Electron paramagnetic resonance parameters of Mn^{4+} ion in h-BaTiO$_3$ crystal from a two-mechanism model

WU XIAO-XUAN[1,4,*], FANG WANG[2], FENG WEN-LIN[2,3] and
ZHENG WEN-CHEN[2,4]

[1]Department of Physics, Civil Aviation Flight University of China, Guanghan 618307,
People's Republic of China
[2]Department of Material Science, Sichuan University, Chengdu 610064,
People's Republic of China
[3]Department of Applied Physics, Chongqing Institute of Technology, Chongqing 400050,
People's Republic of China
[4]International Centre for Materials Physics, Chinese Academy of Sciences,
Shenyang 110016, People's Republic of China
*Corresponding author. E-mail: wxxdd@163.com

Abstract. The EPR parameters (g factors $g_\parallel$, $g_\perp$ and zero-field splitting D) of Mn^{4+} ion in h-BaTiO$_3$ crystal are calculated from the complete high-order perturbation formulas based on a two-mechanism model for the EPR parameters of $3d^3$ ions in trigonal symmetry. In the model, not only the widely used crystal-field mechanism, but also the charge-transfer mechanism (which is not considered in crystal-field theory) are included. The calculated results are in reasonable agreement with the experimental values. The relative importance of charge-transfer mechanism to EPR parameters and the defect structure of Mn^{4+} centre in h-BaTiO$_3$ crystal obtained from the calculations are discussed.

Keywords. Electron paramagnetic resonance; two-mechanism model; defect structure; Mn^{4+}; h-BaTiO$_3$.

PACS Nos 71.70.Ch; 76.30.v; 76.30.Fc; 71.55.-i

1. Introduction

Barium titanate (BaTiO$_3$) represents a material system of fundamental importance for a wide range of technical applications (e.g., in optical computing and metrology [1–3]). There are two polymorphic forms of BaTiO$_3$, one is the well-known perovskite type and the other is the hexagonal polytype BaTiO$_3$ (h-BaTiO$_3$) [4]. The latter crystallizes in the space group p63/mmc at room temperature [4]. In h-BaTiO$_3$ crystal, there are two crystallographically different Ti^{4+} lattice sites.

Both Ti^{4+} sites are surrounded by different trigonally distorted oxygen octahedra. The EPR spectra of h-$BaTiO_3$:Mn^{4+} were measured [5]. From the measurement, the Mn^{4+} ion is found to occupy $Ti^{4+}(1)$ site (where the Ti^{4+}–O^{2-} distances R in $(TiO_6)^{8-}$ octahedron are equal [4,5]) and its EPR parameters (g factors $g_\parallel$, $g_\perp$ and zero-field splitting D) were given [5]. No theoretical explanations for these EPR parameters have been made. Since the g-shifts Δg_i ($=g_i - g_e$, where $i =\parallel$ and $\perp$, $g_e = 2.0023$, the value of free electron) in h-$BaTiO_3$ are very small, the perturbation formulas based on the one-spin-orbit (SO)-parameter model (where only the contribution to EPR parameters due to the SO coupling parameter of central $3d^n$ ion is included) in the conventional crystal-field (CF) theory [6–8] is not effective to explain these EPR parameters. Recently, a two-SO-parameter model is used to explain the small g-shifts of $3d^3$ ions in crystals [9,10]. In the model, the contributions to EPR parameters due to both the SO coupling parameter of $3d^n$ ion and that of ligand ion are considered. The model can explain the small g-shifts of $3d^3$ clusters with ligand having large SO coupling parameter [9,10]. However, it does not hold true for h-$BaTiO_3$:Mn^{4+} because the SO coupling parameter ζ_p^0 (≈ 150 cm^{-1} [10]) of ligand ion O^{2-} is smaller than that ($\zeta_d^0 \approx 405$ cm^{-1} [11]) of central Mn^{4+} ion. In fact, in both one- and two-SO-parameter models, only the contributions to EPR parameters due to the interaction of CF excited states with the ground state via SO coupling (i.e., CF mechanism) are contained. Considering that the charge-transfer (CT) energy levels lower with the increasing valent state of $3d^n$ ion [12], in the system having high valent state $3d^n$ ion (e.g., the studied h-$BaTiO_3$:Mn^{4+}), the contribution to EPR parameters due to the interaction of CT excited states with the ground state (i.e., CT mechanism) becomes important and should be taken into account. Thus, the complete perturbation formulas should include the contributions from both CF and CT mechanisms. In this paper, we establish the complete high-order perturbation formulas based on the two-mechanism model for the EPR parameters of $3d^3$ ions in trigonal symmetry. From these formulas, the EPR parameters and the defect structure of Mn^{4+} in $Ti^{4+}(I)$ site of h-$BaTiO_3$:Mn^{4+} are studied. The results are discussed.

