



Theoretical studies of the g factors and local structure for the tetragonal Nd^{3+} center in SrTiO_3

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ABSTRACT

The anisotropic g factors g_{\parallel} and g_{\perp} and the local structure for the tetragonal Nd^{3+} center in SrTiO_3 are theoretically studied using the perturbation formulas of the g factors for a $4f^3$ ion in tetragonal symmetry. This center is attributed to the impurity Nd^{3+} occupying the dodecahedral Sr^{2+} site in SrTiO_3 , associated with one nearest neighbour interstitial oxygen O_i along $[001]$ (or C_4) axis. The impurity Nd^{3+} is found to suffer the large displacement ($\approx 1.1 \text{ \AA}$) towards the O_i along the C_4 axis due to their strong interaction. The calculated g factors based on the above impurity axial displacement show reasonable agreement with the experimental results.

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1. Introduction

SrTiO_3 doped with Nd^{3+} has aroused interest of researchers due to the unique thermoelectric, [1] luminescence [2–4] and electronic structure [5] properties as well as the applications of the substrates for the high- T_c superconductor films [6,7]. In general, these properties are closely related to the local structure and electronic states of the impurity ion in the host, which can be effectively investigated by means of electron paramagnetic resonance (EPR) technique. For instance, EPR studies were measured for Nd^{3+} doped SrTiO_3 , and the gyromagnetic factors g_{\parallel} and g_{\perp} were determined for the tetragonal Nd^{3+} center decades ago [8,9]. Up to now, however, the above experimental results have not been quantitatively explained, and the information about the local structure of this impurity center has not been obtained either. Usually, such information can be helpful to understand the properties of this model material SrTiO_3 (or other important perovskite-type oxides) containing rare-earth dopants [10,11]. Thus, theoretical studies on the g factors and the local structure for $\text{SrTiO}_3:\text{Nd}^{3+}$ are of special scientific and technical significance. In this work, the EPR spectra and the defect structure of the above Nd^{3+} center in SrTiO_3 are theoretically investigated from the perturbation formulas of the g factors for a $4f^3$ ion under tetragonal symmetry. In the studies, the defect structure model for the impurity center is proposed, by considering the suitable local lattice distortion due to the strong interaction between the impurity and the charge compensator.

2. Calculation

When Nd^{3+} is doped into the lattice of SrTiO_3 , it can occupy the dodecahedral Sr^{2+} site because of their similar ionic radii. Since the impurity Nd^{3+} has extra charge as compared with the host Sr^{2+} , one nearest neighbour interstitial oxygen (labeled as O_i) may occur along $[001]$ (or C_4) axis as the charge compensator and thus form a tetragonally (C_{4v}) distorted dodecahedral $[\text{NdO}_{13}]^{23-}$ cluster. Similar tetragonal impurity center (i.e., $[\text{FeO}_{13}]^{23-}$ cluster) was also reported for Fe^{3+} on the dodecahedral K^+ site in KTaO_3 [12]. In view of the strong electrostatic interaction and chemical bonding between the Nd^{3+} and the negative O_i , the impurity Nd^{3+} is expected to suffer a displacement (labeled as ΔZ) towards the compensator along the C_4 axis. Thus, the local structure of this tetragonal center can be described by the impurity displacement ΔZ .

For an $\text{Nd}^{3+}(4f^3)$ ion under tetragonal symmetry, the ground $4I_{9/2}$ configuration would be separated into five Kramers doublets via the combination of the spin–orbit coupling and tetragonal crystal–field interactions. To study the EPR spectra and the local structure for $\text{SrTiO}_3:\text{Nd}^{3+}$, the perturbation formulas of the g factors for a $4f^3$ ion under tetragonal symmetry are adopted [13]:

$$g_{\parallel} = 2g_j < \Gamma_{\gamma} \hat{J}_z | \Gamma_{\gamma} > + 2 \sum_X' \frac{< \Gamma_{\gamma} | \hat{H}_{CF} | \Gamma_X \gamma_X > < \Gamma_X \gamma_X | \hat{J}_z | \Gamma_{\gamma} >}{E(\Gamma_X) - E(\Gamma)}$$

$$g_{\perp} = g_j < \Gamma_{\gamma} \hat{J}_{\pm} | \Gamma_{\gamma} > . \quad (1)$$

here g_j are the Landé factors for various $2S+1L_J$ configurations, which are given in Refs. [14,15]. The operator $\hat{J}_{\pm} (= \hat{J}_X + i\hat{J}_Y)$ stands for the

