Studies of the EPR Parameters and the Local Tetragonal Distortion of V^{4+}-doped $SrTiO_3$ Crystal

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Z. Naturforsch. **60a,** 433 – 436 (2005); received March 4, 2005

The EPR parameters (g factors $g_\parallel$, $g_\perp$ and hyperfine structure constants $A_\parallel$, $A_\perp$) of V^{4+} ion in the tetragonal phase of $SrTiO_3$ crystal were studied by high-order perturbation formulas based on a two-spin-orbit-parameter model, where the contributions from the spin-orbit-coupling-parameter of central $3d^n$ ion and that of ligands are considered. It is found that the oxygen octahedron surrounding the impurity ion V^{4+} changes from elongation along the tetragonal axis in the pure crystal to compression and the magnitude of tetragonal distortion of oxygen octahedron (characterized by $|\Delta R| = |R_\parallel - R_\perp|$) in V^{4+} center is much greater than the corresponding value in the pure crystal. The cause related to the strong Jahn-Teller effect is discussed.

Key words: Electron Paramagnetic Resonance; Crystal- and Ligand-field; Jahn-Teller Effect; V^{4+}; $SrTiO_3$.

1. Introduction

$SrTiO_3$ has been of considerable theoretical and experimental interest because of its unusual properties [1]. The crystal has a perovskite structure which undergoes a structural phase transition from cubic to tetragonal at ≈ 105 K [1]. The tetragonal phase is the result of the rotation of TiO_6 octahedra around the tetragonal c-axes. The rotation of TiO_6 octahedra leads to slight elongation of the Ti,O bond along the c-axes due to acoustic-optic phonon coupling [2]. So, the TiO_6 octahedron in the tetragonal phase of $SrTiO_3$ is slightly elongated (i. e., the bonding length $R_\parallel > R_\perp$). This was confirmed by X-ray diffraction [3], high-angle double-crystal X-ray diffractometry (HADOX) [4] and neutron diffraction [5] for the pure $SrTiO_3$ crystal, and by EPR and optical spectra studies [6 – 8] for Cr^{3+}-, Fe^{3+}- and Mn^{4+}-doped $SrTiO_3$ (where the impurity ions are used to be the probes, they occupy the Ti^{4+} sites and the charge compensators are not in the vicinity of impurity ions). It should be pointed out that the ground states of these impurity ions in octahedral sites are single orbit states, so there is no Jahn-Teller effect in these systems. Thus, only the small local tetragonal distortion may occur in these impurity centers (e.g. Cr^{3+} centers) [6] because of the size and/or charge mismatch. However, if the impurity ion is a $3d^1$ ion, e. g. V^{4+}, since the ground state of $3d^1$ ion in an elongated octahedron is an orbit doublet, the system is not stable. It can be expected that the Jahn-Teller effect may result in a large change of the $(VO_6)^{8-}$ octahedron from elongation to compression, because in the case of a $3d^1$ ion in a compressed octahedron the ground state is an orbit single state. The EPR spectra of V^{4+} in the tetragonal phase of $SrTiO_3$ ($T = 4.2$ K) were reported [9]. However, no theoretical calculations for these EPR parameters (g factors $g_\parallel$, $g_\perp$ and hyperfine structure constants $A_\parallel$, $A_\perp$) have been made, and the sign and magnitude of the local tetragonal distortion of the oxygen octahedron (characterized by the value $\Delta R = R_\parallel - R_\perp$) have not been given. In order to confirm the above expectation, to explain the EPR parameters and to obtain the local structural data for $SrTiO_3$:V^{4+} system, in this paper, we study the EPR parameters by the high-order perturbation formulas based on the two-spin-orbit-parameter model. The results are discussed.

2. Calculation

Since the spin-orbit-coupling-parameter ($\zeta_p^0 \approx 150\ cm^{-1}$ [10]) of the ligand O^{2-} is close to that

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($\zeta_p^0 \approx 248$ cm^{-1} [11]) of the central $3d^1$ ion, we apply the high-order perturbation formulas of EPR parameters based on the two-spin-orbit-parameter model, where both the contribution to the EPR parameters from the spin-orbit-coupling-parameter of the central $3d^1$ ion and that of ligand ions are considered. Thus, the one-electron basis functions can be expressed as the linear combinations of the d orbitals $|d_r\rangle$ of the central $3d^n$ ion and the p orbitals $|p_r\rangle$ of the ligands, i. e.,

$$|\psi_\gamma\rangle = N_\gamma^{1/2}(|d_\gamma\rangle - \lambda_\gamma|p_\gamma\rangle), \tag{1}$$

where $\gamma = e_g$ or t_{2g} denotes the irreducible representation of the O_h group. N_γ and λ_γ are, respectively, the normalization factors and the orbital mixing coefficients.

