

Theoretical investigations of the g factors and the local structure for the trigonal Zr^{3+} center in X-ray irradiated YSZ

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Abstract

The electron paramagnetic resonance (EPR) g factors $g_{//}$ and g_{\perp} and the local structure for the trigonal Zr^{3+} center in X-ray irradiated yttria-stabilized zirconia (YSZ) are theoretically investigated from the perturbation formulas of the g factors for a d^1 ion in trigonally distorted octahedra. Based on the studies, in this trigonal center (characterized as $[ZrO_6]^{9-}$ cluster associated with two oxygen vacancies V_O along the $[1\ 1\ 1]$ axis), the O^{2-} ions in the ligand triangles are found to displace towards the neighbouring V_O by about $0.42\ \text{\AA}$ due to the electrostatic attraction of the V_O . The above displacement is comparable with that ($\approx 0.36\ \text{\AA}$) obtained from neutron diffraction measurements and those ($\approx 0.24\text{--}0.37\ \text{\AA}$) based on the optical spectral analysis and crystal-field calculations in the previous works. Particularly, partial quenching of the spin-orbit (SO) coupling interaction (i.e., $\gamma(\text{SO}) \approx 0.44$) due to the dynamic Jahn–Teller effect (DJTE) and its influence on the g factors, which were ignored by the previous authors, are taken into account in the present work. The validity of the results is discussed.

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1. Introduction

Yttria-stabilized zirconia (YSZ) is a solid solution of wide range applications due to the remarkable mechanic, thermal, electrical and optical properties. Recently, investigations have been reported on YSZ as electrolyte in solid oxide fuel cell (SOFC) [1–4], high- T_c superconductor thin film substrates [5–7], as well as the properties of optical absorption and upconversion luminescence [8–10], large room temperature magnetoresistance in YSZ doped $La_{0.67}Ba_{0.33}MnO_3$ composite [11]. Particularly, studies on the paramagnetic defects in YSZ due to X-ray irradiation have been carried out by means of electron paramagnetic resonance (EPR) and optical absorption techniques [12–16]. For example, the EPR g factors $g_{//} \approx 1.989$, $g_{\perp} \approx 1.852$ and absorption band (370 nm) were measured for the electron-type trigonally distorted octahedral defect (T -center), which were attributed to the hexa-

coordinated Zr^{3+} ion (i.e., the original Zr^{4+} ion capturing an electron due to X-ray irradiation), midway between two oxygen vacancies (V_O) at the opposite ends of the coordinated cube (see Fig. 1) [12,14,16].

To investigate the observed g factors, the simple perturbation formulas of the g factors for a d^1 ion in trigonally distorted octahedra [12,14] were adopted, with the cubic crystal-field splitting $\Delta (=10D_q)$ or the trigonal splitting δ of the 2T_2 state estimated from other similar systems. Later on, Azzoni et al. [17,18] carried out the studies on the defect structure and crystal-field properties of trigonal six-fold-coordinated Zr^{3+} center in YSZ, by proposing the displacements of about $0.24\text{--}0.37\ \text{\AA}$ for the oxygen ligands towards the V_O along the $[1\ 0\ 0]$ directions. However, there seems to be some imperfectness in their investigations. (i) The parameters D_q (or δ) was adjusted or taken from other systems. In addition, only one splitting (D_q or δ) was included in the simple perturbation formulas [12,14]. (ii) The local structure of the Zr^{3+} defect center was not involved in the studies of the g factors. (iii) Most important, the authors neglected the reduction

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(or quenching) of the spin-orbit (SO) coupling interaction due to the dynamic Jahn–Teller effect (DJTE) for the $[\text{ZrO}_6]^{9-}$ cluster, which has been pointed out by many works for $3d^1$ or $3d^3$ configuration in trigonally distorted environments [19–22]. Instead, a reduction ($\zeta \approx 0.5\zeta_0$) for the SO coupling coefficient was attributed to considerable covalency effect of $\text{Zr}^{3+}-\text{O}^{2-}$ bonding in [14]. Nevertheless, such covalency for the $[\text{ZrO}_6]^{9-}$ cluster in YSZ seems too strong to be regarded as suitable. On the other hand, the above covalency effect was not taken into account in the crystal-field studies [14,17].

