

Theoretical studies of the g factors and local structure for Pt^{3+} in $\alpha\text{-Al}_2\text{O}_3$

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Abstract. The anisotropic g factors and local structure for the trigonal Pt^{3+} centre in $\alpha\text{-Al}_2\text{O}_3$ are theoretically investigated from the perturbation formulas of the g factors for a $5d^7$ ion in trigonal symmetry. The Pt^{3+} impurity is found to experience an outward displacement by about 0.18 Å away from the centre of the oxygen octahedron along the C_3 -axis. The calculated g factors based on the above axial displacement show good agreement with the observed values. Importantly, the pending problem of +3 valence state of the doped Pt in $\alpha\text{-Al}_2\text{O}_3$ is theoretically clarified, and the possibility of Pt^+ ($5d^9$) is thus excluded in this work.

Keywords. Electron paramagnetic resonance (EPR); impurities and defects; Pt^{3+} ; $\alpha\text{-Al}_2\text{O}_3$.

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1. Introduction

Corundum ($\alpha\text{-Al}_2\text{O}_3$) crystals containing platinum have unique surface behaviours [1–4] and catalytic activities [5–7] and thus attract the interest of researchers. In addition, local structure and spectral properties were also extensively investigated for Pt (and other transition-metal ions such as Ni^{2+} , Cr^{3+} , Fe^{3+} and Mn^{4+}) in $\alpha\text{-Al}_2\text{O}_3$ by electron paramagnetic resonance (EPR) technique [8–11]. Among the transition-metal ions, the EPR behaviours in crystals of the first group ($3d^n$) systems have been sufficiently studied, while the third group ($5d^n$) systems are rarely analysed. For example, EPR experiments were performed for Pt-doped $\alpha\text{-Al}_2\text{O}_3$, and the nearly axial g factors were obtained at 4.2 K [11]. Although the above EPR signals were tentatively assigned to the substitutional Pt^+ ($5d^9$) on Al^{3+} site in $\alpha\text{-Al}_2\text{O}_3$ [11], the possibility of Pt^{3+} ($5d^7$) could not be ruled out. Nevertheless, the above axial EPR signal was ascribed to Pt^{3+} on the Al^{3+} site and analysed with the perturbation formulas of the g factors based on the conventional

crystal-field model for a d^7 ion under strong crystal fields [12]. However, the contributions to the g factors arising from the ligand orbital and spin-orbit coupling interactions and the low symmetrical (trigonal) distortion were not taken into account. Meanwhile, these treatments also ignored the local lattice distortion (e.g., impurity axial displacement), which may lead to a different impurity local structure from the host Al^{3+} site in $\alpha\text{-Al}_2\text{O}_3$. Thus, the EPR analysis failed to connect with the defect structure of the impurity centre. As a result, only the isotropic g factor (≈ 2.220 [11]) was analysed in ref. [12], and the local structure information about the Pt impurity in $\alpha\text{-Al}_2\text{O}_3$ was not obtained yet.

Such information would be helpful to understand the properties of this material with $5d^7$ dopants. Meanwhile, microscopic mechanisms of the EPR spectra for Pt^{3+} ($5d^7$) can be different from those for the conventional $3d^n$ ions in crystals and worthy of further investigations. Besides, the pending assignment for Pt^+ or Pt^{3+} in $\alpha\text{-Al}_2\text{O}_3$ also needs to be clarified. To study the EPR spectra and the local structure for Pt-doped $\alpha\text{-Al}_2\text{O}_3$ to a better extent and to clarify the impurity valence state, improved perturbation formulas of the g factors for a $5d^7$ ion in trigonal symmetry are established in this work. In the calculations, the ligand orbital and spin-orbit coupling contributions and the suitable local lattice distortion (e.g., impurity axial displacement due to the size mismatch) are taken into account in a uniform way.