2. Calculation

In the two-mechanism model, the one-electron basis function $|\Psi_\gamma\rangle$ should contain the anti-bonding (related to CF mechanism) and the bonding orbitals (related to CT mechanism). Thus, for $3d^n$ octahedral clusters, we have

$$|\Psi_\gamma\rangle = N_\gamma^X(|d_\gamma\rangle + \lambda_\gamma^X|p_\gamma\rangle), \tag{1}$$

where the subscript γ ($=t$ or e) denotes the irreducible representation t_{2g} or e_g of O_h group. The superscript X ($=a$ or b) represents the anti-bonding or bonding orbitals. $|d_\gamma\rangle$ and $|p_\gamma\rangle$ are the d orbitals of $3d^n$ ion and the p orbitals of the ligand ions. N_γ^X and λ_γ^X are the normalization coefficients and the orbital mixing coefficients.

The Hamiltonian for $3d^3$ ions in trigonal symmetry in the two-mechanism model is given as

Mn^{4+} *ion in h-BaTiO$_3$ crystal*

$$H = H_0 + H'$$
$$H_0 = H_e + H_a$$
$$H' = H_b + H_{\text{tri}} + H_{\text{SO}}^{\text{CF}} + H_{\text{Ze}}^{\text{CF}} + H_{\text{SO}}^{\text{CT}} + H_{\text{Ze}}^{\text{CT}}, \tag{2}$$

where H_e, H_a, H_b, H_{tri}, H_{SO} and H_{Ze} indicate, respectively, the $3d^3$ ions in the cubic part of CF, the diagonal and off-diagonal terms of electrostatic interaction, the trigonal part of CF parameters, the SO coupling interaction and the Zeeman interaction terms. According to the basis functions and Hamiltonian, the high-order perturbation formulas based on the two-mechanism model for the EPR parameters of $3d^3$ ions in trigonal octahedral clusters are established by applying the Macfarlane's perturbation-loop method [7,8]. They are

$$g_\parallel = g_e + \Delta g_\parallel^{\text{CF}} + \Delta g_\parallel^{\text{CT}}$$

$$\Delta g_\parallel^{\text{CF}} = -\frac{8k'_{\text{CF}}\zeta'_{\text{CF}}}{3E_1} - \frac{4k'_{\text{CF}}\zeta_{\text{CF}}\zeta'_{\text{CF}}}{9E_1^2} + \frac{2k_{\text{CF}}\zeta'^2_{\text{CF}}}{9E_1^2} - \frac{4g_s\zeta'^2_{\text{CF}}}{9E_1^2}$$

$$+ \frac{4k_{\text{CF}}\zeta'^2_{\text{CF}}}{9E_3^2} - \frac{8g_s\zeta'^2_{\text{CF}}}{9E_3^2} - \frac{2k_{\text{CF}}\zeta^2_{CF}}{3E_2^2} - \frac{2g_s\zeta^2_{\text{CF}}}{3E_2^2}$$

$$+ \frac{4k'_{\text{CF}}\zeta_{\text{CF}}\zeta'_{\text{CF}}}{9E_1E_3} - \frac{4k'_{\text{CF}}\zeta_{\text{CF}}\zeta'_{\text{CF}}}{3E_1E_2} + \frac{4k'_{\text{CF}}\zeta_{\text{CF}}\zeta'_{\text{CF}}}{3E_2E_3}$$

