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2007 J. Phys.: Condens. Matter 19 456214

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Studies of the spin-Hamiltonian parameters and defect structure for the tetragonal Fe⁵⁺ center in SrTiO₃ crystals using a two-mechanism model

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Received 20 July 2007, in final form 26 September 2007

Published 15 October 2007

Online at stacks.iop.org/JPhysCM/19/456214

Abstract

The high order perturbation formulas for spin-Hamiltonian (SH) parameters (g factors g_{\parallel} , g_{\perp} and zero-field splitting D) for $3d^3$ ions in tetragonal symmetry are established using a cluster approach. In these formulas, not only is the contribution to the SH parameters from the crystal-field (CF) mechanism included, but so also is that from the charge-transfer (CT) mechanism (which is neglected in the widely used CF theory). From these formulas, the g shifts Δg_{\parallel} ($=g_{\parallel} - g_e$, where $g_e \approx 2.0023$, the value for the free electron), Δg_{\perp} ($=g_{\perp} - g_e$) and the zero-field splitting D for the tetragonal Fe⁵⁺ center in SrTiO₃ crystal are calculated. The results (in particular, the positive g shifts, which cannot be explained on the basis of the CF mechanism) are in good agreement with the observed values. The calculation results show that (i) the sign of Δg_i^{CT} ($i = \parallel$ or \perp) due to the CT mechanism is opposite to that of Δg_i^{CF} due to the CF mechanism, but the sign of D^{CT} is the same as that of D^{CF} and (ii) the ratio $|Q^{\text{CT}}/Q^{\text{CF}}|$ (which represents the relative importance of the CT mechanism) takes values of about 143%, 143% and 114% for $Q = \Delta g_{\parallel}$, Δg_{\perp} and D , respectively. This suggests that the positive g shifts are due mainly to the contribution of the CT mechanism; therefore for the high valence state $3d^n$ ions in crystals, the contribution to SH parameters from the CT mechanism should be taken into account. The defect structure of the Fe⁵⁺ center in SrTiO₃ crystal is also obtained from the calculations. The result is consistent with the expectations based on charge compensation and electrostatic interaction.