2. Calculations

For $\alpha\text{-Al}_2\text{O}_3$ containing Pt (in PtO_2), the observed g factors $2 \leq g_{\parallel} < g_{\perp}$ [11] may be attributed to the substitutional Pt^{3+} ($5d^7$) partially reduced from the doped Pt^{4+} on the Al^{3+} site. Although a tetragonally compressed Pt^+ ($5d^9$) cluster may also yield the g factors $2 \leq g_{\parallel} < g_{\perp}$ as proposed in ref. [11], the original trigonal symmetry of the Al^{3+} site seems unlikely to exhibit a tetragonally compressed $[\text{PtO}_6]^{11-}$ cluster. In fact, d^9 (e.g., Ni^+ , Cu^{2+} , Ag^{2+}) ions normally tend to show tetragonally elongated octahedra in oxides [13–16]. Besides, monovalent Pt^+ could only result from very high degree of reduction from the doped Pt^{4+} . Moreover, much fewer charge of Pt^+ replacing the trivalent Al^{3+} would induce some means of charge compensation and probably result in lower local symmetry (e.g., orthorhombic). But this is opposite to the observed axial g factors for Pt-doped $\alpha\text{-Al}_2\text{O}_3$. Thus, the assignment of Pt^{3+} in $\alpha\text{-Al}_2\text{O}_3$ is consistent with that of ref. [12] but inconsistent with that of ref. [11] and can be tentatively regarded as suitable.

For a Pt^{3+} ($5d^7$) ion in strong crystal fields, it can be described as an unpaired E_g electron, associated with the ground orbital doublet ${}^2E_g(t_{2g}^6 e_g)$ of low spin ($S = 1/2$) [12,13]. For a trigonally distorted octahedral $5d^7$ cluster, the ground 2E_g state consists of two components u and v , with the former corresponding to the positive anisotropy Δg ($\approx g_{\perp} - g_{\parallel}$) [12,13]. For a d^7 ion in trigonally distorted octahedra, the perturbation formulas of the g factors were established by considering the contributions from the excited states via the spin-orbit coupling and the cubic crystal-field interactions [12]. However, the contributions from the low symmetrical (trigonal) crystal fields and those from the ligand orbitals and spin-orbit coupling interactions were not taken into account. In order to investigate the trigonal Pt^{3+} centre in $\alpha\text{-Al}_2\text{O}_3$ more exactly, the conventional formulas

in ref. [12] may be improved by including the above contributions. By using the similar perturbation method [12] and the cluster approach [18], we have

$$\begin{aligned} g_{\parallel} &= g_s + \frac{2k\zeta'^2}{E_{1\parallel}^2}, \\ g_{\perp} &= g_s + \frac{2k\zeta'^2}{E_{1\perp}^2} + \frac{3k'\zeta'}{E}, \end{aligned} \quad (1)$$

with

$$\frac{1}{E} = \frac{1}{E_3} + \frac{1}{E_4} + 0.38 \left(\frac{1}{E_3} - \frac{1}{E_4} \right). \quad (2)$$

Here g_s ($=2.0023$) is the spin-only value. E_i ($i = 1, 3, 4$) are the energy separations between the excited ${}^4T_{1b}$, ${}^2T_{2a}$ and ${}^2T_{2b}$ and the ground 2E_g states in trigonal symmetry [12,17]. The subscripts \parallel and \perp in $E_{1\parallel}$ and $E_{1\perp}$ denote the corresponding components of the related energy differences due to the trigonal splittings. They can be obtained from the energy matrices for a $5d^7$ ion in trigonal symmetry:

$$\begin{aligned} E_{1\parallel} &= 10Dq - 4B - 4C - \frac{(V + V')}{(3\sqrt{6})}, \\ E_{1\perp} &= \frac{2[10Dq - 4B - 4C - (V + V')/(3\sqrt{6})][10Dq - 4B - 4C + 2(V + V')/(3\sqrt{6})]}{[4(10Dq - 4B - 4C)^2 - 2(10Dq - 4B - 4C)(V + V')/(3\sqrt{6}) + 7(V + V')^2/54]^{1/2}}, \\ E_3 &= 10Dq + 6B - C + \frac{(V + V')}{(3\sqrt{6})}, \\ E_4 &= 10Dq + 14B + C - \frac{(V + V')}{(3\sqrt{6})}. \end{aligned} \quad (3)$$

In the above formulas, omission of the contributions from the trigonal fields (i.e., $V = V' = 0$) and the ligand orbitals (i.e., $k = k' = 1$ and $\zeta = \zeta'$) can reduce them to the conventional formulas in [12].