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linear combination of the X - and Y -components for the total angular momentum operator \hat{J} . $\Gamma\gamma$ and $\Gamma_x\gamma_x$ denote the basis functions of the lowest and the higher Kramers doublets. It is noted that the off-diagonal matrix elements g_j' may occur in the expansions of Eq. (1) for the \hat{J}_z and \hat{J}_+ interactions between different $^{2S+1}L_J$ configurations. The basis $\Gamma\gamma(\gamma')$ (where γ and γ' are the two components of the Γ irreducible representation) includes the admixtures of various energy levels, i.e., the admixture between the ground $^4I_{9/2}$ and the first excited $^4I_{11/2}$ states via the crystal-field interaction, the admixture among $^2H_{9/2}$, $^4G_{9/2}$ and $^4I_{9/2}$ and that among $^2I_{11/2}$, $^2H_{11/2}$ and $^4I_{11/2}$ via the spin-orbit coupling interaction. In detail, the basis $\Gamma\gamma(\gamma')$ can be written as [13]:

$$|\Gamma\gamma(\gamma')\rangle = \sum_{M_{J1}} C(^4I_{9/2}; \Gamma\gamma(\gamma')M_J) N_{9/2} (|^4I_{9/2}M_{J1}\rangle + \lambda_H|^2H_{9/2}M_{J1}\rangle + \lambda_G|^4G_{9/2}M_{J1}\rangle) + \sum_{M_{J2}} C(^4I_{11/2}; \Gamma\gamma(\gamma')M_J) N_{11/2} (|^4I_{11/2}M_{J2}\rangle + \lambda_{H'}|^2H_{11/2}M_{J2}\rangle + \lambda_{I'}|^2I_{11/2}M_{J2}\rangle), \quad (2)$$

where M_{J1} and M_{J2} are within the ranges of $-9/2$ to $9/2$ and $-11/2$ to $11/2$, respectively. The coefficients $C(^4I_{9/2}; \Gamma\gamma(\gamma')M_J)$ or $C(^4I_{11/2}; \Gamma\gamma(\gamma')M_{J2})$ can be determined by diagonalizing the 22×22 energy matrix containing the $^4I_{9/2}$ and $^4I_{11/2}$ states. N_j ($j=9/2$ and $11/2$) and λ_α ($\alpha=H, G, H'$ and I) are, respectively, the normalization factors and the admixture coefficients for the related configurations, which are usually calculated using the perturbation method in terms of the spin-orbit coupling matrix elements [13].

The crystal-field interaction Hamiltonian \hat{H}_{CF} for a $4f^3$ ion in C_{4v} symmetry may be written in terms of the Stevens operator equivalents [14,15]:

$$\hat{H}_{CF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^4 O_4^4 + B_6^4 O_6^4. \quad (3)$$

here B_k^q ($k=2, 4, 6$; $|q| \leq k$) stands for the crystal-field parameters, which are expressed from the local structure of the impurity center. As mentioned above, the impurity Nd^{3+} may experience the axial displacement ΔZ towards the O_1 . In fact, the O_1 and the Nd^{3+} are actually close to each other along the C_4 axis due to the strong electrostatic attraction, forming the covalent $Nd^{3+}-O^{2-}$ bond. This point is supported by the studies on trivalent Fe^{3+} substituting for K^+ in $KTaO_3$, [12] with the average $Fe^{3+}-O_1$ bond length R_1 about 0.19 \AA smaller than the sum of the radii for both ions. Since Nd^{3+} has the same charge state and the similar ionicity to Fe^{3+} , the $Nd^{3+}-O_1$ bond length R_1 may be approximately taken as $(r_{Nd^{3+}} + r_{O^{2-}}) - 0.19 \approx 2.125 \text{ \AA}$ by using $r_{Nd^{3+}} \approx 0.995 \text{ \AA}$ and $r_{O^{2-}} \approx 1.32 \text{ \AA}$ [16]. For convenience, the local impurity-ligand bond lengths and angles are divided into four groups (see Fig. 1):

$$R_1 = \left[\frac{a^2}{4} + \left(\frac{a}{2} - \Delta Z \right)^2 \right]^{1/2}, \quad R_2 = (R_0^2 + \Delta Z^2)^{1/2}, \quad R_3 = \left[\frac{a^2}{4} + \left(\frac{a}{2} + \Delta Z \right)^2 \right]^{1/2}, \quad R_4 = R_l \quad (4)$$

$$\theta_1 = \text{tg}^{-1} \left(\frac{a}{a - 2\Delta Z} \right), \quad \theta_2 = \frac{\pi}{2} + \text{tg}^{-1} \left(\frac{\Delta Z}{R_0} \right), \quad \theta_3 = \frac{\pi}{2} + \text{tg}^{-1} \left(\frac{a}{a + 2\Delta Z} \right), \quad \theta_4 = 0.$$

here $a \approx 3.906 \text{ \AA}$ [17,18] is the lattice constant of $SrTiO_3$. Thus, the crystal-field parameters are determined from the superposition model [19] and the local geometrical relationship of the studied system:

$$B_k^q = \sum_{j=1}^4 \bar{A}_k K_k^q(\theta_j, \phi_j) \left(\frac{R_0}{R_j} \right)^{t_k}, \quad (5)$$

where $K_k^q(\theta_j, \phi_j)$ are the coordination factors [19,20] based on the above local impurity-ligand bond lengths and angles in Eq.