1. Introduction

SrTiO₃ is a classical displacive soft mode system where the ferroelectric phase is suppressed by zero-point fluctuation of the soft mode leading to quantum paraelectricity [1, 2]. This crystal, doped with transition metal impurities, shows photochromic behavior and has been investigated using optical and electron paramagnetic resonance (EPR) spectra [3–5]. From the EPR study [6], a tetragonal Fe⁵⁺ (3d³) impurity center was found in the cubic phase of SrTiO₃. A probable assignment of the tetragonal center would be as a substitutional Fe⁵⁺ ion (for Ti⁴⁺) perturbed by an unknown diamagnetic ion Mⁿ⁺ at a Ti site in an adjacent oxygen octahedron (i.e., an Fe⁵⁺–O²⁻–Mⁿ⁺ defect) [6]. However, the detail of Mⁿ⁺ and the defect structure of this Fe⁵⁺ center were not given [6]. Considering that the impurity Fe⁵⁺ carries extra charge compared with the replaced Ti⁴⁺ ion, the charge compensation is required to maintain electric neutrality. Thus we expect $n < 4$. Since the effective charge of Mⁿ⁺ ($n < 4$) at the Ti⁴⁺ site is negative, we also expect that the O²⁻ ion intervening in the Fe⁵⁺ and Mⁿ⁺ is displaced towards the Fe⁵⁺ along the C₄ axis by $\Delta R = R_0 - R_1$ (where R₁ is the distance between Fe⁵⁺ and the intervening O²⁻ ion and R₀ is the Fe⁵⁺–O²⁻ distance for the other five O²⁻ ions in (FeO₆)⁷⁻ octahedron) and the tetragonal (C_{4v}) Fe⁵⁺ center is formed. In order to confirm the expectations, the spin-Hamiltonian (SH) parameters (g factors g_{\parallel} , g_{\perp} and zero-field splitting D) of the Fe⁵⁺ center should be studied. The experimental values of g_{\parallel} , g_{\perp} for the Fe⁵⁺ center are greater than g_e (≈ 2.0023 , the value for the free electron). The positive g shift Δg_i ($=g_i - g_e$, where $i = \parallel$ or \perp), cannot be explained by the conventional crystal-field (CF) theory [7, 8] (where $\Delta g_i \approx -\frac{8k\zeta_d}{3\Delta}$, i.e., only the contribution to the g shift due to the spin-orbit (SO) coupling parameter of the central 3dⁿ ion is included, and so it is called the one-SO-parameter model). As an improvement, a two-SO-parameter model [9–11] based on the cluster approach was developed to explain the slightly negative and even positive g shift Δg for 3d³ ions in octahedral clusters. In the model, both the contribution to Δg from the SO parameter of the central 3d³ ion and that from the SO parameter of ligand ion are considered, and the positive Δg is attributed to the large contribution due to the great SO parameter of the ligand. However, the model is not effective in explaining the positive Δg_i in SrTiO₃:Fe⁵⁺ because the SO parameter ζ_p^0 (≈ 150 cm⁻¹ [7]) of the ligand ion O²⁻ is much smaller than that ($\zeta_d^0 \approx 579$ cm⁻¹ [12]) of the central Fe⁵⁺ ion. So, one should consider the other cause here. It should be noted that in both one- and two-SO-parameter models, only the contribution from the CF excited states (i.e., the CF mechanism) to SH parameters is considered. In fact, not only CF excited states, but also the charge-transfer (CT) excited states (i.e., the CT mechanism) can contribute to SH parameters (including Δg_i) [13, 14]. Since in many cases the energy differences between the CT excited states and the ground state are much larger than those between CF excited states and ground state [15–17], the contributions of the CT mechanism to the SH parameters are much smaller and can be omitted. However, for a 3dⁿ ion having a high valence state (i.e., Fe⁵⁺) in crystals, the energy differences between CT excited states and the ground state may become small [15] and so the contribution to SH parameters should be taken into account. In this paper, we first establish the high order perturbation formulas including both CF and CT mechanisms using a cluster approach for the SH parameters g_{\parallel} , g_{\perp} and D for 3d³ ions in tetragonal octahedral clusters. From these formulas, the SH parameters of SrTiO₃:Fe⁵⁺ are calculated. The results (including the defect structure of the tetragonal Fe⁵⁺ center based on the above expectations and the relative importance of the CT mechanism) are discussed.

2. Calculation

The Hamiltonian including CF and CT mechanisms for 3d³ ions in tetragonal symmetry can be expressed as

$$\begin{aligned}
H &= H_0 + H' \\
H_0 &= H_e + H_a \\
H' &= H_b + H_{\text{tetra}} + H_{\text{SO}}^{\text{CF}} + H_{\text{Ze}}^{\text{CF}} + H_{\text{SO}}^{\text{CT}} + H_{\text{Ze}}^{\text{CT}}
\end{aligned} \tag{1}$$

in which H_e , H_a , H_b , H_{tetra} , H_{SO} and H_{Ze} denote, respectively, the $3d^n$ ion in the cubic part of the CF, the diagonal and off-diagonal terms of the electrostatic interaction, the tetragonal part of the CF, the SO coupling Hamiltonian and Zeeman interaction terms. The superscripts CF and CT stand for terms (or parameters) in CF and CT mechanisms, respectively. The one-electron basis function related to both mechanisms is written as

$$|\Psi_\gamma\rangle = N_\gamma^X (|d_\gamma\rangle + \lambda_\gamma^X |p_\gamma\rangle), \tag{2}$$

where the subscript X ($=a$ or b) stands for the anti-bonding orbitals (related to the CF mechanism) or bonding orbitals (related to the CT mechanism). The subscript γ ($=t_{2g}$ or e_g) denotes the irreducible representation of the O_h group. $|d_\gamma\rangle$ and $|p_\gamma\rangle$ are the d orbitals of $3d^n$ ion and the p orbitals of ligands, respectively. N_γ^X and λ_γ^X are the normalization coefficient and orbital mixing coefficient.