When the ligand orbital and spin-orbit coupling contributions are introduced on the basis of the cluster approach, the spin-orbit coupling coefficients ζ , ζ' and the orbital reduction factors k , k' in eq. (1) are expressed as [18]

$$\begin{aligned} \zeta &= N_t \left(\zeta_d^0 + \frac{\lambda_t^2 \zeta_p^0}{2} \right), \quad \zeta' = (N_t N_e)^{1/2} \left(\zeta_d^0 - \frac{\lambda_t \lambda_e \zeta_p^0}{2} \right), \\ k &= N_t \left(1 + \frac{\lambda_t^2}{2} \right), \quad k' = (N_t N_e)^{1/2} \left[1 - \frac{\lambda_t (\lambda_e + \lambda_s A)}{2} \right]. \end{aligned} \quad (4)$$

Here ζ_d^0 and ζ_p^0 are the spin-orbit coupling coefficients of the free $5d^7$ and the ligand ions, respectively. A stands for the integral $R \langle ns | \partial/\partial y | np_y \rangle$, with the reference distance R . N_γ and λ_γ (or λ_s) are, respectively, the normalization factors and the orbital admixture

coefficients, with the subscripts γ ($= e$ and t) denoting the irreducible representations E_g and T_{2g} of the O_h group. They are determined from the approximate relationships [18]

$$\begin{aligned} N^2 &= N_t^2[1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}], \\ N^2 &= N_e^2[1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}], \end{aligned} \quad (5)$$

and the normalization conditions [18]

$$\begin{aligned} N_t(1 - 2\lambda_t S_{dpt} + \lambda_t^2) &= 1, \\ N_e(1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) &= 1. \end{aligned} \quad (6)$$

Here N is the average covalency factor, characteristic of the covalency effect (or reduction of the Racah parameters B and C) of the central ion in crystals. $S_{d\gamma}$ (and S_{ds}) are the group overlap integrals. Usually, the orbital admixture coefficients increase with the increase of the corresponding group overlap integrals, and one can approximately apply the proportional relationship $\lambda_e/S_{dpe} \approx \lambda_s/S_{ds}$ between the orbital admixture coefficients and the related group overlap integrals within the same irreducible representation E_g .

The trigonal field parameters V and V' can be obtained from the superposition model [19] and the local geometrical relationship of the studied system:

$$\begin{aligned} V &= (9/7) \bar{A}_2(R) \sum_i \left(\frac{R}{R_i}\right)^{t_2} (3 \cos^2 \beta_i - 1) + \bar{A}_4(R) \sum_i \left(\frac{R}{R_i}\right)^{t_4} \\ &\quad \times \left[\left(\frac{20}{21}\right) (35 \cos^4 \beta_i - 30 \cos^2 \beta_i + 3) + \left(\frac{20\sqrt{2}}{3}\right) \sin^3 \beta_i \cos \beta_i \right], \\ V' &= \times \left(\frac{-3\sqrt{2}}{7}\right) \bar{A}_2(R) \sum_i \left(\frac{R}{R_i}\right)^{t_2} (3 \cos^2 \beta - 1) + \bar{A}_4(R) \sum_i \left(\frac{R}{R_i}\right)^{t_4} \\ &\quad \times \left[\left(\frac{5\sqrt{2}}{21}\right) (35 \cos^4 \beta_i - 30 \cos^2 \beta_i + 3) + \left(\frac{10}{3}\right) \sin^3 \beta_i \cos \beta_i \right]. \end{aligned} \quad (7)$$

