Theoretical Investigations of the Defect Structure and the *g* Factors of a Tetragonal Ni^{3+} Center in $PbTiO_3$

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The defect structure and the anisotropic *g* factors of a tetragonal Ni^{3+} center in $PbTiO_3$ are theoretically investigated from improved perturbation formulas of the *g* factors for a $3d^7$ ion with low spin $S = 1/2$ in tetragonally elongated octahedra, established in this work. Based on the studies, the distance between the impurity Ni^{3+} and the center of the oxygen octahedron is found to be about 0.14 Å, which is smaller than that (≈ 0.3 Å) for the host Ti^{4+} site due to the inward shift (≈ 0.16 Å) towards the center of the oxygen octahedron. The theoretical *g* factors based on the above defect structure agree well with the observed values.

Key words: Defect Structures; Electron Paramagnetic Resonance; Crystal-Fields and Spin Hamiltonian; Ni^{3+}; $PbTiO_3$.

1. Introduction

As an ideal prototype ferroelectric $PbTiO_3$ undergoes the mainly displacive phase transition from a paraelectric cubic (*Pm*3*m*) to a ferroelectric tetragonal (*P*4*mm*) structure [1, 2]. Usually, the properties of this material depend strongly on the microscopic structure (e. g., atomic displacements) and can be probed by some paramagnetic transition metal ions (such as Cr^{3+}, Fe^{3+}, Mn^{4+}). These investigations were carried out by means of electron paramagnetic resonance (EPR) technique [3 – 7]. For instance, the EPR spectra of Ni^{3+} ($3d^7$) with low spin $S = 1/2$ in a $PbTiO_3$ crystal have been observed, and the anisotropic *g* factors $g_\parallel$ and $g_\perp$ for one tetragonal Ni^{3+} center were also measured at 77 K [7]. Until now, however, the above EPR experimental results have not been theoretically interpreted, and the defect structure, e. g., impurity displacement along the crystalline axis, of this center has not been determined, either. Compared with the works on common high spin $S = 3/2$ systems [e. g., $3d^3$ (Cr^{3+}, Mn^{4+}) and $3d^7$ (Fe^+, Co^{2+}) ions in oxides], studies on the low spin ($S = 1/2$) $3d^7$ ions (e. g., Ni^{3+}) are relatively rare. Information about the defect structure in $PbTiO_3$ may be helpful for the understanding of properties of this material with transition metal dopants, therefore investigations on the local structure and the *g* factors for the above tetragonal Ni^{3+} center are of significance.

In this work, the anisotropic *g* factors and the defect structure of a tetragonal Ni^{3+} center in $PbTiO_3$ are theoretically studied by improved perturbation formulas of the *g* factors for a $3d^7$ ion with low spin $S = 1/2$ in tetragonal symmetry. In these formulas, the contributions of the spin-orbit coupling coefficient and the s- and p-orbitals of the ligands are taken into account.

2. Calculations

In $PbTiO_3$, both the host Pb and Ti atoms suffer large displacements from their corresponding oxygen planes by about 0.47 and 0.3 Å at room temperature, resulting in a colossal tetragonality of 6.5% along with a 0.75 C/m^2 spontaneous polarization [2, 8]. When a Ni^{3+} ion enters the lattice, it prefers to locate at the octahedral Ti^{4+} site due to their similar ionic radii and charge, forming the $[NiO_6]^{9-}$ cluster. The local structure of the studied impurity center may be described by the effective distance $\Delta Z'$ between the impurity and the center of the oxygen octahedron, which would be dissimilar to that ($\Delta Z \approx 0.3$ Å [2]) for the host Ti^{4+} site due to the charge and / or size mismatching substitution.

A Ni^{3+} ($3d^7$) ion in strong crystal-fields (e. g., oxides) can be characterized as an unpaired electron in e_g state, associated with the ground orbital doublet ^2E_g ($t_{2g}{}^6e_g$) having a low spin ($S = 1/2$) [9, 10]. This point is different from other $3d^7$ ions (e. g., Co^{2+} and Fe^+) in oxides, with the ground orbital triplet $^4T_{1g}$ ($t_{2g}{}^4e_g{}^3$) of high spin $S = 3/2$. As the ligand octahedron is elongated, the ground ^2E_g state of the $[NiO_6]^{9-}$ cluster would be split into two orbital singlets $\varepsilon(|x^2-y^2\rangle)$ and $\theta(|z^2\rangle)$, with the latter lying lowest [10].