In order to make further investigations on the g factors and the defect structure for the above trigonal Zr^{3+} center in X-ray irradiated YSZ, theoretical studies on the g factors and optical absorption band are carried out in this paper based on the improved perturbation formulas of the g factors for a $4d^1$ ion in trigonally distorted octahedra. In these formulas, the contributions to the g factors from both the cubic and trigonal splittings are considered, which are calculated from the generalized crystal-field model and the local structural parameters of the studied system. Based on the studies, the displacements of the oxygen ligands due to the two V_{O} and the reduction effect of the SO coupling coefficient due to the DJTE are also determined. The validity of the results is discussed.

2. Calculations

In X-ray irradiated YSZ, the Zr^{3+} center was observed and attributed to the original Zr^{4+} capturing an electron on irradiation, associated with two V_{O} along the $[1\ 1\ 1]$ (or C_3) axis [12,14,16], i.e., the trigonal (D_{3d}) $[\text{ZrO}_6]^{9-}$ cluster. Since the effective charge of the V_{O} is positive, the oxygen ions in the ligand triangles near the V_{O} may be expected to shift towards the latter along the $[1\ 0\ 0]$ directions by an amount ΔX due to the electrostatic attraction. Thus, the local structure of this center can be characterized by the displacement ΔX of the ligands (see Fig. 1).

For a $4d^1(\text{Zr}^{3+})$ ion in trigonally distorted octahedra, its orbital triplet 2T_2 of cubic case would be split into an orbital doublet 2E and a singlet 2A_1 , with the 2A_1 lying lowest [23]. In the simple perturbation formulas of the g factors used in [12,14], the contributions from the cubic and trigonal field splittings Δ and δ were not included completely. By using the perturbation procedure similar to that of Abragam et al. [23], the improved perturbation formulas of the g factors $g_{//}$ and g_{\perp} for a $4d^1$ ion under octahedral trigonal symmetry can be derived [24]:

$$g_{//} = g_s - (g_s + k) \frac{\zeta^2}{E_2^2},$$

$$g_{\perp} = g_s - 2k \frac{\zeta}{E_2} - 4k \frac{\zeta}{E_1} - (g_s - 2k) \frac{\zeta^2}{(2E_2^2)}, \quad (1)$$

where g_s ($=2.0023$) is the spin-only value. k is the orbital reduction factor, and ζ the SO coupling coefficient for the

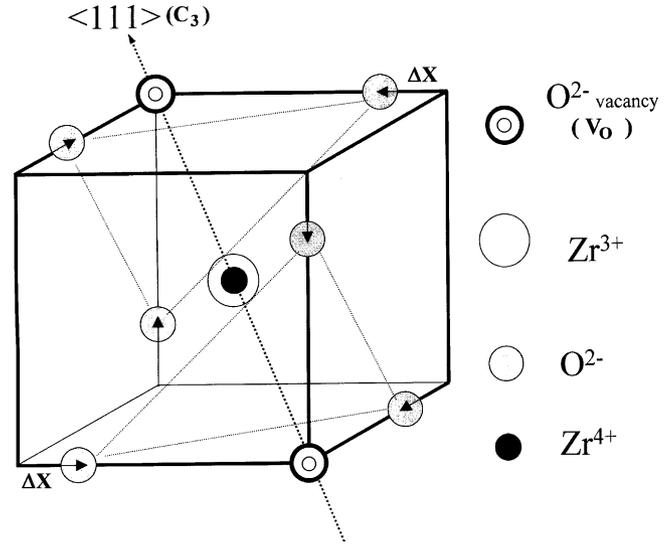


Fig. 1. The local structure of the trigonal Zr^{3+} center in X-ray irradiated YSZ. The Zr^{3+} is formed by the original Zr^{4+} capturing an electron on irradiation, associated with two V_{O} along the $[1\ 1\ 1]$ (or C_3) axis. The O^{2-} ions in the ligand triangles undergo a displacement ΔX towards the neighbouring V_{O} along the $[1\ 0\ 0]$ directions.