From the above Hamiltonian and basis function, the high order perturbation formulas based on the two-mechanism model for the SH parameters of $3d^3$ ions in tetragonal octahedral clusters are derived by using the perturbation-loop method [18, 19]. They are

$$\begin{aligned}
g_{\parallel} &= g_e + \Delta g_{\parallel}^{\text{CF}} + \Delta g_{\parallel}^{\text{CT}} \\
\Delta g_{\parallel}^{\text{CF}} &= -\frac{8k'_{\text{CF}}\zeta'_{\text{CF}}}{3E_1} - \frac{4k'_{\text{CF}}\zeta_{\text{CF}}\zeta'_{\text{CF}}}{9E_1^2} + \frac{2k_{\text{CF}}\zeta_{\text{CF}}^2}{9E_1^2} - \frac{4g_e\zeta_{\text{CF}}^2}{9E_1^2} + \frac{4k_{\text{CF}}\zeta_{\text{CF}}^2}{9E_3^2} - \frac{8g_e\zeta_{\text{CF}}^2}{9E_3^2} \\
&\quad - \frac{2k_{\text{CF}}\zeta_{\text{CF}}^2}{3E_2^2} - \frac{2g_e\zeta_{\text{CF}}^2}{3E_2^2} + \frac{4k'_{\text{CF}}\zeta_{\text{CF}}\zeta'_{\text{CF}}}{9E_1E_3} - \frac{4k'_{\text{CF}}\zeta_{\text{CF}}\zeta'_{\text{CF}}}{3E_1E_2} \\
&\quad + \frac{4k'_{\text{CF}}\zeta_{\text{CF}}\zeta'_{\text{CF}}}{3E_2E_3} + \frac{140k'_{\text{CF}}\zeta'_{\text{CF}}Dt}{9E_1^2} \\
\Delta g_{\parallel}^{\text{CT}} &= \frac{8k'_{\text{CT}}\zeta'_{\text{CT}}}{3E_n} - \frac{8k'_{\text{CT}}\zeta'_{\text{CT}}(2Ds + 6Dt)}{3E_n^2} \\
g_{\perp} &= g_e + \Delta g_{\perp}^{\text{CF}} + \Delta g_{\perp}^{\text{CT}} \\
\Delta g_{\perp}^{\text{CF}} &= \Delta g_{\parallel}^{\text{CF}} - \frac{210k'_{\text{CF}}\zeta'_{\text{CF}}Dt}{9E_1^2} \\
\Delta g_{\perp}^{\text{CT}} &= \Delta g_{\parallel}^{\text{CT}} + \frac{8k'_{\text{CT}}\zeta'_{\text{CT}}(3Ds - 5Dt)}{3E_n^2} \\
D &= D^{\text{CF}} + D^{\text{CT}} \\
D^{\text{CF}} &= \frac{35Dt\zeta_{\text{CF}}^2}{9E_1^2} - \frac{35Dt\zeta_{\text{CF}}^2}{9E_3^2} - \frac{35BDt\zeta_{\text{CF}}\zeta'_{\text{CF}}}{9E_2E_3^2} \\
D^{\text{CT}} &= \frac{4(3Ds - 5Dt)\zeta_{\text{CT}}^2}{9E_n^2},
\end{aligned} \tag{3}$$

where E_i ($i = 1-3$) are the zero-order energy denominators which can be calculated from the cubic field parameters Dq and Racah parameters B and C in the systems studied [18, 19]. E_n is the lowest level of CT bands. D_s and D_t are tetragonal field parameters. The SO coupling parameters ζ , ζ' and the orbital reduction factors k , k' related to CF and CT mechanisms are