The perturbation formulas of the g factors $g_\parallel$ and $g_\perp$ for the lowest θ irreducible representation of the $3d^7$ ion in tetragonally elongated octahedra have been established by including the contributions from the excited states via the metal spin-orbit coupling coefficient and the cubic crystal-field interactions [10]. However, the contributions from the low symmetrical (tetragonal) crystal-fields and the orbital reduction factor due to the covalent reduction of the orbital angular momentum interaction were not taken into account. In addition, the contributions from the ligand spin-orbit coupling coefficient and the ligand orbitals were neglected as well. In order to investigate the Ni^{3+} center in $PbTiO_3$, the conventional formulas in [10] are to be improved by including the above contributions. By using the perturbation method similar to that in [10], the new formulas of the g factors for the tetragonally elongated $3d^7$ cluster can be derived as follows:

$$\begin{aligned} g_\parallel &= g_s + 2k'\zeta'^2/E_{1\parallel}{}^2 - 4k\zeta(1/E_{2\parallel} - 1/E_{5\parallel}), \\ g_\perp &= g_s + 2k'\zeta'^2/E_{1\perp}{}^2 \\ &\quad + 3k\zeta/E_\perp - k'\zeta'(1/E_{2\perp} - 1/E_{5\perp}), \end{aligned} \tag{1}$$

with

$$1/E_\perp = 1/E_{3\perp} + 1/E_{4\perp} + 0.38(1/E_{3\perp} - 1/E_{4\perp}). \tag{2}$$

Here g_s ($= 2.0023$) is the spin-only value. E_i ($i = 1, 2, 3, 4, 5$) are the energy separations between the excited $^4T_{1b}$, $^2T_{1a}$, $^2T_{2a}$, $^2T_{2b}$ and $^2T_{1b}$ and the lowest $^2E(\theta)$ states in tetragonal symmetry. The subscripts α ($= \parallel$ and $\perp$) denote the various components of the related energy differences due to the tetragonal splittings. They can be obtained from the energy matrices of the $3d^7$ ion in tetragonal symmetry:

$$\begin{aligned} E_{1\parallel} &= 10Dq - 4B - 4C, \\ E_{1\perp} &= 10Dq - 4B - 4C - 3Ds + 5Dt, \\ E_{2\parallel} &= 10Dq + 2B - C, \\ E_{2\perp} &= 10Dq + 2B - C + 3Ds - 5Dt, \\ E_{3\perp} &= 10Dq + 6B - C - 3Ds + 5Dt, \\ E_{4\perp} &= 10Dq + 14B + C - 3Ds + 5Dt, \\ E_{5\parallel} &= 10Dq + 6B - C, \\ E_{5\perp} &= 10Dq + 6B - C + 3Ds - 5Dt, \end{aligned} \tag{3}$$

where B and C are the Racah parameters of the $3d^7$ ion in crystals. Dq is the cubic field parameter, and Ds and Dt are the tetragonal ones. Obviously, when neglecting the contributions from the tetragonal distortion (i. e., $Ds = 0$ and $Dt = 0$), the above formulas return to those of the previous work [10].

In the above formulas, the spin-orbit coupling coefficients ζ, ζ' and the orbital reduction factors k, k' denote the anisotropic (diagonal and off-diagonal) contributions for the irreducible representations γ ($= e_g$ and t_{2g}) in the $3d^7$ octahedral clusters. They can be expressed as

$$\begin{aligned} \zeta &= N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0/2), \\ \zeta' &= (N_tN_e)^{1/2}(\zeta_d^0 - \lambda_t\lambda_e\zeta_p^0/2), \\ k &= N_t(1 + \lambda_t^2/2), \\ k' &= (N_tN_e)^{1/2}[1 - \lambda_t(\lambda_e + \lambda_s A)/2], \end{aligned} \tag{4}$$

where ζ_d^0 and ζ_p^0 are the spin-orbit coupling coefficients of the free $3d^7$ and the ligand ions, respectively. N_γ and λ_γ (or λ_s) are, respectively, the normalization factors and the orbital admixture coefficients. A is the integral $R\langle ns|\frac{\partial}{\partial y}|np_y\rangle$, where R is the impurity-ligand distance of the studied systems. By applying the semiempirical method similar to that in [12], the molecular orbital coefficients N_γ and λ_γ (or λ_s) can be determined by the normalization conditions

$$\begin{aligned} &N_t(1 - 2\lambda_t S_{dpt} + \lambda_t^2) = 1, \\ &N_e(1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) = 1, \end{aligned} \tag{5}$$

and the approximate relationship

$$\begin{aligned} N^2 &= N_t^2[1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}], \\ N^2 &= N_e^2[1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}]. \end{aligned} \tag{6}$$

Here $S_{dp\gamma}$ (and S_{ds}) are the group overlap integrals, N is the average covalency factor, characteristic of the covalency effect (or reduction of the Racah parameters B and C) of the central ion in crystals. In general, the admixture coefficients increase with increasing the group overlap integrals, and one can approximately adopt the proportional relationship between the admixture coefficients and the related group overlap integrals, i. e., $\lambda_e/S_{dpe} \approx \lambda_s/S_{ds}$ within the same irreducible representation e_g.