$4d^1$ ion in crystals. E_1 is the energy difference between the ground state 2A_1 and the original 2E state of cubic case, and E_2 is that between 2A_1 and the excited state 2E due to trigonal splitting of the cubic 2T_2 state [23,24]. They can be written in terms of the cubic field parameter D_q and the trigonal field parameter V as [9,16]

$$E_1 = 10D_q, \quad E_2 = V \quad (2)$$

The parameters D_q and V can be calculated from the local geometrical relationship (see Fig. 1) of the impurity center, by using the generalized crystal-field model [22,25–27]:

$$D_q = \sum_{j=1}^2 -\frac{3}{8\sqrt{2}} \sin^3 \beta_j \cos \beta_j \text{eq} \frac{\langle r^4 \rangle}{R_j^5},$$

$$V = \sum_{j=1}^2 \left[9(3 \cos^2 \beta_j - 1) \text{eq} \frac{\langle r^2 \rangle}{(14R_j^3)} + 5(35 \cos^4 \beta_j - 30 \cos^2 \beta_j + 3) \text{eq} \frac{\langle r^4 \rangle}{(42R_j^5)} + 5\sqrt{2} \sin^3 \beta_j \cos \beta_j \text{eq} \frac{\langle r^4 \rangle}{(6R_j^5)} \right], \quad (3)$$

where q ($=-2e$) is the effective charge of the oxygen ligand. In view of the overlap between the central metal ion and the ligand orbitals [22,25–27], the SO coupling coefficient ζ and the expectation values $\langle r^n \rangle$ in crystals can be reasonably expressed in terms of the average reduction factor N ($\approx k^{1/2}$) [23,28,29]:

$$\begin{aligned} \zeta &\approx 500N^2 \text{ cm}^{-1}, & \langle r^2 \rangle &\approx 3.857N^2 \text{ a.u.}, \\ \langle r^4 \rangle &\approx 29.389N^2 \text{ a.u.} \end{aligned} \quad (4)$$

From Fig. 1, the local structural parameters R_j and β_j can be determined from the corresponding effective impurity-ligand distance R_0 and angle β_0 (in absence of perturbation due to the V_O) and the displacement ΔX . For the Zr^{4+} site in YSZ, the $\text{Zr}^{4+}-\text{O}^{2-}$ distance is about $\sqrt{3}a/4$ ($\approx 2.226 \text{ \AA}$ [16,17]), and the angle β_0 of the $\text{Zr}^{4+}-\text{O}^{2-}$ bond related to the C_3 axis is about 70.53° .

In the above formulas, only the average reduction factor N and the displacement ΔX are unknown. Substituting these values into Eqs. (1)–(3) and fitting the calculated optical absorption band (or D_q) and the g factors to the observed values, we have

$$N \approx 0.983, \quad \Delta X \approx 0.42 \text{ \AA}. \quad (6)$$

The corresponding results are shown in Table 1. One can find that the theoretical D_q shows reasonable agreement with the observed result. However, the calculated g factors are inconsistent with the experimental data, regardless of the values of N and ΔX . Even though one adopts significant covalency effect (i.e., $k = N^2 \approx 0.5$) suggested in [14], the theoretical results are still in poor agreement with experiment by adjusting the ΔX . So, it seems that the optical absorption and g factors cannot be satisfactorily explained in the scheme of static crystal-field theory.