Here $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters. For transition-metal ions in the octahedra, $\bar{A}_4(R) \approx (3/4)Dq$ and $\bar{A}_2(R) \approx 10.8 \bar{A}_4(R)$ are proved approximately valid in crystals [20–22] and reasonably adopted here. t_2 (≈ 3) and t_4 (≈ 5) are the power-law exponents [19]. β_i are the angles between the directions of the distances R_i and the C_3 -axis at the host Al^{3+} site. For the regular Al^{3+} site in $\alpha-Al_2O_3$, the structural parameters are $R_1 \approx 1.966 \text{ \AA}$, $\beta_1 \approx 46.7^\circ$, $R_2 \approx 1.857 \text{ \AA}$ and $\beta_2 \approx 62.7^\circ$ [23,24]. Thus, the reference distance R can be taken as the average cation–anion distance $\bar{R} = (R_1 + R_2)/2 \approx 1.9115 \text{ \AA}$. From these formulas, the trigonal distortion (or local structure) of the impurity centre is correlated to the g factors, particularly the anisotropy $\Delta g (= g_\perp - g_\parallel)$.

From the spectral analysis for Pt^{3+} in $\alpha-Al_2O_3$, the cubic field parameter $Dq \approx 2500 \text{ cm}^{-1}$ and the covalency factor $N \approx 0.64$ were obtained [25]. By using the free-ion parameters $B_0 \approx 924 \text{ cm}^{-1}$ and $C_0 \approx 3810 \text{ cm}^{-1}$ [26], the Racah parameters $B \approx N^2 B_0$ and $C \approx N^2 C_0$ can be acquired as well. From the distance \bar{R} and the Slater-type self-consistent field (SCF) functions [27,28], the related integrals are calculated: $S_{dpt} \approx 0.0216$, $S_{dpe} \approx 0.0629$, $S_{ds} \approx 0.0505$, $A \approx 1.2445$. Then the molecular orbital coefficients $N_t \approx 0.647$, $N_e \approx 0.678$, $\lambda_t \approx 0.761$, $\lambda_e \approx 0.604$ and $\lambda_s \approx 0.485$ are determined

Table 1. The anisotropic g factors for the trigonal Pt^{3+} centre in $\alpha-Al_2O_3$ at 4.2 K.

	g_{\parallel}	g_{\perp}	$\Delta g (= g_{\perp} - g_{\parallel})$
Cal. ^a	2.025	2.314	0.289
Cal. ^b	2.002	2.492	0.490
Cal. ^c	2.018	2.323	0.305
Expt. [11]	2.011 (6)	2.328 (4)	0.317 (10)

^aCalculations based on the host structural parameters of the Al^{3+} site in $\alpha-Al_2O_3$ (i.e., taking the impurity displacement $\Delta Z = 0$) and inclusion of the ligand contributions.

^bCalculations based on the impurity displacement ΔZ in eq. (8) and omission of the ligand contributions (i.e., taking $\zeta = \zeta' = N\zeta_d^0$ and $k = k' = N$).

^cCalculations based on the impurity displacement and the inclusion of ligand contributions.

from eqs (5) and (6). Utilizing the free-ion values ζ_d^0 ($\approx 5011 \text{ cm}^{-1}$ [26]) for Pt^{3+} and $\zeta_p^0 \approx 151 \text{ cm}^{-1}$ for O^{2-} [29], the parameters $\zeta \approx 3268 \text{ cm}^{-1}$, $\zeta' \approx 3296 \text{ cm}^{-1}$, $k \approx 0.834$ and $k' \approx 0.358$ are calculated from eq. (4). Substituting these data into eq. (1), the g factors (Cal.^a) are calculated and shown in table 1.