$$+ \frac{8k'_{\text{CF}}\zeta'_{\text{CF}}v}{9E_1^2} - \frac{4\sqrt{2}k'_{\text{CF}}\zeta_{\text{CF}}v'}{3E_1E_4} - \frac{4\sqrt{2}k_{\text{CF}}\zeta'_{\text{CF}}v'}{3E_1E_4}$$

$$\Delta g_\parallel^{\text{CT}} = \frac{8k'_{\text{CT}}\zeta'_{\text{CT}}}{3E_n} + \frac{8k'_{\text{CT}}\zeta'_{\text{CT}}v}{9E_n^2}$$

$$g_\perp = g_e + \Delta g_\perp^{\text{CF}} + \Delta g_\perp^{\text{CT}}$$

$$\Delta g_\perp^{\text{CF}} = g_\parallel - \frac{4k'_{\text{CF}}\zeta'_{\text{CF}}v}{9E_1^2} + \frac{4\sqrt{2}k'_{\text{CF}}\zeta_{\text{CF}}v'}{3E_1E_4} + \frac{8\sqrt{2}k_{\text{CF}}\zeta'_{\text{CF}}v'}{3E_1E_4}$$

$$\Delta g_\perp^{\text{CT}} = g_\parallel^{\text{CT}} - \frac{12k'_{\text{CT}}\zeta'_{\text{CT}}v}{9E_n^2}$$

$$D = D^{\text{CF}} + D^{\text{CT}}$$

$$D^{\text{CF}} = \frac{2\zeta'^2 v}{9E_1^2} - \frac{2\zeta'^2 v}{9E_3^2} - \frac{2\sqrt{2}v'\zeta\zeta'}{3E_1E_4} - \frac{\sqrt{2}v'\zeta\zeta'}{E_2E_3} - \frac{\sqrt{2}v'\zeta\zeta'}{3E_3E_4}$$

$$- \frac{\sqrt{2}v'\zeta\zeta'}{E_2E_4} - \frac{8v'B\zeta\zeta'}{E_1E_4E_5} - \frac{4\sqrt{2}v'B_4\zeta'^2}{E_3E_4E_5} - \frac{9\sqrt{2}v'B\zeta'^2}{2E_2^2E_3}$$

$$D^{\text{CT}} = -\frac{2\zeta'^2_{\text{CT}}v}{9E_n^2} \tag{3}$$

in which E_i ($i = 1$–5) are the zero-order energy denominators depending upon the cubic field parameter Dq and Racah parameters B and C [7,8]. v and v' are the trigonal field parameters. E_n is the CT energy level. For the $(\text{MnO}_6)^{8-}$ cluster, we have $E_n \approx 30{,}000$ cm^{-1} [13,14]. The SO coupling parameters ζ, ζ' and the orbital reduction factors k, k' concerning both mechanisms are

$$\zeta_{\mathrm{CF}} = (N_t^a)^2[\zeta_d^0 + (\lambda_t^a)^2\zeta_p^0/2],$$
$$\zeta'_{\mathrm{CF}} = N_t^a \cdot N_e^a[\zeta_d^0 - \lambda_t^a\lambda_e^a\zeta_p^0/2],$$
$$\zeta_{\mathrm{CT}} = N_t^a \cdot N_t^b[\zeta_d^0 + \lambda_t^a\lambda_t^b\zeta_p^0/2],$$
$$\zeta'_{\mathrm{CT}} = N_t^a \cdot N_e^b[\zeta_d^0 - \lambda_t^a\lambda_e^b\zeta_p^0/2],$$
$$k_{\mathrm{CF}} = (N_t^a)^2[1 + 2\lambda_t^a S_{dp}(t_{2g}) + (\lambda_t^a)^2/2],$$
$$k'_{\mathrm{CF}} = N_t^a \cdot N_e^a[1 + \lambda_t^a S_{dp}(t_{2g}) + \lambda_e^a S_{dp}(e_g) - \lambda_t^a\lambda_e^a/\sqrt{2}],$$
$$k_{\mathrm{CT}} = N_t^a N_t^b\{1 + (\lambda_t^a + \lambda_t^b)S_{dp}(t_{2g}) + \lambda_t^a\lambda_t^b/2\},$$
$$k'_{\mathrm{CT}} = N_t^a N_e^b[1 + \lambda_e^b S_{dp}(e_g) + \lambda_t^a S_{dp}(t_{2g}) - \lambda_t^a\lambda_e^b/2], \tag{4}$$