The tetragonal field parameters Ds and Dt can be determined from the local structure of the impurity center by using the superposition model [13]:

$$\begin{aligned} Ds &= (2/7)\bar{A}_2[2(3\cos^2\theta - 1)R_0/R_2)^{t2} \\ &\quad + (R_0/R_{11})^{t2} + (R_0/R_{12})^{t2}], \\ Dt &= (4/21)\bar{A}_4 \\ &\quad \cdot [(35\cos^4\theta - 30\cos^2\theta + 3 - 7\sin^4\theta) \\ &\quad \cdot (R_0/R_2)^{t4} + 2(R_0/R_{11})^{t4} + 2(R_0/R_{12})^{t4}], \end{aligned} \tag{7}$$

with

$$\begin{aligned} &R_{11} \approx R_\parallel - \Delta Z', \quad R_{12} \approx R_\parallel + \Delta Z', \\ &R_2 \approx (R_\perp^2 + \Delta Z'^2)^{1/2}. \end{aligned} \tag{8}$$

Here $\bar{A}_2$ and $\bar{A}_4$ are the intrinsic parameters, with the reference (average) bond length R_0. For $3d^n$ ions in octahedra, $\bar{A}_4(R_0) \approx (3/4)Dq$ and $\bar{A}_2(R_0) \approx 10.8\bar{A}_4(R_0)$ are valid in many crystals [13–15]. t_2 (≈ 3) and t_4 (≈ 5) are the power-law exponents [13]. R_{11} and R_{12} are the impurity-ligand distances in the C_4 axis, and R_2 ($\times 4$) are the bonding lengths between Ni^{3+} and the four planar oxygen ions. Because of the new distance $\Delta Z'$, the impurity-ligand bonding lengths are usually unlike the host Ti-O distances $R_\parallel \approx 2.076$ Å and $R_\perp \approx 1.952$ Å [2,8] parallel and perpendicular to the C_4 axis for the center of the oxygen octahedron in the host $PbTiO_3$. θ is the angle between R_2 and the C_4 axis. Thus, the defect structure (or tetragonal distortion) of the impurity center is connected with the tetragonal field parameters Ds and Dt and hence with the g factors, particularly the anisotropy Δg ($= g_\perp - g_\parallel$).

Since the ionic radius r_i (≈ 0.74 Å [16]) of the impurity Ni^{3+} is slightly smaller than the radius r_h (≈ 0.745 Å [16]) of the host Ti^{4+}, the effective (or average) impurity-ligand distance may be approximately modified by an amount $(r_i - r_h)/2$ [17–19], yielding $R_0 \approx \bar{R} \approx 1.990$ Å. From the distance R_0 and the Slater-type SCF functions [20,21], the group overlap integrals $S_{dpt} \approx 0.0120$, $S_{dpe} \approx 0.0383$, $S_{ds} \approx 0.0307$ and $A \approx 1.2975$ are calculated.