$$\begin{aligned}
\zeta_{\text{CF}} &= N_t^a N_t^b [\zeta_d^0 + \lambda_t^a \lambda_t^b \zeta_p^0 / 2] \\
\zeta'_{\text{CF}} &= N_t^a N_e^a [\zeta_d^0 - \lambda_t^a \lambda_e^a \zeta_p^0 / 2] \\
k_{\text{CF}} &= (N_t^a)^2 [1 + 2\lambda_t^a S_{\text{dp}}(t_{2g}) + (\lambda_t^a)^2 / 2] \\
k'_{\text{CF}} &= N_t^a N_e^a [1 + \lambda_t^a S_{\text{dp}}(t_{2g}) + \lambda_e^a S_{\text{dp}}(e_g) - \lambda_t^a \lambda_e^a / 2]
\end{aligned}$$

$$\begin{aligned}
\zeta_{\text{CT}} &= N_t^a N_t^b [\zeta_d^0 + \lambda_t^a \lambda_t^b \zeta_p^0/2] \\
\zeta'_{\text{CT}} &= N_t^a N_e^b [\zeta_d^0 - \lambda_t^a \lambda_e^b \zeta_p^0/2] \\
k_{\text{CT}} &= N_t^a N_t^b [1 + (\lambda_t^a + \lambda_t^b) S_{\text{dp}}(t_{2g}) + \lambda_t^a \lambda_t^b/2] \\
k'_{\text{CT}} &= N_t^a N_e^b [1 + \lambda_e^b S_{\text{dp}}(e_g) + \lambda_t^a S_{\text{dp}}(t_{2g}) - \lambda_t^a \lambda_e^b/2]
\end{aligned} \tag{4}$$

in which $S_{\text{dp}}(\gamma)$ is the group overlap integral.

For the compound studied, $\text{SrTiO}_3:\text{Fe}^{5+}$, we have [14, 20]

$$B \approx 800 \text{ cm}^{-1} \quad C \approx 3050 \text{ cm}^{-1} \quad Dq \approx 2020 \text{ cm}^{-1}. \tag{5}$$

Thus, the energy denominators E_i can be acquired. The CT energy level $E_n \approx 20\,000 \text{ cm}^{-1}$ for the $(\text{FeO}_6)^{7-}$ cluster [21]. The group overlap integrals $S_{\text{dp}}(e_g) \approx 0.0650$ and $S_{\text{dp}}(t_{2g}) \approx 0.0221$ are calculated from the Slater-type SCF functions [22, 23] with the metal–ligand distance $R_0 \approx 1.95 \text{ \AA}$ [24] in SrTiO_3 . From equation (2), we have the normalization relationship

$$N_\gamma^X [1 + 2\lambda_\gamma^X S_{\text{dp}}(\gamma) + (\lambda_\gamma^X)^2]^{1/2} = 1 \tag{6}$$

and the orthonormal relation

$$\lambda_\gamma^b = -\frac{1 + \lambda_\gamma^a S_{\text{dp}}(\gamma)}{\lambda_\gamma^a + S_{\text{dp}}(\gamma)}. \tag{7}$$

Thus, if the parameter λ_γ^a is known, the remaining molecular orbital (MO) coefficients λ_γ^b , N_γ^a and N_γ^b can be obtained. The parameter λ_γ^a ($=\lambda_t^a = \lambda_e^a$) is an adjustable parameter.

From the superposition model [25], the tetragonal field parameters in the Fe^{5+} center in SrTiO_3 studied here can be expressed as

$$\begin{aligned}
D_s &= \frac{2}{7} \bar{A}_2(R_0) \left[1 - \left(\frac{R_0}{R_0 - \Delta R} \right) \right]^{t_2} \\
D_t &= \frac{8}{21} \bar{A}_4(R_0) \left[1 - \left(\frac{R_0}{R_0 - \Delta R} \right) \right]^{t_4},
\end{aligned} \tag{8}$$