It can be found that these results are not in good agreement with the experimental data, especially the anisotropy Δg is smaller than the observed value [11], suggesting that the local trigonal distortion based on the host Al^{3+} site is underestimated for the impurity centre. This means that the Pt^{3+} impurity may not occupy exactly the host Al^{3+} site in $\alpha-Al_2O_3$ but experience an axial off-centre shift. In order to obtain good agreement between the theoretical and experimental g factors, Pt^{3+} is expected to suffer an outward displacement ΔZ away from the centre of the oxygen octahedron along the C_3 -axis so as to yield larger trigonal distortion and better anisotropy Δg . Fitting the calculated g factors to the experimental data, one can obtain

$$\Delta Z \approx 0.18 \text{ \AA}. \quad (8)$$

Here the displacement direction away from the centre of the oxygen octahedron is defined as positive. The corresponding theoretical results (Cal.^c) are also given in table 1. To clarify the importance of the covalency and ligand contributions, the calculated g factors (Cal.^b) based on omission of the ligand orbital and spin-orbit coupling contributions (i.e., taking $\zeta = \zeta' = N\zeta_d^0$ and $k = k' = N$) are given in table 1.

3. Discussion

Table 1 reveals that the calculated g factors (Cal.^c) for the Pt^{3+} centre in $\alpha-Al_2O_3$ based on the axial outward displacement ΔZ in this work are in better agreement with the observed values than those (Cal.^a) based on the host structural parameters of the ideal Al^{3+} site and those (Cal.^b) based on omission of the ligand contributions.

- (1) From the positive sign of the displacement ΔZ , the Pt^{3+} impurity is found not to occupy the regular Al^{3+} site in $\alpha-Al_2O_3$ but to experience an outward displacement away from the centre of the oxygen octahedron along the C_3 -axis. This point can be illustrated by the displacement model for impurity ions under trigonally-distorted octahedral environments [30,31]. According to the displacement model,

when a host cation is replaced by an impurity with larger size or higher charge, the local environment may become tense and the electrostatic interactions acting upon the impurity would be stronger than those upon the host cation, which may push the impurity further away from the centre of the octahedron. Inversely, as the host cation is substituted by an impurity of smaller size or lower charge, the local environment may become loose and the electrostatic interactions acting upon the impurity would be weaker and thus make the impurity shift towards the centre of the octahedron. The ionic radius of the Pt^{3+} impurity ($\approx 0.725 \text{ \AA}$ [32]) which is larger than that of the host Al^{3+} ($\approx 0.51 \text{ \AA}$ [32]) may bring forward further displacement away from the centre of the oxygen octahedron. Therefore, the moderate and positive displacement ($\Delta Z \approx 0.18 \text{ \AA}$) of Pt^{3+} can be understood. If this impurity displacement is neglected, the theoretical g factors (Cal.^a) are not as good as those (Cal.^c) including the displacement. Particularly, the calculated anisotropy Δg is smaller than the observed value. Furthermore, these discrepancies cannot be removed by adjusting the spectral parameters Dq and N . It is noted that the off-centre displacement of an impurity ion in crystals may be a difficult problem involving various physical and chemical properties of the impurity and host crystals. Particularly, the present calculations are based on the cluster approach containing only six nearest-neighbour oxygen ligands (i.e., $[\text{PtO}_6]^{9-}$ cluster), whereas the contributions from the rest of the lattice are not taken into account. The above treatments are valid when the clusters are roughly uncoupled with the lattice, the electrostatic potential generated by the rest of the lattice is approximately flat and the cluster size is big enough to include some nearest-neighbour ions. Thus, the theoretical study of this work should be regarded as only an approach to this problem, and the impurity axial displacement ΔZ obtained here is actually a tentative one. In order to evaluate the accuracy of the present results and to make more exact investigations of the local structure and the EPR spectra for $\alpha\text{-Al}_2\text{O}_3:\text{Pt}^{3+}$, one should apply the more powerful and reliable density function theory (DFT) calculations [33–36].