where $S_{dp}(\gamma)$ is the group overlap integrals. For the $(\mathrm{MnO}_6)^{8-}$ cluster in the studied h-BaTiO$_3$:Mn^{4+}, from the Slater-type SCF functions [15,16] and the metal–ligand distance $R \approx 1.96$ Å [4], we obtain $S_{dp}(t_{2g}) \approx 0.02701$ and $S_{dp}(t_{2g}) \approx 0.07745$.

From eq. (1), the molecular orbital (MO) coefficients N_γ^X and λ_γ^X can be related by the normalization correlation

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

and the orthonormal relation

$$\lambda_\gamma^b = -\frac{1 + \lambda_\gamma^a S_{dp}(\gamma)}{\lambda_\gamma^a + S_{dp}(\gamma)}. \tag{6}$$

Thus, the coefficients λ_γ^b, N_γ^a and N_γ^b can be calculated from the coefficient λ_γ^a. We take λ_γ^a ($=\lambda_t^a = \lambda_e^a$) as the adjustable parameter.

No optical spectra of h-BaTiO$_3$:Mn^{4+} were reported. So, we estimate the optical spectra parameters Dq, B and C from those obtained in similar system. Mn^{4+} in h-BaTiO$_3$ and SrTiO$_3$ crystals replace the Ti^{4+} ion and the metal–ligand distances R in both crystals are close to each other (for SrTiO$_3$, $R \approx 1.95$ Å [17]). Considering that for $3d^n$ clusters, the Racah parameters B and C decrease slightly with the increasing distance R [18,19] and the cubic field parameter $Dq \propto R^{-n}$ ($n = 5 \pm 1.5$ [20,21]), from the optical spectra parameters of SrTiO$_3$:Mn^{4+} [22], we obtain for h-BaTiO$_3$:Mn^{4+},

$$Dq \approx 1780 \text{ cm}^{-1}, \quad B \approx 738 \text{ cm}^{-1}, \quad C \approx 2820 \text{ cm}^{-1}. \tag{7}$$

Thus, the energy denominators E_i can be calculated.

From the superposition model [23], the trigonal field parameters in the studied system can be calculated from the following formulas:

$$v = \frac{18}{7}\bar{A}_2(R_0)\left(\frac{R_0}{R}\right)^{t_2}(3\cos^2\theta - 1)$$
$$+\frac{40}{21}\bar{A}_4(R_0)\left(\frac{R_0}{R}\right)^{t_4}(35\cos^4\theta - 30\cos^2\theta + 3)$$
$$+\frac{40\sqrt{2}}{3}\bar{A}_4(R_0)\left(\frac{R_0}{R}\right)^{t_4}\sin^2\theta\cos\theta$$

Mn⁴⁺ ion in h-BaTiO₃ crystal

$$v' = -\frac{6\sqrt{2}}{7}\bar{A}_2(R_0)\left(\frac{R_0}{R}\right)^{t_2}(3\cos^2\theta - 1)$$

$$+\frac{10\sqrt{2}}{21}\bar{A}_4(R_0)\left(\frac{R_0}{R}\right)^{t_4}(35\cos^4\theta - 30\cos^2\theta + 3)$$

$$+\frac{10}{3}\bar{A}_4(R_0)\left(\frac{R_0}{R}\right)^{t_4}\sin^2\theta\cos\theta \tag{8}$$