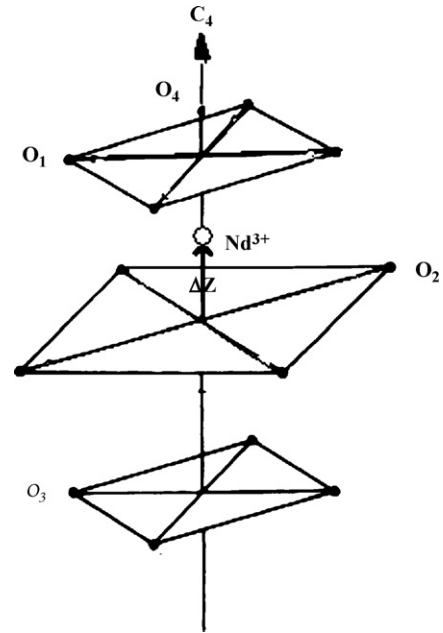


Fig. 1. Local structure for the tetragonal Nd^{3+} center in $SrTiO_3$. The impurity Nd^{3+} on the dodecahedral Sr^{2+} site experiences the large displacement ΔZ ($\approx 1.1 \text{ \AA}$) towards the nearest neighbour interstitial oxygen O_1 (labeled as O_4) along the C_4 axis.

(4). The quantities \bar{A}_k and t_k are the intrinsic parameters (with the reference distance R_0) and the power-law exponents, respectively. Here the reference distance is taken as the cation-anion distance for the host Sr^{2+} site in $SrTiO_3$, i.e., $R_0 = a/\sqrt{2} \approx 2.762 \text{ \AA}$. From Ref. [21], the power-law exponents $t_2 \approx 3.5$, $t_4 \approx t_6 \approx 6$ and the intrinsic parameters $\bar{A}_2 \approx 522 \text{ cm}^{-1}$, $\bar{A}_4 \approx 66.3 \text{ cm}^{-1}$ and $\bar{A}_6 \approx 4.1 \text{ cm}^{-1}$ are obtained for the similar tetragonal $Nd^{3+}-O^{2-}$ cluster in $CaWO_4:Nd^{3+}$. These parameters are approximately adopted for $SrTiO_3:Nd^{3+}$ here.

The free-ion parameters of the Coulomb repulsion ($F^2 \approx 71,090 \text{ cm}^{-1}$, $F^4 \approx 50,917 \text{ cm}^{-1}$ and $F^6 \approx 34,173 \text{ cm}^{-1}$), the two-body interaction parameters ($\alpha \approx 20.8 \text{ cm}^{-1}$, $\beta \approx -651 \text{ cm}^{-1}$ and $\gamma \approx 1868 \text{ cm}^{-1}$) and the spin-orbit coupling coefficient ($\zeta_{4f} \approx 875 \text{ cm}^{-1}$) were acquired for the similar $Nd^{3+}-O^{2-}$ combination in $YAG:Nd^{3+}$ [22]. These values can also be applied here. In consideration of the covalency between the Nd^{3+} 4f orbitals and the O^{2-} 2p orbitals for the $Nd^{3+}-O^{2-}$ bonds in $SrTiO_3:Nd^{3+}$, the orbital reduction factor k (≈ 0.9818) [23] for the $Nd^{3+}-F$ bonds in $CaF_2:Nd^{3+}$ may also be used here due to the similarity in covalency for the ligands O^{2-} and F^- [24,25]. Thus, there is only one unknown parameter, i.e., the impurity displacement ΔZ , in the formulas of the g factors. Substituting these values into Eq. (1)

and fitting the theoretical results to the experimental data, one can obtain $\Delta Z \approx 1.1 \text{ \AA}$. Here the displacement direction towards the interstitial oxygen O_1 is defined as positive. The calculated g factors together with the anisotropy $\Delta g (=g_{||} - g_{\perp})$ and the average $\bar{g} [= (g_{||} + 2g_{\perp})/3]$ are compared with the observed values in Table 1. In order to clarify the importance of the contributions from the compensator O_1 and the impurity displacement, the results (Cal.^a) based on omission of the crystal-fields arising from the O_1 (i.e., taking the distance $R_1 \rightarrow \infty$ in Eq. (5)) and those (Cal.^b) based on omission of

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