Studies of the g Factor for Cr^{4+} Ion in $Bi_4Ge_3O_{12}$ Crystal from Crystal-field and Charge-transfer Mechanisms

Xiao-Xuan Wu[a,b,c], Wen-Chen Zheng[b,c], and Sheng Tang[b]

[a] Department of Physics, Civil Aviation Flying Institute of China, Guanghan 618307, P. R. China
[b] Department of Material Science, Sichuan University, Chengdu 610064, P. R. China
[c] International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, P. R. China

Reprint requests to Prof. W.-C. Zheng. Fax: +86-28-85416050; E-mail: zhengwc1@163.com.

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The complete third-order perturbation formulas of the g factors $g_\parallel$ and $g_\perp$ for $3d^2$ ions in tetragonal MX_4 clusters have been obtained by a cluster approach. In these formulas, in addition to contributions to the g factors from the crystal-field mechanism in the crystal-field theory, the contributions from the charge-transfer mechanism are included. From these formulas, the g factors $g_\parallel$ and $g_\perp$ for a Cr^{4+} ion in a $Bi_4Ge_3O_{12}$ crystal are calculated. The results agree with the observed values. The calculated $\Delta g_i (i = \parallel \text{ or } \perp)$ value due to the charge-transfer is opposite in sign and about 20% greater than that due to the crystal-field mechanism. So, for the $3d^n$ ions having a high valence in crystals, a reasonable explanation of the g factors should take both the crystal-field and charge-transfer mechanisms into account.

Key words: Electron Paramagnetic Resonance; Crystal- and Ligand- field Theory; Charge-Transfer Mechanism; Cr^{4+}, $Bi_4Ge_3O_{12}$.

1. Introduction

For transition-metal ($3d^n$) ions in crystals, the g factor of the ground state should deviate from the free-ion value g_e (≈ 2.0023). The shift of the g factor is caused by admixtures or influences of excited states via spin-orbit (SO) coupling [1]. In the classical crystal-field (CF) theory [1], only the admixtures of CF excited states via SO coupling of the central $3d^n$ ion are considered (so it is called the one-SO-parameter model). Since the SO coupling parameter of the ligand increases with its atomic number and hence with the increasing covalency of the $3d^n$ cluster [2], the contribution to g factor (or g-shift $\Delta g = g - g_e$) from the SO coupling parameter of the ligand should be taken into account in the case of $3d^n$ clusters having strong covalency. Considering this, a two-SO-parameter model based on the cluster approach was developed recently [3 – 6]. In this model, the contributions to the g factor from the SO coupling parameter of ligands are included in addition to that from the central $3d^n$ ion. This model is preferable to the one-SO-parameter model in the explanations of g factors of $3d^n$ ions in covalency crystals. However, in the one- and two-SO-parameter models only the contributions to the g factor due to admixtures of CF excited states are considered, while the contributions due to charge transfer (CT) excited states are neglected because their energies are often much higher than those of CF excited states. It is worth noticing that for the isoelectronic $3d^n$ ion series of crystals, the energies of the CT bands lower with increasing valence state, and hence with increasing atomic number of the $3d^n$ ion [7], so the contributions due to admixtures of CT excited states may be considered in the cases of $3d^n$ ions having a high valence (e.g., $3d^2$ Cr^{4+} and Mn^{5+} ions) in crystals. Thus, a reasonable explanation of the g factor in the above cases should include the contributions due to both the CF and CT mechanisms [8, 9]. In this paper, the complete high-order perturbation formulas (including both the CF and CT mechanisms) of the g factors $g_\parallel$ and $g_\perp$ for $3d^2$ ions in tetragonal MX_4 clusters are obtained from a cluster approach in which both the anti-bonding orbitals in the CF mechanism and the bonding orbitals in the CT mechanism are included. From these formulas, the g factors $g_\parallel$ and $g_\perp$ for Cr^{4+} ions in $Bi_4Ge_3O_{12}$ crystals are calculated (note: because of the success of Cr^{4+} in tetrahedral oxo-coordination as near infrared lasing center, the calculations are of interest). The results are discussed.