From the g factor of $SrTiO_3$:V^{4+}, it can be expected that the ground state is $^2B_2$ ($|d_{xy}\rangle$). Thus, from the above one-electron basis function and the perturbation methods, the high-order perturbation formulas of $3d^1$ ion in the tetragonal symmetry can be derived as

$$\begin{aligned}
g_\parallel &= g_s - 8k'\zeta'/E_1 - k\zeta^2/(E_2)^2 - 4k'\zeta\zeta'/(E_1E_2) - g_s\zeta^2/(E_2)^2, \\
g_\perp &= g_s - 2k\zeta/E_2 + k\zeta^2/(E_2)^2 - 2k\zeta'^2/(E_1E_2) + 2k'\zeta\zeta'/(E_1E_2) - 2g_s\zeta'^2/(E_1)^2 - g_s\zeta^2/2(E_2)^2, \\
A_\parallel &= P(-k-4/7) + P'\Big[-8k'\zeta'/E_1 - 6k\zeta/(7E_2) - 4k\zeta^2/(7E_2)^2 \\
&\qquad - 6k\zeta'^2/(7E_1E_2) - 22k'\zeta\zeta'/(7E_1E_2) - 6g_s\zeta'^2/7(E_1)^2 - 17g_s\zeta^2/14(E_2)^2\Big], \\
A_\perp &= P(2/7-k) + P'\Big[-11k\zeta/(7E_2) + 11/14k\zeta^2/(E_2)^2 - 11k\zeta'^2/(7E_1E_2) \\
&\qquad + 11k'\zeta\zeta'/(7E_1E_2) - 11/7g_s\zeta'^2/(E_1)^2 - 11/28g_s\zeta^2/(E_2)^2\Big],
\end{aligned} \tag{2}$$

in which g_s (≈ 2.0023) is the spin-only value. κ is the core polarization constant. The energy separations E_i can be written as

$$\begin{aligned}
E_1 &= E(^2B_1) - E(^2B_2) \approx 10Dq, \\
E_2 &= E(^2E) - E(^2B_2) = 5D_t - 3D_s,
\end{aligned} \tag{3}$$

where Dq is the cubic field parameter, and D_s and D_t are the tetragonal field parameters.

The spin-orbit-parameters ζ, ζ', the orbital reduction factors k, k' and the dipolar hyperfine structure parameters P, P' in (2) can be expressed as

$$\begin{aligned}
\zeta &= N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0/2), \\
\zeta' &= (N_tN_e)^{1/2}(\zeta_d^0 - \lambda_t\lambda_e\zeta_p^0/2), \\
k &= N_t[1 - 2\lambda_t S_{dp}(t_{2g}) + \lambda_t^2/2], \\
k' &= (N_tN_e)[1 - \lambda_t S_{dp}(t_{2g}) - \lambda_e S_{dp}(e_g) - \lambda_e\lambda_t/2], \\
P &= N_tP_0, \quad P' = (N_tN_e)^{1/2}P_0,
\end{aligned} \tag{4}$$

where ζ_d^0 and ζ_p^0 are the spin-orbit-parameter of the d electrons of a free $3d^1$ ion and that of p electrons of a free ligand ion. P_0 is the dipolar hyperfine structure constant of the free $3d^1$ ion. For the studied $SrTiO_3$:V^{4+} system, ζ_d^0 and ζ_p^0 are given above and $P_0 \approx 136 \cdot 10^{-4}$ cm^{-1} [12, 13]. $S_{dp}(r)$ are the group overlap integrals. For $SrTiO_3$:V^{4+}, from the Slater-type SCF functions [14, 15] and the metal-ligand distance $R_0 \approx 1.95$ Å [3–5] we obtain $S_{dp}(e_g) \approx 0.1297$ and $S_{dp}(t_{2g}) \approx 0.0508$. In (2) we assume that the mixing coefficients $\lambda_\gamma = \lambda_e \approx \lambda_t$ and the coefficient λ_γ is taken as an adjustable parameter. Thus, the normalization factors N_r can be calculated from the normalization relation