in which the intrinsic parameter $\bar{A}_4(R_0) \approx 3/4Dq$ [23–25] validated for $3d^n$ ions in octahedral clusters and the intrinsic parameter $\bar{A}_2(R_0) \approx (8\text{–}12)\bar{A}_4(R_0)$ are found for $3d^n$ ions in many crystals [24–27]. We take $\bar{A}_2(R_0) \approx 9\bar{A}_4(R_0)$ here. θ is the angle between the direction of distance R and C_3-axis. Since the nature of impurity Mn^{4+} differs from that of the replaced host ion Ti^{4+}, the local angle θ in the Mn^{4+} impurity centre may be unlike the corresponding angle θ_h in the host crystal. We introduce an impurity-induced angular distorted factor t and assume $\theta = t\theta_h$ ($t = 1$ represents the angle θ being uncharged). Thus, we have two adjustable parameters λ_γ^a and t in the above formulas. By fitting the calculated EPR parameters $g_\parallel, g_\perp$ and D to the experimental values, we yield

$$\lambda_\gamma^a \approx -0.633, \quad t \approx 0.964. \tag{9}$$

The parameters in eq. (4) used in the calculations can be obtained from the MO coefficients. They are ζ_{CF} (cm⁻¹) = 318.4, ζ'_{CF} (cm⁻¹) = 281.0, $k_{CF} = 0.8534$, k'_{CF} = 0.5498, ζ_{CT} (cm⁻¹) = 145.5, ζ'_{CT} (cm⁻¹) = 210.7, $k_{CT} = 0.2277$, $k'_{CT} = 0.7183$. The comparison of EPR parameters between the calculation and experiment are shown in table 1.

3. Discussion

The above calculations show that the angular distorted factor $t \neq 1$, suggesting that the defect structure of Mn^{4+} impurity centre is different from the corresponding structure in the host h-BaTiO₃ crystal.

The sign of D was not given in ref. [5]. From the above calculations, we suggest that D is negative. The relative importance of CT mechanism to EPR parameter Q ($= \Delta g_\parallel$, $\Delta g_\perp$ or D) can be characterized by $|Q^{CT}/Q^{CF}|$. The values of $|Q^{CT}/Q^{CF}|$

Table 1. The EPR parameters $g_\parallel$, $g_\perp$ and D (cm⁻¹) for Mn^{4+} at Ti^{4+}(I) site of h-BaTiO₃.

$\Delta g_\parallel^{CF}$	$\Delta g_\parallel^{CT}$	$g_\parallel$ (total)	$g_\parallel$ (expt. [5])
−0.0242	0.0134	1.9915	1.9901(8)
$\Delta g_\perp^{CF}$	$\Delta g_\perp^{CT}$	$g_\perp$ (total)	$g_\perp$ (expt. [5])
−0.0237	0.0135	1.9921	1.9932(8)
D^{CF}	D^{CT}	D (total)	D (expt. [5])
−0.1179	0.0026	−0.1154	−0.1160*

*The sign is not given in ref. [5].

are about 55, 56 and 2.2 for $Q = \Delta g_\parallel$, $\Delta g_\perp$ or D, respectively. The large difference between $|\Delta g_i^{CT}/\Delta g_i^{CF}|$ and $|D^{CT}/D^{CF}|$ is due to the values of Δg_i in both CF and CT mechanisms coming mainly from the second-order perturbation terms, but those of D from the third-order perturbation terms. From eq. (3), one can find that the value of $|\Delta g_i^{CT}/\Delta g_i^{CF}|$ is roughly related to the ratio $|E_1/E_n|$, but that of $|D^{CT}/D^{CF}|$ to $|E_1/E_n|^2$. Since $|E_1/E_n| < 1$, the large difference between $|\Delta g_i^{CT}/\Delta g_i^{CF}|$ and $|D^{CT}/D^{CF}|$ can be understood. In fact, the large difference between $|\Delta g_i^{CT}/\Delta g_i^{CF}|$ and $|D_{CT}/D_{CF}|$ can also be found for $3d^2$ ions in trigonal tetrahedral clusters in crystals [28]. In addition, in the expressions of Δg_i^{CT} and Δg_i^{CF}, the dominant second-order terms are independent of the trigonal field parameters. So, the relative importance of $|\Delta g_i^{CT}/\Delta g_i^{CF}|$ is insensitive to the trigonal distortion and so the value of $|\Delta g_\parallel^{CT}/\Delta g_\parallel^{CF}|$ is close to that of $|\Delta g_\perp^{CT}/\Delta g_\perp^{CF}|$. However, the zero-field splitting D is caused by the trigonal (or other low symmetry) distortion. According to eq. (3), it can be seen that D^{CF} depends on the trigonal field parameters v and v', but D^{CT} depends on only the parameter v'. So, the relative importance in magnitude and ever in sign may be related to the trigonal distortion of the studied system.