As mentioned before, the contributions of the DJTE in the $[\text{ZrO}_6]^{9-}$ cluster, which may lead to significant reduction or quenching of the SO coupling interaction, should be taken into account [19–22]. Thus, an additional reduction factor $\gamma(\text{SO})$ can be introduced for the SO coupling coefficient in Eq. (4), i.e., $\zeta \approx 500 \gamma(\text{SO}) N^2 \text{ cm}^{-1}$. By fitting the calculated g factors to the observed values, one can obtain

$$\gamma(\text{SO}) \approx 0.44. \quad (7)$$

The corresponding theoretical results are shown in Table 1. For comparison, the calculated results of the g factors and the optical absorption band by the previous works [12,14,17] are collected in Table 1. In addition, the theoretical values based

on the above $\gamma(\text{SO})$ and neglecting of the displacement of the oxygen ligands (i.e., $\Delta X = 0$) are also shown in Table 1.

3. Discussions

From Table 1, one can find that the theoretical D_q and g factors based on the displacement ΔX and $\gamma(\text{SO})$ in Eqs. (6) and (7) are in better agreement than those obtained in [12,14,17] and those based on the perturbation formulas of present work and neglecting of ΔX or $\gamma(\text{SO})$ with the observed values. There are several points that may be discussed here.

- (1) The validity of the adjustable parameters in Eqs. (6) and (7) can be illustrated as follows: (i) The average reduction factor N (≈ 0.983 , or $k \approx 0.967$) is close to unit, suggesting that the covalency effect for the $\text{Zr}^{3+}-\text{O}^{2-}$ bonds in YSZ is weak. For the isoelectronic ($4d^1$) $\text{Mo}^{5+}-\text{O}^{2-}$ bonds in CaWO_4 , the orbital reduction factor $k \approx 0.85$ was obtained [28]. Considering that the Zr^{3+} has lower valence state, the larger k or weaker covalency effect for the $\text{Zr}^{3+}-\text{O}^{2-}$ bonds in this work can be regarded as reasonable. Therefore, the $\text{Zr}^{3+}-\text{O}^{2-}$ bonds in YSZ may be mainly ionic. (ii) The displacement ΔX ($\approx 0.42 \text{ \AA}$) of the oxygen ligands towards the V_O obtained in this work is also comparable with that ($\approx 0.36 \text{ \AA}$) obtained from neutron diffraction measurements [30], and those ($\approx 0.24-0.37 \text{ \AA}$) obtained from the optical spectral analysis and crystal-field calculations in the previous works [17,18]. Considering the strong electrostatic attraction between the oxygen ions in ligand triangles and the nearest V_O , the large displacement ΔX can be understood (see Fig. 1). (iii) The significant reduction of the SO coupling coefficient due to the DJTE is described by $\gamma(\text{SO}) \approx 0.44$, whose contributions to the g factors cannot be satisfactorily accounted for on the basis of covalent bonding [20,24]. This value is much larger than that (≈ 0.075) for the trigonal $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ cluster in methylammonium aluminum alum [19], where the SO coupling coefficient ($\zeta_0 \approx 154 \text{ cm}^{-1}$ [23]) is much smaller for the free Ti^{3+} ion. Thus, the weak SO coupling interaction

Table 1

The optical absorption band (in cm^{-1}) and the EPR g factors for the trigonal Zr^{3+} center in X-ray irradiated YSZ

	Cal. ^a	Cal. ^b	Cal. ^c	Cal. ^d	Cal. ^e	Cal. ^f	Expt. [12,16,18]
Δ ($=10D_q$)	20000	–	26052	27022	14024	27022	27027
$g_{//}$	1.998	2.0023	1.995	1.943	1.999	1.991	1.989 (4)
g_{\perp}	1.107	1.853	1.815	1.660	1.876	1.851	1.852 (28)

^a Calculations based on the simple perturbation formulas of the g factors in [12].

^b Calculations based on the simple perturbation formulas of the g factors in [14].

^c Calculations based on crystal-field approach and the strong covalency reduction ($\zeta \approx 0.5\zeta_0$) of SO coupling coefficient in [17].

^d Calculations based on the improved perturbation formulas Eq. (1), the displacement ΔX and neglecting of the reduction of the SO coupling coefficient due to the DJTE in present work.