2. Calculation

Considering the contributions from the CF and CT mechanisms, the one-electron basis functions of a tetrahedral $3d^n$ MX_4 Cluster can be expressed as a linear combination of atomic orbitals (LCAO), i. e.

$$\begin{aligned} \Psi_t^X &= N_t^X(|d_t> + \lambda_\sigma^X|\sigma_t> + \lambda_\pi^X|\pi_t>), \\ \Psi_e^X &= N_e^X(|d_e> + \sqrt{3}\lambda_\pi^X|\pi_e>), \end{aligned} \tag{1}$$

with the normalization correlation

$$\begin{aligned} N_e^X &= [1 + 3(\lambda_\sigma^X)^2 + 6\lambda_\pi^X S_{dp}(\pi)]^{-1/2}, \\ N_t^X &= [1 + (\lambda_\sigma^X)^2 + (\lambda_\pi^X)^2 + 2\lambda_\sigma^X S_{dp}(\sigma) \\ &\quad + 2\lambda_\pi^X S_{dp}(\pi)]^{-1/2}, \end{aligned} \tag{2}$$

where the superscript $X = a$ or b stands for the antibonding or bonding orbitals. The subscript e or t denotes the irreducible representation of T_d group. $|d_t>$ and $|d_e>$ denote the d orbitals of a $3d^n$ ion. $|\pi_t>$, $|\pi_e>$ and $|\sigma_t>$ are the p orbitals of the ligands. N_t^X and N_e^X are the normalization coefficients, and λ_π^X and λ_σ^X are the orbital mixing coefficients, $S_{dp}(\pi) = <d_t|\pi_t> = <d_e|\pi_e>/\sqrt{3}$ and $S_{dp}(\sigma) = <d_t|\sigma_t>$ are the group overlap integrals.

The perturbation formulas can be obtained from Macfarlane's perturbation- loop methods [10, 11], in which the complete spin Hamiltonian including both CF and CT mechanisms for $3d^2$ ions in a tetragonal MX_4 cluster can be expressed as

$$\begin{aligned} \hat{H} &= \hat{H}_0 + \hat{H}', \\ \hat{H}_0 &= \hat{H}_c + \hat{H}_a, \\ \hat{H}' &= \hat{H}_b + \hat{H}_{tetra} + \hat{H}_{SO}^{CF} + \hat{H}_{Ze}^{CF} + \hat{H}_{SO}^{CT} + \hat{H}_{Ze}^{CT}, \end{aligned} \tag{3}$$

where $\hat{H}_c$, $\hat{H}_a$, $\hat{H}_b$, $\hat{H}_{tetra}$, $\hat{H}_{SO}$ and $\hat{H}_{Ze}$ are the cubic field, the diagonal and off-diagonal terms of electrostatic Coulomb interaction, the tetragonal field, the SO coupling Hamiltonian and the Zeeman interaction terms, respectively. The superscripts CF and CT stand for the corresponding terms related to CF and CT mechanisms. Thus, from the above one-electron basis functions and Macfarlane's perturbation methods [10, 11], the complete third-order perturbation formulas of g factors for $3d^2$ ions in a tetragonal MX_4 cluster can be derived as

$$\begin{aligned} g_\parallel &= g_e + \Delta g_\parallel^{CF} + \Delta g_\parallel^{CT}, \\ \Delta g_\parallel^{CF} &= g_e - 4k'_{CF}\zeta'_{CF}/E_1 - [(g_e - k_{CF}/2)(\zeta'_{CF})^2 + k'_{CF}\zeta'_{CF}\zeta_{CF}]/E_1^2 - (g_e - k_{CF}/2)(\zeta'_{CF})^2/E_2^2 \\ &\quad - k'_{CF}\zeta_{CF}\zeta'_{CF}/(E_1E_2) + 28k'_{CF}\zeta_{CF}D_t/E_1^2, \\ \Delta g_\parallel^{CT} &= 4(k'_{CT}\zeta'_{CT}/E_n + k_{CT}\zeta_{CT}/E_a) - 8[2k'_{CT}\zeta'_{CT}(D_s + 5D_t/4)/E_n^2 - k_{CT}\zeta_{CT}(5D_t - 3D_s)/E_a^2], \end{aligned} \tag{4}$$

$$\begin{aligned} g_\perp &= g_e + \Delta g_\perp^{CF} + \Delta g_\perp^{CT}, \quad \Delta g_\perp^{CF} = \Delta g_\parallel^{CF} - 35k'_{CF}\zeta'_{CF}D_t/E_1^2, \\ \Delta g_\perp^{CT} &= \Delta g_\parallel^{CT} + 12(2k'_{CT}\zeta'_{CT}(D_s + 5D_t/4)/E_n^2 - k_{CT}\zeta_{CT}(5D_t - 3D_s)/E_a^2), \end{aligned} \tag{5}$$

