T_{2g}$ three-fold orbital ground state of Ir^{4+} may suffer the Jahn-Teller effect, characterized by compression of the impurity-ligand bonds (or increase of the bonding angle β) along the C_3 axis. Therefore, the positive angular distortion $\Delta\beta$ obtained in this work suggests that the influence of the Jahn-Teller effect on the local structure of the $[IrO_6]^{-8}$ cluster seem to be stronger than that of the charge or size mismatching substitution of Nb by Ir.

- When the ligand orbital and spin-orbit coupling contributions were neglected, the theoretical results (Cal. °) do not show good agreement with the observed values, i.e., the calculated Δg is much (one order in magnitude) larger than the exact result. In fact, due to the high valence state of Ir^{4+} belonging to the third transition-metal ions, it has some covalency even in oxides. This point can be illustrated by the small covalency factor N [$\approx$ 0.815, which is comparable with the fitted orbital reduction factor k $\approx$ 0.75 based on the cubic case in the previous work (Possenriede *et al.*, 1989)] and the moderate orbital admixture coefficients ($\lambda_\pi \approx$ 0.484, $\lambda_\sigma \approx$ 0.394 and $\lambda_s \approx$ 0.316) obtained in this work. Further, by neglecting the contributions from the ligand orbitals and the spin-orbit coupling coefficients, good agreement between theory and experiment can hardly be achieved, by adjusting the values of N and $\Delta\beta$. Therefore, the anisotropic contributions to the EPR parameters from different (π and σ) components of the spin-orbit coupling (including both of the metal and the ligands) and the orbital angular momentum (orbital reduction factor) interactions should be taken into account based on the cluster approach.

- The experimental $A_\perp$ was not obtained due to the unresolved EPR signals (Possenriede *et al.*, 1989). According to the present studies, $5d^5$ ions in trigonally compressed octahedra would yield $|g_\perp/g_{//}| > 1$ and $|A_\perp/A_{//}| < 1$. In addition, the fitted core polarization constant κ ($\approx$ 0.80) in this work is also in consistence with the expectation (0.86 ~ 0.9) of some earlier studies (Raizman and Suss, 1980; Davies and Owen, 1969) and can be regarded as reasonable.

CONCLUSION

In conclusion, the EPR parameters and the local structure for the trigonal Ir^{4+} center in $KNbO_3$ are theoretically studied based on the cluster approach. The metal-ligand bonding angle β related to the C_3 axis in the impurity center is found to be about 0.47° larger than that in the host due to the Jahn-Teller effect and the charge or size mismatching substitution, which leads to compression of the ligand octahedron in the impurity center.

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