For $PbTiO_3:Ni^{3+}$, to our knowledge, no optical spectrum data were reported. However, the value $Dq \approx 1800\ cm^{-1}$ and the reduction of the spin-orbit coupling coefficient ($\zeta/\zeta_0 \approx 0.74$) of the central ion were obtained from optical spectra and crystal-field analysis for the $[NiO_6]^{9-}$ cluster in $Al_2O_3:Ni^{3+}$ [10]. Here, the ionic radius $r_h \approx 0.67$ Å [16] and the average cation-anion distance $\bar{R} \approx 1.912$ Å [16], yielding the effective impurity-ligand distance $R_0 \approx 1.947$ Å. Note that the crystal structures for corundum and $PbTiO_3$ are different. Fortunately, in consideration of the fact (i) that the crystal-field strength and the covalency around the impurity Ni^{3+} may be insensitive to the whole lattice structures of the hosts, but mainly dependent upon its distances from the six nearest oxygen ions (i. e., the octahedral $[NiO_6]^{9-}$ cluster) and (ii) that the effective Ni^{3+}-O^{2-} distances for both crystals are close to each other, the spectral parameters of $Al_2O_3:Ni^{3+}$ [10] can be considered here as the reference. According to the relationship $Dq \propto R_0^{-5}$ [22,23] and the fact that the Racah parameters (or the average covalency factor N) increase slightly with increasing the distance R_0 [24], one can approximately obtain $Dq \approx 1700\ cm^{-1}$ and $N \approx 0.74$ for the studied system. Thus the molecular orbital coefficients $N_t \approx 0.740$, $N_e \approx 0.758$, $\lambda_t \approx 0.605$, $\lambda_e \approx 0.481$ and $\lambda_s \approx 0.386$ can be calculated from (5) and (6). By using the free-ion values $\zeta_d^0 \approx 776\ cm^{-1}$ [25] for Ni^{3+} and $\zeta_p^0 \approx 603\ cm^{-1}$ [26–28] for O^{2-}, the parameters $\zeta \approx 656\ cm^{-1}$, $\zeta' \approx 516\ cm^{-1}$, $k \approx 0.875$ and $k' \approx 0.527$ are acquired from (4). Based on the relationships $B \approx N^2 B_0$ and $C \approx N^2 C_0$ [29] and the values $B_0 \approx 1115\ cm^{-1}$ and $C_0 \approx 5450\ cm^{-1}$ [30] for the free Ni^{3+}, the Racah parameters in (3) can be obtained as $B \approx 602\ cm^{-1}$ and $C \approx 2943\ cm^{-1}$ for the studied $PbTiO_3:Ni^{3+}$.

Thus only the local distance $\Delta Z'$ between the impurity and the center of the oxygen octahedron are unknown in the formulas of the g factors. Substituting the known values into (1) and fitting the calculated g factors to the observed values, we have

$$\Delta Z' \approx 0.144\ \text{Å}. \tag{9}$$

The corresponding g factors (Cal. [d]) are shown in Table 1. For comparison, the theoretical values (Cal. [a]) based on the conventional formulas in the previous work [i. e., $Ds = 0$ and $Dt = 0$ in (3)], those (Cal. [b]) based on the formulas (1) in this work and the host structure parameters (i. e., $\Delta Z' \approx \Delta Z \approx 0.3$ Å), and those (Cal. [c]) based on the local distance $\Delta Z'$ in (9) but neglecting the ligand

Table 1. The g factors for the tetragonal Ni^{3+} center in PbTiO$_3$.

	Cal.[a]	Cal.[b]	Cal.[c]	Cal.[d]	Expt. [7]
$g_\parallel$	2.0170	2.0122	2.0440	2.0226	2.0128(2)
$g_\perp$	2.2073	2.1785	2.1456	2.4833	2.4819(2)
$\Delta g(=g_\perp - g_\parallel)$	0.1903	0.1663	0.1016	0.4607	0.4691(4)

[a] Calculations based on the conventional formulas of the previous work [10] in the absence of the tetragonal crystal-field contributions [i. e., $Ds = 0$ and $Dt = 0$ in (3)].

[b] Calculations based on the formulas (1) in this work and the structural parameters of the host Ti^{4+} site (i. e., $\Delta Z' \approx \Delta Z \approx 0.3$ Å).

[c] Calculations based on the local distance $\Delta Z'$ in (9) and neglecting of the ligand orbital and spin-orbit coupling contributions (i. e., $\zeta = \zeta' = N\zeta_\mathrm{d}^0, k = k' = N$) in this work.

[d] Calculations based on both the local distance $\Delta Z'$ in (9) and the ligand orbital and spin-orbit coupling contributions in this work.

orbital and spin-orbit coupling contributions (i. e., $\zeta = \zeta' = N\zeta_\mathrm{d}^0$, $k = k' = N$) are also shown in Table 1.

3. Discussion

From Table 1, one can find that the theoretical g factors (Cal. [d]) based on the distance $\Delta Z'$ in (9) of this work agree better with the observed values than those (Cal. [b]) based on the host structural parameters of the Ti^{4+} site and those (Cal. [c]) in the absence of the ligand orbital and spin-orbit coupling contributions.