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

The tetragonal field parameters D_s and D_t can be calculated from the superposition model [16]. From the model, we have

$$\begin{aligned}
D_s &= (4/7)\bar{A}_2(R_0)[(R_0/R_\perp)^{t_2} - (R_0/R_\parallel)^{t_2}], \\
D_t &= (16/21)\bar{A}_4(R_0)[(R_0/R_\perp)^{t_4} - (R_0/R_\parallel)^{t_4}],
\end{aligned} \tag{6}$$

where the power-law exponents are $t_2 \approx 3$ and $t_4 \approx 5$ [17–19]. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are intrinsic parameters. For a $3d^n$ MX_6 octahedral cluster, $\bar{A}_4(R_0) = 3/4Dq$ [16, 18, 19] and $\bar{A}_2(R_0) \approx (9 \sim 12)\bar{A}_4(R_0)$ [18–21]. We take $\bar{A}_2(R_0) = 12\bar{A}_4(R_0)$ here. To our best knowledge, the value of Dq for the $(VO_6)^{8-}$ cluster is not reported, so we estimate it as follows: According to the spectrochemical series [22], for a $3d^n$ ion, $Dq(F^-) < Dq(O^{2-})$, for example, $Dq(F^-)$ in $KMgF_3$:Cr^{3+} is about 1,560 cm^{-1} [23] and $Dq(O^{2-})$

in $Al_2O_3:Cr^{3+}$ is above 1,800 cm^{-1} [24, 25]. Thus, from $Dq \approx$ 2,012 cm^{-1} for the $(VF_6)^{2-}$ octahedral cluster [26], we estimate $Dq \approx$ 2,400 cm^{-1} for the studied $(VO_4)^{8-}$ cluster. In the tetragonal phase of $SrTiO_3:V^{4+}$ we have the bonding length $R_\perp \approx R_0 \approx 1.95$ Å [3–5], and the bonding length $R_\parallel$ is taken as an adjustable parameter. The core polarization constant κ is related only to the hyperfine structure constants $A_\parallel$ and $A_\perp$, it is also taken as the adjustable parameter. Thus, by fitting the calculated EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ to the observed values, we obtain for the tetragonal $SrTiO_3:V^{4+}$ system

$$\lambda_\gamma \approx 0.4646, \quad R_\parallel \approx 1.859 \text{ Å}, \quad \kappa \approx 0.58. \qquad (7)$$

Comparisons between the calculated EPR parameters and the experimental values are shown in Table 1.

Table 1. g Factors and hyperfine structure constants for V^{4+} in the tetragonal phase of $SrTiO_3$.

	$g_\parallel$	$g_\perp$	$A_\parallel$ (10^{-4} cm^{-1})	$A_\perp$ (10^{-4} cm^{-1})
Calculation	1.9421	1.8951	−146.76	−44.37
Experiment [9]	1.9420(50)	1.8945(50)	−146.78(5)[a]	−44.04(5)[a]

[a] The sign is not given in [9].

3. Discussion

The above calculations suggest that the bonding length $R_\parallel < R_\perp$, that is to say, the oxygen octahedron in the V^{4+} center in the tetragonal $SrTiO_3$ crystal is compressed. This point is, as expected above, opposite to that in the pure $SrTiO_3$ [3–5] and the Cr^{3+}-, Fe^{3+}- and Mn^{4+}-doped $SrTiO_3$ crystals [6–8]. The magnitude of the tetragonal distortion $|\Delta R| = |R_\parallel - R_\perp|$ is 0.091 Å for the V^{4+} center in the tetragonal $SrTiO_3$. This value is much greater than the value ($\approx 5 \cdot 10^{-4}$ Å [3–5, 7, 8]) in pure $SrTiO_3$ and Fe^{3+}- and Mn^{4+}-doped $SrTiO_3$ at 4.2 K and that ($\approx 16 \cdot 10^{-4}$ Å [6]) in Cr^{3+}-doped $SrTiO_3$. Considering that the impurity V^{4+} has the same charge as the replaced Ti^{4+} ion in $SrTiO_3$, tetragonal distortion due to charge compensation can be excluded. In addition, since the ionic radius ($\approx$ 0.63 Å [27]) of V^{4+} is close to that ($\approx$ 0.68 Å [27]) of the replaced Ti^{4+}, one has to visualize that off-center displacement of the impurity is the cause of the large tetragonal distortion. So, the large tetragonal distortion of the V^{4+} center in the tetragonal phase of $SrTiO_3$ is attributed to the Jahn-Teller effect, because V^{4+} in $SrTiO_3$ is a Jahn-Teller system. It can be expected that even for V^{4+} in cubic $SrTiO_3$, the Jahn-Teller effect may result in a tetragonal elongation of the oxygen octahedron. Noteworthy, for the $3d^1$ ions Ti^{3+} and Cr^{5+} in the tetragonal phase of $SrTiO_3$ [28, 29], since $R_\parallel > R_\perp$, the ground state is an orbital doublet, an additional distortion due to the Jahn-Teller effect and/or the off-center displacement of an impurity ion (only for Cr^{5+}) can occur, which leads the symmetry of the octahedron being orthorhombic and the orbital degeneracy of the doublet is removed. So, if a $3d^1$ ion is in an octahedral site with tetragonal distortion, the tetragonal distortion should be compressed and even the corresponding octahedron in the host crystal is elongated.

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