^e Calculations based on the improved perturbation formulas Eq. (1), the reduction of the SO coupling coefficient due to the DJTE and neglecting of the ΔX in present work.

^f Calculations based on the improved perturbation formulas Eq. (1), the ΔX and the reduction of the SO coupling coefficient due to the DJTE in present work.

in this system cannot depress the DJTE, which may become very strong. As a result, the SO coupling interaction is almost completely quenched in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. However, for the much larger SO coupling coefficient ($\zeta_0 \approx 500 \text{ cm}^{-1}$ [23]) of Zr^{3+} in the studied $[\text{ZrO}_6]^{9-}$ cluster, the DJTE may not be strong enough and then the SO coupling interaction is only partially quenched [20]. Therefore, the larger value of $\gamma(\text{SO})$ for $\text{YSZ}:\text{Zr}^{3+}$ obtained in this work can be understood.

- (2) When the displacement ΔX is neglected (see Cal.^e in Table 1), the theoretical results are not as good as those including it, particularly, the D_q is only about half of the observed value. This means that the estimated crystal-field strength based on the original R_0 ($\approx 2.226 \text{ \AA}$) is too small. Thus, as the oxygen ions undergo the shift ΔX towards the V_O , the impurity-ligand bonding length decreases to R_j ($\approx 2.012 \text{ \AA}$) so as to increase the value of D_q (see Eq. (3)). Therefore, the observed optical absorption band ($\approx 27027 \text{ cm}^{-1}$) may be attributed to the six oxygen ligands suffering a large displacement ΔX . In addition, incomplete consideration of the contributions to the g factors from cubic and trigonal field splittings (Δ and δ) in the simple perturbation formulas of the previous works [12,14,17] leads to the theoretical g factors which do not show good agreement with the experimental results (see Cal.^{a,b,c} in Table 1). Therefore, the improved perturbation formulas of the g factors adopted in this work seem to be more reasonable.
- (3) There are some errors in the calculations due to the following: (i) The approximation of the theoretical model and the calculation formulas (as well as the related parameters) may bring some errors to the final results. (ii) In the perturbation formulas Eq. (1), the magnitudes of g_{\parallel} and g_{\perp} depend largely upon the terms ζ^2/E_2^2 (~ 0.005) and $\zeta/E_2 + \zeta/E_1$ (~ 0.08), respectively. Then, the higher order perturbation contributions can be expected to be much smaller. So, the convergence of the formulas may be regarded as valid, under the condition of the strong cubic and trigonal crystal-fields in this work. (iii) Recent studies on the oscillator strength of optical transitions for the Zr^{3+} center in YSZ revealed that local axial distortions without inversion symmetry account for the experimental optical absorption and EPR spectra [18]. The authors preferred C_{3v} to the strict D_{3d} symmetry i.e., the displacements of the oxygen ions in upper ($\Delta X_2 \approx 0.37 \text{ \AA}$) and lower ligand triangles ($\Delta X_1 \approx 0.24\text{--}0.37 \text{ \AA}$) may not be equivalent [16,18]. For the sake of reduction of number of the adjustable parameters, only one displacement ΔX (i.e., D_{3d} approach) is applied for simplicity in this work. Considering the above errors, one can approximately estimate that $\Delta X \approx 0.42 \pm 0.07 \text{ \AA}$ for the two groups of ligands, which is also in accordance with the result ($\approx 0.36 \text{ \AA}$) of neutron diffraction measurements [30].

In summary, the EPR g factors and the local structure for the trigonal Zr^{3+} center in X-ray irradiated YSZ are theoretically investigated on the basis of the improved perturbation formulas for the g factors. The contributions to the g factors from the reduction of the SO coupling coefficient due to the DJTE and the displacement of the ligands due to the V_O are also analyzed.