1.) The local distance $\Delta Z'$, smaller than the host ΔZ, can be illustrated by the modification of local structure properties around the impurity Ni^{3+} replacing the Ti^{4+}. Since the impurity has less charge compared with the host Ti^{4+}, leading to a decrease in the electrostatic interactions within the oxygen octahedron and hence to an inward displacement of the impurity toward the center of the octahedron. Furthermore, the slightly smaller impurity Ni^{3+} (≈ 0.74 Å [16]) regarding the host Ti^{4+} (≈ 0.745 Å [16]) would also induce some local relaxation along the C_4 axis, and then the decreasing interactions may yield another shift of the impurity towards the center of the octahedron. Consequently, the resultant distance $\Delta Z'$ of the impurity from the center of the oxygen octahedron is significantly (about half) smaller than the host ΔZ. Unlikely, the distance ($\Delta Z' \approx 0.26$ Å or the smaller inward displacement of about 0.04 Å for the impurity ion) was obtained for the trivalent Cr^{3+} in the same crystal by EPR analyses [31], where the radius (≈ 0.755 Å [16]) of the impurity Cr^{3+} is larger than that of the host Ti^{4+}. In this case, the local tension arising from size mismatching substitution may yield an outward displacement of the impurity Cr^{3+} and then largely cancel its original inward shift due to the charge unbalance. Thus the impurity displacements of both Ni^{3+} and Cr^{3+} in PbTiO$_3$ can be understood. It should be noted that the problem of impurity structure (displacement) in crystals is essentially a difficult one, which is connected with many complicated physical and chemical properties of the impurity and host materials. Therefore, the impurity displacement acquired in this work, based on EPR analyses, remains to be further checked with other theoretical (e. g., DFT) and experimental (e. g., EXAFS) studies.

2.) The results (Cal. [a]), based on the previous treatments in the absence of the tetragonal distortion, are smaller than the experimental data, since neglecting of Ds and Dt leads to increase of the energy denominators in (1) – (3). Thus, the conventional formulas in the previous work [10] seem difficult to yield reasonable g factors for PbTiO$_3$:Ni^{3+} by considering only the contributions from the cubic crystal-field. The calculation results (Cal. [b]) based on the host structure parameters for Ti^{4+} (i. e., $\Delta Z' \approx \Delta Z$) also show disagreement with the observed values, especially the theoretical $g_\perp$ and anisotropy Δg are, respectively, by 12% and 65% smaller than the experimental findings. This means that the tetragonal distortion based on the host structural data of the Ti^{4+} site are not suitable to the studies of the g factors. On the other hand, when the ligand orbital and spin-orbit coupling contributions were neglected, the theoretical results (Cal. [c]) are not as good as those including the above contributions, i. e., the calculated Δg is much (by about 80%) smaller than the exact result. For the studied system, due to the high valence state of Ni^{3+}, it may exhibit significant covalency even in oxides. This point is supported by the small covalency factor N (≈ 0.74) and the moderate orbital admixture coefficients ($\lambda_\mathrm{t} \approx 0.605$, $\lambda_\mathrm{e} \approx 0.481$ and $\lambda_\mathrm{s} \approx 0.386$) obtained in this work. Further, by neglecting the anisotropic contributions (i. e., the differences between ζ and ζ', and k and k') 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 $\Delta Z'$. Therefore, the contributions to the g factors from the spin-orbit coupling coefficient and the orbitals of the ligands should be taken into account.

3.) In the above calculations, the displacements of the oxygen ions are not considered. For example, the oxygen plane perpendicular to the C_4 axis would also shift away from the Ni^{3+} due to decrease in the electrostatic attraction compared to the host $[TiO_6]^{8-}$ cluster. In fact, the above displacements may be negligible because of the inward shift of the impurity and hence of its increasing electrostatic attraction. It is noted that in the host $PbTiO_3$ the actual Ti-O distance ΔZ at 77 K would be slightly different from (e. g., larger than) that (≈ 0.3 Å) at room temperature. This means that the inward displacement of the impurity would be slightly larger. Thus, the distance $\Delta Z'$ obtained in this work can be regarded as an effective and tentative one, as the influence of the above points is approximately assumed to be absorbed in the fitted value $\Delta Z'$.

4. Summary

The g factors and the defect structure for the tetragonal Ni^{3+} center in $PbTiO_3$ are theoretically studied, based on the improved formulas of the g factors for a low spin ($S = 1/2$) $3d^7$ ion in tetragonally elongated octahedra established in this work. The distance between the impurity Ni^{3+} and the center of the oxygen octahedron is found to be about 0.14 Å, which is smaller than that (≈ 0.3 Å) for the host Ti^{4+} site. The significant inward shift (≈ 0.16 Å) of the impurity towards the center of the octahedron may be attributed to the charge and / or size mismatching substitution of Ti^{4+} by Ni^{3+}.

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