



EPR g factors and defect structures for V^{4+} and Cr^{5+} in the rutile-type crystals



Minjie Wang, Lianxuan Zhu*

College of Sciences, Henan Agricultural University, Zhengzhou 450002, China

ARTICLE INFO

Article history:

Received 3 February 2016

Received in revised form

19 March 2016

Accepted 21 March 2016

Available online 29 March 2016

PACS numbers:

75.10.Dg

76.30.Fc

71.70.Ch

Keywords:

Crystal structures

EPR

g -factor

Charge-transfer (CT) excited states

Impurity

ABSTRACT

The g -factor formulas for V^{4+} and Cr^{5+} ions in the rutile-type crystals are deduced from Jahn-Teller effect and contributions of the charge transfer levels. The tetragonal distortions $\Delta R = -0.0045$, -0.0045 and -0.0067 nm, and $\Delta\theta = 0^\circ$, -0.001° and 0° , for $GeO_2:V^{4+}$, $TiO_2:V^{4+}$ and $TiO_2:Cr^{5+}$, respectively. The calculations of the g -factors agree well with the experimental values. The contributions of the charge transfer levels to g factors increase with the increasing valence state. It must be taken into account in the precise calculations of g factors for the high valence state d^1 ions in crystals.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Rutile-type crystals TiO_2 and GeO_2 have been of considerable theoretical and experimental interest because of their unique optical, dielectric, magnetic and catalytic properties when doped with transition-metal (TM) ions [1–9]. Their properties most closely relate to the electronic levels and structures of TM impurity centers in crystals. Electron Paramagnetic Resonance (EPR) is a very efficient technique to probe the local magnetic and structural properties of crystals [10,11]. So, the EPR spectra of $TiO_2:V^{4+}$ and $GeO_2:V^{4+}$ were carried out by the cw and pulsed experiment and the anisotropic g -factors were measured [12]. The g -factor of $TiO_2:Cr^{5+}$ was also obtained by Weckhuysen in 1993 [13]. Gallay et al. established a simple point-charge model to interpret the g -factors of $TiO_2:V^{4+}$ and $GeO_2:V^{4+}$ [12]. In such a model, the near-neighbor oxygen ions are taken into account, and the radial averages $\langle r^2 \rangle$ and $\langle r^4 \rangle$ were adjusted for comparison to experimental EPR g -factor. However, the model did not take into account some

important factors, including charge-transfer levels, spin-orbit coupling interactions in ligand orbitals and local lattice deformations caused by the Jahn-Teller effect. In fact, they are very important of the analysis of the EPR spectra.

In this paper, the complete high-order perturbation formulas are established based on Jahn-Teller effect, contributions of the charge-transfer (CT) levels, and that of the spin-orbit coupling effect. The EPR g -factors are calculated for $GeO_2:V^{4+}$, $TiO_2:V^{4+}$ and $TiO_2:Cr^{5+}$ crystals. It is found that the contribution of the CT levels to the EPR g -factors for Cr^{5+} ions is critical and cannot be ignored, because the energies of the CT levels decline and the impurity-ligand orbital admixtures become more obvious owing to higher valence.

2. Theory and formulas

The O-Ti (or O-Ge) octahedral is minorly elongated in the pure rutile-type crystals TiO_2 and GeO_2 , with four shorter perpendicular bonds and two longer parallel bonds. The planar bond angles (θ) are slightly different from the ideal value 90° for an equilateral octahedron. The V^{4+} ion replaces the host Ti^{4+} and Ge^{4+} in $TiO_2:V^{4+}$ and $GeO_2:V^{4+}$, and the Cr^{5+} ion replaces the host Ti^{4+} ion in $TiO_2:Cr^{5+}$.

* Corresponding author. College of Sciences, Henan Agricultural University, NO. 95 Wenhua Road, Zhengzhou City, Henan Province 450002, China.

E-mail address: zhulianxuan@henau.edu.cn (L. Zhu).