where the power-law exponents are $t_2 \approx 3$ and $t_4 \approx 5$ [25, 26]. The intrinsic parameter $\bar{A}_4(R_0) \approx (3/4)Dq$ for $3d^n$ ions in octahedral clusters [25–27] and $\bar{A}_2(R_0) \approx (9-12)\bar{A}_4(R_0)$ are obtained for $3d^n$ ions in many crystals [26–29]. The mean value is used, i.e., $\bar{A}_2(R_0) \approx 10.5\bar{A}_4(R_0)$ here. Thus in the above formulas, only the parameters λ_γ^a and ΔR are not known. By fitting the calculated SH parameters g_{\parallel} , g_{\perp} and D to the observed values, we derive

$$\lambda_\gamma^a \approx -0.736 \quad \Delta R \approx 0.096 \text{ \AA}. \tag{9}$$

Thus the coefficients λ_γ^b , N_γ^a and N_γ^b can be calculated from equations (6) and (7). The parameters in equation (4) obtained from these coefficients are

$$\begin{aligned}
\zeta_{\text{CF}} &\approx 411 \text{ cm}^{-1}, & \zeta'_{\text{CF}} &\approx 365 \text{ cm}^{-1}, & k_{\text{CF}} &\approx 0.8208, & k'_{\text{CF}} &\approx 0.4512, \\
\zeta_{\text{CT}} &\approx 238 \text{ cm}^{-1}, & \zeta'_{\text{CT}} &\approx 305 \text{ cm}^{-1}, & k_{\text{CT}} &\approx 0.2398, & k'_{\text{CT}} &\approx 0.7407.
\end{aligned} \tag{10}$$

The comparison of the calculated and experimental SH parameters is shown in table 1.

3. Discussion

The above calculations show that in order to reasonably explain the SH parameters g_{\parallel} , g_{\perp} and D for the tetragonal Fe^{5+} center in the cubic phase of SrTiO_3 , the O^{2-} ion intervening in Fe^{5+} and the unknown diamagnetic ion M^{n+} should be displaced towards the Fe^{5+} ion by

Table 1. Spin-Hamiltonian parameters (g factors g_{\parallel} , g_{\perp} and zero-field splitting D , D in cm^{-1}) for the tetragonal Fe^{5+} centers in the cubic phase of SrTiO_3 .

$\Delta g_{\parallel}^{\text{CF}}$	$\Delta g_{\parallel}^{\text{CT}}$	g_{\parallel} (total)	g_{\parallel} (expt. [6])
-0.0237	0.0338	2.0124	2.0132(10)
$\Delta g_{\perp}^{\text{CF}}$	$\Delta g_{\perp}^{\text{CT}}$	g_{\perp} (total)	g_{\perp} (expt. [6])
-0.0221	0.0317	2.0119	2.0116(10)
D^{CF}	D^{CT}	D (total)	D (expt. [6])
-0.1269	-0.1444	-0.2713	$\pm 0.2705(5)$

$\Delta R = 0.096 \text{ \AA}$. The displacement ΔR is consistent with our expectations based on the charge compensation (i.e. the charged state $n < 4$ for the diamagnetic M^{n+} in the adjacent oxygen octahedron) and the electrostatic interaction between M^{n+} and the intervening O^{2-} ion. In fact, the $\text{Fe}^{5+}\text{-O}^{2-}\text{-Al}^{3+}$ (i.e. $M^{n+} = \text{Al}^{3+}$) defect was found in cubic SrTiO_3 [30]; it is a strong validating indication of the above defect structure for the tetragonal Fe^{5+} centers in SrTiO_3 crystal. So, the defect structure of the tetragonal Fe^{5+} center in SrTiO_3 is reasonable.