References

[1] L Mager, G Pauliat, M H Garret, D Rytz and G Roosen, *Opt. Mater.* **4**, 381 (1995)
[2] M B Klein, Photorefractive materials and their applications I: Fundamental phenomena, in: *Topics in applied physics* edited by P Gunter and J P Huignard (Springer-Verlag, Berlin, 1988) Vol. 61
[3] P Gunter and J P Huignard (eds), Photorefractive materials and their applications II, *Topies in applied physics* (Springer-Verlag, Berlin, 1989) Vol. 62
[4] R W G Wyckoff, *Crystal structure* (John Wiley & Sons, Inc., New York, 1964) Vol. 2
[5] R Bottcher, H T Langhammer, T Muller and H P Abicht, *J. Phys.: Condens. Matter* **17**, 4925 (2005)
[6] A Abragam and B Bleaney, *Electron paramagnetic resonance of transition ions* (Oxford University Press, London, 1970)
[7] R M Macfarlane, *J. Chem. Phys.* **47**, 2066 (1967)
[8] R M Macfarlane, *Phys. Rev.* **B1**, 989 (1970)
[9] M L Du, *Phys. Rev.* **B46**, 5274 (1992)
[10] M L Du and C Rudowicz, *Phys. Rev.* **B46**, 8974 (1992)
[11] J S Griffith, *The theory of transition metal ions* (Cambridge University Press, London, 1961)
[12] A B P Lever, *Inorganic electronic spectroscopy* (Elsevier, Amsterdam, 1984)
[13] G Blasse and P H M de Korte, *J. Inorg. Nucl. Chem.* **43**, 1505 (1981)
[14] T Yamase, T Kobayashi and S F A Kettle, *J. Electrochem. Soc.* **143**, 1678 (1996)
[15] E Clementi, D L Raimondi and W P Reinhardt, *J. Chem. Phys.* **47**, 1300 (1967)
[16] E Clementi and D L Raimondi, *J. Chem. Phys.* **38**, 2686 (1963)
[17] M Sato, Y Soejima, N Ohama, A Okazaki, H J Scheel and K A Muller, *Phase Transitions* **5**, 207 (1985)
[18] V Luana, M Bermejo, M Florez, J M Recio and L Pueyo, *J. Chem. Phys.* **90**, 6409 (1989)
[19] J C Zahner and H G Drickamer, *J. Chem. Phys.* **47**, 1300 (1967)
[20] D Hernandez, F Rodriguez, M Moreno and H U Gudel, *Physica* **B265**, 186 (1999)

[21] M Moreno, M T Barrinso and J A Aramburu, *J. Phys.: Condens. Matter* **4**, 9481 (1992)
[22] Z Bryknar, V Trepakov, Z Potucek and L Jastrabik, *J. Lumin.* **87–89**, 605 (2000)
[23] J D Newman and B Ng, *Rep. Prog. Phys.* **52**, 699 (1989)
[24] W C Zheng, X X Wu, Q Zhou and Y Mei, *Spectrochim. Acta* **A66**, 126 (2007)
[25] W L Yu, *J. Phys.: Condens. Matter* **6**, 5105 (1994)
[26] T H Yeom, S H Choh, M L Du and M S Tang, *Phys. Rev.* **B53**, 3415 (1996)
[27] C Rudewicz and Y Y Zhou, *J. Magn. Magn. Mater.* **111**, 153 (1992)
[28] W C Zheng, X X Wu, Q Zhou and Y Mei, *Chem. Phys. Lett.* **406**, 192 (2005)