- (2) The valence state of Pt was tentatively assumed to be +1 in the previous work [11], since a tetragonally compressed d^9 cluster may yield similar g factors ($2 \leq g_{\parallel} < g_{\perp}$) to the experimental results. Nevertheless, the possibility of Pt^{3+} cannot be excluded [11]. Physically, there seems to be some imperfections in the previous assignment [11]. First, the original trigonal symmetry of the Al^{3+} site in $\alpha\text{-Al}_2\text{O}_3$ make it difficult to yield a tetragonally compressed $[\text{PtO}_6]^{11-}$ cluster. Secondly, d^9 ions tend to exhibit tetragonally elongated octahedra in oxides [13–16]. Thirdly, monovalent Pt^+ could only be produced through very high degree of reduction from the original Pt^{4+} . More importantly, the fewer charge of Pt^+ replacing the host Al^{3+} could induce considerable local charge unbalance. Thus, some means of charge compensation might occur, e.g., a non-axial oxygen vacancy, which would result in lower (orthorhombic or monoclinic) local symmetry. Obviously, this is opposite to the observed axial g factors for Pt-doped $\alpha\text{-Al}_2\text{O}_3$ [11]. If one would deliberately adopt the previous assignment of Pt^+ centre [11] and analyse the EPR results with the g formulas for a d^9 ion under tetragonally compressed octahedra [13], the best results $g_{\parallel} \approx 2.001$ and $g_{\perp} \approx 2.233$ could be obtained based on the optimal tetragonal compression ratio $\tau \approx 0.5$. So, the above results are not as good as

- those (Cal.^c) based on the present assignment of the trigonal Pt³⁺ centre with the impurity displacement ΔZ . Thus, the pending problem of the valence state for Pt in α -Al₂O₃ is clarified in this work, and the probability of Pt⁺ may be excluded here.
- (3) When the contributions from the ligand orbitals and the spin-orbit coupling interactions are neglected, the calculation results (Cal.^b) are not as good as those containing these contributions, e.g., the theoretical g_{\perp} is larger than the observed value. Although the spin-orbit coupling coefficient of the ligand oxygen is much smaller than that of the Pt³⁺ impurity, the small metal–ligand distance R (≈ 1.9115 Å) can result in very strong covalency ($N \approx 0.64 \ll 1$) and significant impurity–ligand orbital admixtures (~ 0.5 – 0.7). Therefore, the perturbation formulas of the g factors containing the ligand contributions in this work seem more applicable than those without these contributions in the previous calculations [12]. Thus, to investigate the g factors better for Pt³⁺ in α -Al₂O₃ (or other similar trigonal environments), the contributions from the ligand orbitals and the low symmetrical distortions should be taken into account in the EPR analysis.
 - (4) Apart from the axial EPR signal ascribed to the trigonal Pt³⁺ centre, another isotropic signal with $g \approx 2.220$ (1) was also observed at 79 K [11]. This spectrum can be attributed to the dynamical Jahn–Teller effect of the [PtO₆]⁹⁻ cluster via vibration interactions, which may actually exhibit only dynamical average of the parallel and perpendicular g components and thus conceal the anisotropy at lower (4.2 K) temperature. Interestingly, the theoretical g factors (Cal.^c) of this work will yield an average value of 2.221, which is close to the observed isotropic g factor at higher temperature and can be regarded as reasonable.

4. Conclusion

The g factors and the local structure for the trigonal Pt³⁺ centre in α -Al₂O₃ are theoretically investigated from the perturbation formulas of these parameters for a $5d^7$ ion in trigonal symmetry. It is found that the Pt³⁺ impurity does not occupy the exact Al³⁺ site but it experiences an outward displacement of about 0.18 Å away from the centre of the octahedron along the C_3 -axis. The observed axial EPR spectra are suitably attributed to the trigonal Pt³⁺ on Al³⁺ site, and the possibility of the previously supposed tetragonally compressed Pt⁺ is theoretically excluded. Thus, the pending problem of the valence state for the doped Pt in α -Al₂O₃ is clarified in this work.