References

- [1] S.K. Pratihari, A.D. Sharma, R.N. Basu, H.S. Maiti, J. Power Sources 129 (2004) 138.
- [2] S.P. Jiang, Y.Y. Duan, J.G. Love, J. Electrochem. Soc. 149 (2002) A1175.
- [3] J.W. Yan, Z.G. Lu, Y. Jiang, Y.L. Dong, C.Y. Yu, W.Z. Li, J. Electrochem. Soc. 149 (2002) A1132.
- [4] J. Liu, W. Liu, Z. Lu, L. Pei, L. Jia, L. He, W. Su, Solid State Ionics 118 (1999) 67.
- [5] L. Kang, Z.F. Di, S.Z. Yang, Y.J. Feng, P.H. Wu, Supercond. Sci. Technol. 15 (2002) 320.
- [6] A.N. Khodan, J.P. Contour, D. Michel, O. Durand, R. Lyonnet, M. Mihet, J. Cryst. Growth 209 (2000) 828.
- [7] M. Krellmann, D. Selbmann, U. Schmatz, F. Weiss, J. Alloys Compd. 251 (1997) 307.
- [8] B. Savoini, J.E. Munoz-Santiuste, R. Gonzalez, G.K. Cruz, C. Bonardi, R.A. Carvalho, J. Alloys Compd. 323–324 (2001) 748.
- [9] J.E. Munoz-Santiuste, B. Savoini, R. Gonzalez, J. Alloys Compd. 323–324 (2001) 768.
- [10] A.A. Kaminskii, Ann. Phys. (Paris) 16 (1991) 639.
- [11] Z.C. Xia, S.L. Yuan, W. Feng, L.J. Zhang, G.H. Zhang, J. Tang, L. Liu, S. Liu, G. Peng, D.W. Niu, L. Chen, Q.H. Zheng, Z.H. Fang, C.Q. Tang, Solid State Commun. 128 (2003) 291.
- [12] C.B. Azzoni, A. Paleari, Phys. Rev. B 40 (1989) 6518.
- [13] C.B. Azzoni, A. Paleari, Phys. Rev. B 40 (1989) 9333.
- [14] V.M. Orera, R.I. Merino, Y. Chen, R. Cases, P.J. Alonso, Phys. Rev. B 42 (1990) 9782.
- [15] R.I. Merino, V.M. Orera, E.E. Lomonova, S.K.H. Batygov, Phys. Rev. B 52 (1990) 6510.
- [16] C.B. Azzoni, L. Bolis, P. Camagni, G.C. Campagnoli, M. De Simone, Radiat. Eff. Defects Solids 134 (1995) 485.
- [17] C.B. Azzoni, A. Paleari, Phys. Rev. B 44 (1991) 6858.
- [18] C.B. Azzoni, L. Bolis, A. Paleari, G. Samoggia, F. Scardina, Phys. Rev. B 51 (1995) 15942.
- [19] N. Rumin, C. Vincent, D. Walsh, Phys. Rev. 7 (1973) 1811.
- [20] F.S. Ham, Phys. Rev. 138 (1965) A1727.
- [21] R.M. Macfarlane, J.Y. Wong, M.D. Sturge, Phys. Rev. 166 (1968) 250.
- [22] M.G. Zhao, Chin. Phys. Lett. 20 (2003) 2229.
- [23] A. Abragam, B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Oxford University Press, London, 1970.
- [24] M. Narayana, V.S. Sivasankar, S. Radhakrishna, Phys. Status Solidi (b) 105 (1981) 11.
- [25] M.G. Zhao, J. Chem. Phys. 109 (1998) 8003.
- [26] M.G. Zhao, M. Chiu, Phys. Rev. B 49 (1994) 12556.
- [27] M.G. Zhao, Y. Lei, J. Phys.: Condens. Matter 9 (1997) 529.
- [28] A.S. Chakravarty, Introduction to the Magnetic Properties of Solids, Wiley-Interscience Publication, New York, 1980.
- [29] J.W. Richardson, M.J. Blackman, J.E. Ranschak, J. Chem. Phys. 58 (1973) 3010.
- [30] D. Steele, B.E.F. Fender, J. Phys. C 7 (1974) 1.