where the zero-order energy separations $E_1 \approx \Delta$ and $E_2 \approx \Delta + 8B + 2C$ (in which, B and C are the Racah parameters in crystals, $\Delta = 10D_q$ is the cubic field parameter). E_n and E_a are the energy levels of CT excited states. D_s and D_t are the tetragonal field parameters. The SO coupling parameters and the orbit reduction factors related to the CF and CT mechanisms are

$$\zeta_{CF} = (N_t^a)^2\{\zeta_d^0 + [\sqrt{2}\lambda_\pi^a\lambda_\sigma^a - (\lambda_\pi^a)^2/2]\zeta_p^0\}, \quad \zeta'_{CF} = N_t^a \cdot N_e^a\{\zeta_d^0 + [\lambda_\pi^a\lambda_\sigma^a/\sqrt{2} + (\lambda_\pi^a)^2/2]\zeta_p^0\},$$

$$\zeta_{CT} = N_t^a \cdot N_t^b\{\zeta_d^0 + [\frac{\lambda_\pi^a\lambda_\sigma^b + \lambda_\pi^b\lambda_\sigma^a}{\sqrt{2}} - \frac{\lambda_\pi^a\lambda_\pi^b}{2}]\zeta_p^0\}, \quad \zeta'_{CT} = N_t^b \cdot N_e^a\{\zeta_d^0 + [\frac{\lambda_\pi^a\lambda_\sigma^b}{\sqrt{2}} + \frac{\lambda_\pi^a\lambda_\pi^b}{2}]\zeta_p^0\},$$

$$k_{CF} = (N_t^a)^2[1 - (\lambda_\pi^a)^2/2 + \sqrt{2}\lambda_\pi^a\lambda_\sigma^a + 2\lambda_\sigma^a S_{dp}(\sigma) + 2\lambda_\pi^a S_{dp}(\pi)],$$

$$k'_{\mathrm{CF}} = N_\mathrm{t}^\mathrm{a} \cdot N_\mathrm{e}^\mathrm{a}[1-(\lambda_\pi^\mathrm{a})^2/2+\lambda_\pi^\mathrm{a}\lambda_\sigma^\mathrm{a}/\sqrt{2}+4\lambda_\pi^\mathrm{a}S_\mathrm{dp}(\pi)+\lambda_\sigma^\mathrm{a}S_\mathrm{dp}(\sigma)],$$

$$k_{\mathrm{CT}} = N_\mathrm{t}^\mathrm{a}N_\mathrm{t}^\mathrm{b}\{1+\left[\frac{\lambda_\pi^\mathrm{a}\lambda_\sigma^\mathrm{b}+\lambda_\pi^\mathrm{b}\lambda_\sigma^\mathrm{a}}{\sqrt{2}}-\frac{\lambda_\pi^\mathrm{a}\lambda_\pi^\mathrm{b}}{2}\right]+(\lambda_\sigma^\mathrm{a}+\lambda_\sigma^\mathrm{b})S_\mathrm{dp}(\sigma)+(\lambda_\pi^\mathrm{a}+\lambda_\pi^\mathrm{b})S_\mathrm{dp}(\pi)],$$

$$k'_{\mathrm{CT}} = N_\mathrm{t}^\mathrm{b}N_\mathrm{e}^\mathrm{a}\{1+\left[\frac{\lambda_\pi^\mathrm{a}\lambda_\sigma^\mathrm{b}}{\sqrt{2}}-\frac{\lambda_\pi^\mathrm{a}\lambda_\pi^\mathrm{b}}{2}\right]+\lambda_\sigma^\mathrm{b}S_\mathrm{dp}(\sigma)(3\lambda_\pi^\mathrm{a}+\lambda_\pi^\mathrm{b})S_\mathrm{dp}(\pi)], \tag{6}$$

where ζ_d^0 and ζ_p^0 are the SO coupling parameter of the $3d^2$ ion and the ligand in free state. If the contributions due to the CT mechanism (i.e., the terms related to the superscript or subscript CT) are neglected, the above formulas become those in the two-SO-parameter model [6].