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References

- [1] N A Deskins, D H Mei and M Dupuis, *Surface Sci.* **603**, 2793 (2009)
- [2] B Habibi, M H Pournaghi-Azar, H Razmi and H Abdolmohammad-Zadeh, *Int. J. Hydrogen Energy* **33**, 2668 (2008)

- [3] N P Socolova, *Colloids and Surfaces* **A239**, 125 (2004)
- [4] V A Nasluzov, V V Rivanenkov, A M Shor, K M Neyman and N Rösch, *Chem. Phys. Lett.* **374**, 487 (2003)
- [5] S Albertazzi, P Arpentinier, F Basile, P D Gallo, G Fornasari, D Gary and A Vaccari, *Appl. Catal.* **A247**, 1 (2003)
- [6] J L Margitfalvi and I Borbáth, *J. Mol. Catal.* **A202**, 313 (2003)
- [7] J L Margitfalvi, I Borbáth, M Hegedűs and S Göbölös, *Appl. Catal.* **A219**, 171 (2001)
- [8] S A Marshall, T T Kikuchi and A R Reinberg, *Phys. Rev.* **125**, 453 (1962)
- [9] M D Sturge, *Phys. Rev.* **130**, 639 (1963)
- [10] I N Geifman and M D Glinchuk, *Sov. Phys. Solid State* **13**, 872 (1971)
- [11] S Geschwind, P Kisliuk, M P Klein, J P Remeika and D L Wood, *Phys. Rev.* **126**, 1684 (1962)
- [12] R Lacroix, U Hochli and K A Müller, *Helv. Phys. Acta* **37**, 627 (1964)
- [13] A Abragam and B Bleaney, *Electron paramagnetic resonance of transition ions* (Oxford University Press, London, 1970)
- [14] Y V Yablokov and T A Ivanova, *Coordination Chem. Rev.* **190–192**, 1255 (1999)
- [15] M A Augustyniak-Jabłokow, *J. Phys. Chem. Solids* **62**, 1319 (2001)
- [16] L A Boatner, R W Reynolds, Y Chen and M M Abraham, *Phys. Rev.* **B16**, 86 (1977)
- [17] Y Tanabe and S Sugano, *J. Phys. Soc. Japan* **9**, 753 (1954); **9**, 766 (1954)
- [18] X Y Gao, S Y Wu, W H Wei and W Z Yan, *Z. Naturforsch.* **A60**, 145 (2005)
- [19] D J Newman and B Ng, *Rep. Prog. Phys.* **52**, 699 (1989)
- [20] D J Newman, D C Pryce and W A Runciman, *Am. Mineral.* **63**, 1278 (1978)
- [21] A Edgar, *J. Phys.* **C9**, 4303 (1976)
- [22] H N Dong and W D Chen, *Z. Naturforsch.* **A61**, 83 (2006)
- [23] K Moorjani and N Meavoy, *Phys. Rev.* **132**, 504 (1963)
- [24] D S McClure, *J. Chem. Phys.* **38**, 2289 (1963)
- [25] R Muller and H H Gunthard, *J. Chem. Phys.* **44**, 365 (1966)
- [26] C A Morrison, *Crystal fields for transition-metal ions in laser host materials* (Springer, Berlin, 1992)
- [27] E Clementi and D L Raimondi, *J. Chem. Phys.* **38**, 2686 (1963)
- [28] E Clementi, D L Raimondi and W P Reinhardt, *J. Chem. Phys.* **47**, 1300 (1967)
- [29] E K Hodgson and I Fridovich, *Biochem. Biophys. Res. Commun.* **54**, 270 (1973)
- [30] S Y Wu and W C Zheng, *Phys. Rev.* **B65**, 224107 (2002)
- [31] H N Dong, S Y Wu and W C Zheng, *J. Phys. Chem. Solids* **64**, 695 (2003)
- [32] R C Weast, *CRC handbook of chemistry and physics* (CRC Press, Boca Raton, 1989) p. F187
- [33] J M Garcia-Lastra, J A Aramburu, M T Barriuso and M Moreno, *Chem. Phys. Lett.* **385**, 286 (2004)
- [34] M Moreno, J A Aramburu, J M Garcia-Lastra and M T Barriuso, *J. Mol. Structure (Theochem)* **759**, 195 (2006)
- [35] J A Aramburu, J I Paredes, M T Barriuso and M Moreno, *Phys. Rev.* **B61**, 6525 (2000)
- [36] M T Barriuso, J A Aramburu and M Moreno, *J. Mol. Structure (Theochem)* **537**, 117 (2001)