The impurity ions V^{4+} and Cr^{5+} are surrounded by six O^{2-} ions to form an octahedral cluster in the crystals. When V^{4+} or Cr^{5+} is in an octahedral field, the energy level 2D would be split into 2E_g and ${}^2T_{2g}$ levels. The lower 2E_g level is further separated into two orbital singlets ${}^2A_{1g}(|d(z^2)\rangle)$ and ${}^2B_{1g}(|d(xy)\rangle)$, while the original lower orbital triplet ${}^2T_{2g}$ is split into three orbital singlets ${}^2B_{2g}(\langle d(xz)|)$, ${}^2B_{3g}(\langle d(yz)|)$ and ${}^2B_{1g}(\langle d(x^2-z^2)|)$. Thus, the perturbation formulas of the g factors may be written as

$$\begin{aligned} g_x &= g_e + \Delta g_x^L + \Delta g_x^T, \\ g_y &= g_e + \Delta g_y^L + \Delta g_y^T, \\ g_z &= g_e + \Delta g_z^L + \Delta g_z^T, \\ \Delta g_x^L &= -\frac{2k'_L \xi'_L \xi_L}{W_1^2} - \frac{2k'_L \xi'_L}{W_2} + \frac{k_L \xi_L^2}{2W_2^2} - \frac{k_L \xi_L^2}{2W_3^2} + \frac{2k'_L \xi'_L \xi_L}{W_3 W_1}, \\ \Delta g_y^L &= -\frac{2k'_L \xi'_L \xi_L}{W_1^2} - \frac{k_L \xi_L^2}{2W_2^2} - \frac{2k'_L \xi'_L}{W_3} + \frac{k_L \xi_L^2}{2W_3^2} + \frac{2k'_L \xi'_L \xi_L}{W_1 W_2}, \\ \Delta g_z^L &= -\frac{8k'_L \xi'_L}{W_1} + \frac{2k'_L \xi'^2}{W_1^2} + \frac{k_L \xi_L^2}{2W_2^2} - \frac{k_L \xi_L^2}{2W_3^2} + \frac{k_L \xi_L^2}{W_2 W_3}, \\ \Delta g_x^T &= \frac{2\xi'_T k'_T}{W_n} - \frac{3\xi'^2_T k'_T}{W_m W_n}, \\ \Delta g_y^T &= \frac{2\xi'_T k'_T}{W_n} - \frac{3\xi'^2_T k'_T}{W_m W_n}, \\ \Delta g_z^T &= \frac{8\xi'_T k'_T}{W_m} + \frac{6\xi'^2_T k'_T}{W_n^2}, \end{aligned} \quad (1)$$

in which g_0 (~ 2.0023) is the free-ion g value; the superscript (or subscript) L denote the crystal-field mechanism and T is related to the CT levels. The SO coupling parameters ξ and ξ' as well as the orbital reduction factors k and k' are expressed below:

$$\xi_L = A_t^a \left[\xi_d^0 + \frac{3}{2} (\mu_t^a)^2 \xi_p^0 \right],$$

$$\xi'_L = \sqrt{A_t^a A_e^a} \left(\xi_d^0 - \frac{3}{2} \mu_t^a \mu_e^a \xi_p^0 \right),$$

$$k_L = A_t^a \left[1 + 2\sqrt{3} \mu_t^a G_t + \frac{3}{2} (\mu_t^a)^2 \right],$$

$$k'_L = \sqrt{A_t^a A_e^a} \left(1 + \sqrt{3} \mu_t^a G_t + \sqrt{3} \mu_e^a G_e - \frac{3}{2} \mu_t^a \mu_e^a \right),$$

$$\xi_T = \sqrt{A_t^a A_t^b} \left(\xi_d^0 + \frac{3}{2} \mu_t^a \mu_t^b \xi_p^0 \right),$$