The sign of the calculated Δg_i^{CT} is opposite due to the CF mechanism, and that of the calculated D^{CT} is the same due to the CF mechanism when compared with the corresponding Δg_i^{CF} and D^{CF} (see table 1). The relative importance of the CT mechanism (characterized by $|Q^{\text{CT}}/Q^{\text{CF}}|$) takes values of about 143% and 114% for $Q = \Delta g_i$ and D , respectively. That is to say, the contributions to Δg_i and D due to the CT mechanism are greater than those due to the CF mechanism. So, the positive g shift Δg_i is due mainly to the contribution from the CT mechanism. It appears that for high valence $3d^n$ ions in crystals the contribution from the CT mechanism to the SH parameters is important, and so one should apply a two-mechanism model (i.e. with CF and CT mechanisms) to explain the SH parameters.

Acknowledgments

This project was supported by the National Natural Science Foundation of China (grant no 10274054) and the CAAC Scientific Research Base of Civil Aviation Flight Technology and Safety.

References

- [1] Muller K A and Burkhard H 1979 *Phys. Rev. B* **19** 3593
- [2] Zhong W and Vanderbilt D 1996 *Phys. Rev. B* **53** 5047
- [3] Muller K A, Von Waldkirch Th and Berlinger W 1971 *Solid State Commun.* **9** 1097
- [4] Faughnan B W and Kiss Z J 1968 *Phys. Rev. Lett.* **21** 1331
- [5] Faughnan B W 1971 *Phys. Rev. B* **4** 3623
- [6] Kool Th W and Glasbeek M 1977 *Solid State Commun.* **22** 193
- [7] Abragam A and Bleaney B 1970 *Electron Paramagnetic Resonance of Transition Ions* (Oxford: Oxford University Press)
- [8] Griffith J S 1964 *The theory of Transition-Metal Ions* (Cambridge: Cambridge University Press)
- [9] Du M L and Zhao M G 1989 *Phys. Status Solidi b* **153** 249
- [10] Du M L and Rudowicz C 1992 *Phys. Rev. B* **46** 8974
- [11] Zheng W C and Wu S Y 1998 *J. Phys. Chem. Solids* **59** 503
- [12] Uylings P H M, Raassen A J J and Wyart J F 1984 *J. Phys. B: At. Mol. Phys.* **17** 4103
- [13] Aramburu J A and Moreno M 1987 *Solid State Commun.* **62** 513
- [14] Zheng W C and Wu X X 2005 *J. Phys. Chem. Solids* **66** 1701
- [15] Lever A B P 1984 *Inorganic Electronic Spectroscopy* (Amsterdam: Elsevier)

- [16] Brik M G and Ogasawara K 2006 *Phys. Rev. B* **74** 040105
- [17] Moreno M, Aramburu J A and Barriuso M T 2004 *Struct. Bonding* **106** 127
- [18] Macfarlane R M 1967 *J. Chem. Phys.* **47** 2066
- [19] Macfarlane R M 1970 *Phys. Rev. B* **1** 989
- [20] Brik M G and Avram N M 2006 *J. Phys. Chem. Solids* **67** 1599
- [21] Michel-Calendinl F M and Muller K A 1981 *Solid State Commun.* **40** 255
- [22] Clementi E, Raimondi D L and Reinhardt W P 1967 *J. Chem. Phys.* **47** 1300
- [23] Clementi E and Raimondi D L 1963 *J. Chem. Phys.* **38** 2686
- [24] Wyckoff R W G 1964 *Crystal Structures* vol 2 (New York: Wiley)
- [25] Newman D J and Ng B 1989 *Rep. Prog. Phys.* **52** 699
- [26] Yu W L, Zhang X M, Yang L X and Zen B Q 1994 *Phys. Rev. B* **50** 6756
- [27] Zheng W C, Wu X X, Zhou Q and Mei Y 2007 *Spectrochim. Acta A* **66** 126
- [28] Rudowicz C and Zhou Y Y 1992 *J. Magn. Magn. Mater.* **111** 153
- [29] Yeom T H, Choh S H, Du M L and Tang M S 1996 *Phys. Rev. B* **53** 3415
- [30] Schirimer O F, Berlinger W and Muller K A 1976 *Solid State Commun.* **18** 1505