According to the method in [3, 4], one can obtain the approximate relationship

$$\begin{aligned} f_\mathrm{e} &= (N_\mathrm{e}^\mathrm{a})^4[1+6\lambda_\pi^\mathrm{a}S_\mathrm{dp}(\pi)+9(\lambda_\pi^\mathrm{a})^2S_\mathrm{dp}^2(\pi)],\\ f_\mathrm{t} &= (N_\mathrm{t}^\mathrm{a})^4[1+2\lambda_\sigma^\mathrm{a}S_\mathrm{dp}(\sigma)+2\lambda_\pi^\mathrm{a}S_\mathrm{dp}(\pi)\\ &\quad +2\lambda_\sigma^\mathrm{a}\lambda_\pi^\mathrm{a}S_\mathrm{dp}(\sigma)S_\mathrm{dp}(\pi)\\ &\quad +(\lambda_\sigma^\mathrm{a})^2S_\mathrm{dp}^2(\sigma)+(\lambda_\pi^\mathrm{a})^2S_\mathrm{dp}^2(\pi)] \end{aligned} \tag{7}$$

where $f_\mathrm{e} \approx f_\mathrm{t} \approx (B/B_0+C/C_0)/2$, B_0 and C_0 are the Racah parameters of the free $3d^n$ ion. For a free Cr^{4+} ion [12], $B_0 \approx 1039\ \mathrm{cm}^{-1}$ and $C_0 \approx 4238\ \mathrm{cm}^{-1}$. For the studied $Bi_4Ge_3O_{12} : Cr^{4+}$, from the optical spectra [13], we have

$$B \approx 600\ \mathrm{cm}^{-1}, \quad C \approx 2700\ \mathrm{cm}^{-1}. \tag{8}$$

Thus, $f_\mathrm{e} \approx f_\mathrm{t} \approx 0.607$. The group overlap integrals are related to the impurity-ligand distance R in the $3d^n$ cluster. Since the ionic radius r_i of the impurity is often unlike the radius r_h of the replaced host ion, the impurity-ligand distance R in crystal may be different from the corresponding R_h in the pure or host crystal. We can estimate the distance R by using the approximate formula [14]

$$R \approx R_\mathrm{h} + \frac{1}{2}(r_\mathrm{i} - r_\mathrm{h}). \tag{9}$$

For the $Bi_4Ge_3O_{12} : Cr^{4+}$ crystal, $R_\mathrm{h} \approx 1.739$ Å [15], r_i (Cr^{4+}) ≈ 0.55 Å and $r_\mathrm{h}(Ge^{4+}) \approx 0.53$ Å [16]. Then, we have $R \approx 1.75$ Å. From the value of R and the Slater-type self-consistent field (SCF) functions [17, 18], we obtain the group overlap integrals $S_\mathrm{dp}(\pi) \approx 0.0336$ and $S_\mathrm{dp}(\sigma) \approx -0.1068$. Substituting the values of f_γ, $S_\mathrm{dp}(\pi)$ and $S_\mathrm{dp}(\sigma)$ into (2) and (7), we calculate the parameters N_t^a, N_e^a, λ_π^a and $\lambda_\sigma^\mathrm{a}$ related to the CF mechanism. They are shown in Table 1.

Table 1. The LACO molecular orbital coefficients for $Bi_4Ge_3O_{12} : Cr^{4+}$ crystal.

N_t^a	N_e^a	λ_π^a	$\lambda_\sigma^\mathrm{a}$	N_t^b	N_e^b	λ_π^b	λ^b
0.9111	0.8972	−0.3197	0.4747	0.4261	0.4454	1.1276	−1.6743

Table 2. The g factors $g_\parallel$ and $g_\perp$ for $Bi_4Ge_3O_{12} : Cr^{4+}$ crystal.

Calculation				Experiment [23]
$\Delta g_\parallel^\mathrm{CF}$	$\Delta g_\parallel^\mathrm{CT}$	$g_\parallel^\mathrm{CF}$	$g_\parallel$ (total)	$g_\parallel$
−0.0919	0.0218	1.910	1.932	1.931(1)
$\Delta g_\perp^\mathrm{CF}$	$\Delta g_\perp^\mathrm{CT}$	$g_\perp^\mathrm{CT}$	$g_\perp$ (total)	$g_\perp$
−0.1005	0.0201	1.902	1.922	1.919(1)

From the orthonormal relationship, we have

$$\begin{aligned} \lambda_\pi^\mathrm{b} &= -\frac{1+3\lambda_\pi^\mathrm{a}S_\mathrm{dp}(\pi)}{3[\lambda_\pi^\mathrm{a}+S_\mathrm{dp}(\pi)]},\\ \lambda_\sigma^\mathrm{b} &= -\frac{1+\lambda_\pi^\mathrm{a}\lambda_\pi^\mathrm{b}+(\lambda_\pi^\mathrm{a}+\lambda_\pi^\mathrm{b})S_\mathrm{dp}(\pi)+\lambda_\sigma^\mathrm{a}S_\mathrm{dp}(\sigma)}{\lambda_\sigma^\mathrm{a}+S_\mathrm{dp}(\sigma)}. \end{aligned} \tag{10}$$

Applying the above parameters to (10) and then to (2), the parameters λ_π^b, $\lambda_\sigma^\mathrm{b}$, N_t^b and N_e^b, related to the CT mechanism, are calculated. They are collected in Table 1.