$$\xi'_T = \sqrt{A_e^b A_t^a} \left(\xi_d^0 - \frac{3}{2} \mu_t^a \mu_e^b \xi_p^0 \right),$$

$$\begin{aligned} k_T &= \sqrt{A_t^a A_t^b} \left(1 + \sqrt{3} \mu_t^b G_t + \sqrt{3} \mu_t^a G_t + \frac{3}{2} \mu_t^a \mu_e^b \right), \\ k'_T &= \sqrt{A_t^a A_e^b} \left(1 + \sqrt{3} \mu_e^b G_e + \sqrt{3} \mu_t^a G_t - \frac{3}{2} \mu_t^a \mu_e^b \right), \end{aligned} \quad (2)$$

where $\xi_0 d$ and $\xi_0 p$ are the spin-orbit parameter of free d^1 ion and that of free ligand ion. We have $\xi_0 d(V^{4+}) = 248 \text{ cm}^{-1}$ [14], $\xi_0 d(Cr^{5+}) = 383 \text{ cm}^{-1}$ and $\xi_0 p(O^{2-}) = 150 \text{ cm}^{-1}$ [15,16]. $AM Y$ denotes the normalization coefficient and $\mu M \tau$ is the orbital mixing coefficient. The superscript M (a or b) represents the anti-bonding or the bonding orbital, and the subscript Y (t or e) indicates the cubic irreducible representations. They can be determined as follows:

$$A_Y^M = \frac{1}{1 + 2\sqrt{3} \mu_Y^M G_Y + 3(q_Y^M)^2},$$

$$\mu_Y^b = -\frac{1 + \sqrt{3} \mu_Y^a G_Y}{3\mu_Y^a + \sqrt{3} G_Y},$$

$$N^2 = (A_t^a)^2 \left[1 + 3(\mu_t^a)^2 G_t + 2\sqrt{3} \mu_t^a G_t \right],$$

$$N^2 = (A_e^a)^2 \left[1 + 3(\mu_e^a)^2 G_e + 2\sqrt{3} \mu_e^a G_e \right], \quad (3)$$

where N is the average covalency factor. W_m and W_n are the lowest CT energy levels. G_Y ($Y = t$ or e) represents the group overlap integral which can be obtained from the Slater-type self-consistent field (SCF) functions [17,18]. W_i ($i = 1-3$) denote the zero-order energy levels for d^1 ion and can be expressed in terms of the cubic field parameter D_q and the rhombic field parameters D_s , D_t , D_ξ and D_η . They are expressed as

$$W_1 = 10D_q,$$

$$W_2 = -12D_s + 10D_t + D_\xi - 16D_\eta$$

$$W_3 = -12D_s + 10D_t - D_\xi - 16D_\eta \quad (4)$$

The rhombic field parameters D_s , D_t , D_ξ and D_η can be calculated from the superposition model [19]. They are given by

$$D_s = \frac{1}{7} \bar{A}_2(R) \left[\left(\frac{R}{R_\perp} \right)^3 - \left(\frac{R}{R_\parallel} \right)^3 \right],$$

$$D_t = \frac{2}{21} \bar{A}_4(R) \left[4 \left(\frac{R}{R_\perp} \right)^5 + (7 \cos 2\theta + 3) \left(\frac{R}{R_\parallel} \right)^5 \right],$$

$$D_\xi = \frac{1}{7} \bar{A}_2(R) \left(\frac{R}{R_\perp} \right)^3 \cos \theta,$$

$$D_\eta = \frac{5}{21} \bar{A}_4(R) \left(\frac{R}{R_\perp} \right)^5 \cos \theta, \quad (5)$$

here $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters varying with the average bonding length R ($= R_\parallel + 2R_\perp$)/3. They can be determined from the cubic crystal field parameter Dq via the relation [20–22]:

Download English Version:

<https://daneshyari.com/en/article/1408901>

Download Persian Version:

<https://daneshyari.com/article/1408901>

[Daneshyari.com](https://daneshyari.com)