For the $Bi_4Ge_3O_{12} : Cr^{4+}$ crystal, $\zeta_\mathrm{d}^0(Cr^{4+}) \approx 327\ \mathrm{cm}^{-1}$ [12] and $\zeta_\mathrm{p}^0(O^{2-}) \approx 150\ \mathrm{cm}^{-1}$ [4], thus, from the above parameters and those in Table 1, the parameters in (6) can be calculated. They are

$$\begin{aligned} &\zeta_\mathrm{CF} \approx 238\ \mathrm{cm}^{-1}, && \zeta'_\mathrm{CF} \approx 260\ \mathrm{cm}^{-1},\\ &k_\mathrm{CF} \approx 0.5075, && k'_\mathrm{CF} \approx 0.6950,\\ &\zeta_\mathrm{CT} \approx 181\ \mathrm{cm}^{-1}, && \zeta'_\mathrm{CT} \approx 136\ \mathrm{cm}^{-1},\\ &k_\mathrm{CT} \approx 0.8123, && k'_\mathrm{CT} \approx 0.5286. \end{aligned} \tag{11}$$

From the density functional calculations on the $(CrO_4)^{4-}$ tetrahedral cluster [19], one can get $E_\mathrm{n} \approx$

40400 cm^{-1} and $Ea \approx 43600$ cm^{-1} for the Cr^{4+}-O^{2-} distance $R \approx 1.75$ Å. The cubic field parameter $\Delta(=10D_q)$ is estimated from the $^3A_2 \rightarrow {}^3T_2$ transition. This band (which is in the vicinity of 8000 cm^{-1}) is broadened by vibronic interactions [13] and we estimate $D_q \approx 760$ cm^{-1}.

From the empirical superposition model [20], the tetragonal field parameters can be written as

$$\begin{aligned} D_s &= 4\bar{A}_2(R)(3\cos^2\theta - 1)/7, \\ D_t &= 4\bar{A}_4(R)(7\sin^4\theta + 35\cos^4\theta \\ &\quad - 30\cos^2\theta + 3)/21, \end{aligned} \tag{12}$$

where $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters. For a $3d^n$ ion in a tetrahedron we have $\bar{A}_4(R) = 27D_q/16$ [6, 20]. The ratio $\bar{A}_2(R)/\bar{A}_4(R) \approx 9 \sim 12$ for a $3d^n$ ion in many crystals [5, 6, 21, 22] and we take $\bar{A}_2(R)/\bar{A}_4(R) \approx 9$ here. θ is the angle between the R direction and the C_4 axis. As in the case of the bonding length R, the bonding angle θ in the impurit-ligand cluster may be different from that in the pure or host crystal, and so we take the angle θ as an adjustable parameter. By fitting the calculated $g_\parallel$ and $g_\perp$ values to the observed values, we obtain $\theta \approx 55.9^\circ$, which is smaller than that ($\approx 58.06^\circ$ [15]) in pure $Bi_4Ge_3O_{12}$ crystal. Comparisons between the calculated and experimental g factors $g_\parallel$ and $g_\perp$ (including the contributions $\Delta g_i{}^{CF}$ and $\Delta g_i{}^{CT}$ $(i = \parallel$ or $\perp)$ due to the CF and CT mechanisms) are shown in Table 2.

3. Discussion

From Table 2 it can be seen that the calculated $g_\parallel$ and $g_\perp$ values based on the CF and CT mechanisms are closer to the observed values than those based on only the CF mechanism. The calculated $\Delta g_i{}^{CT}(i = \parallel$ or $\perp)$ due to CT mechanism is opposite in sign and about 20% in magnitude, compared with that due to the CF mechanism. So, for high valence state $3d^n$ ions in crystals, reasonable explanations of the g factors should take the CF and CT mechanisms into account.

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