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Theoretical investigations of the Jahn–Teller distortions for V^{3+} and Cr^{4+} in α-Al_2O_3

Zhi-Hong Zhang [a,*], Shao-Yi Wu [a,b], Min-Quan Kuang [a]

[a] Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu 610054, PR China
[b] International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, PR China

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ABSTRACT

The spin Hamiltonian parameters (zero-field splittings D, g factors $g_{//}$ and $g_{\perp}$, the hyperfine structure constants and the spin–lattice coupling coefficients $|G_{-}|$, $|G_{15}|$, $|G_{51}|$ and $|G_{44}|$) for V^{3+} and Cr^{4+} in α-Al_2O_3 are theoretically investigated from the perturbation formulas of these parameters for a $3d^2$ ion under trigonally distorted octahedra. In these formulas, the contributions from the dynamical Jahn–Teller effect, the configuration interactions and the ligand orbital and spin–orbit coupling interactions are quantitatively taken into account in a uniform way based on the ligand field model. The impurity-ligand bond angles related to the C_3 axis are found to experience the variations of about 1.5–1.9° due to the dynamical Jahn–Teller nature, yielding more regular octahedra around the $3d^2$ impurities. In addition, the size mismatching substitution of the smaller host Al^{3+} by the larger impurities may also bring forward some contributions to the local angular distortions. All the calculated spin Hamiltonian parameters based on the above angular variations show reasonable agreement with the experimental data for both centers. The improvements are achieved in this work by adopting the uniform model and formulas and much fewer adjustable parameters as compared with the previous treatments.

1. Introduction

As a promising laser host [1–3], corundum (α-Al_2O_3) crystals attract much interest of the researchers due to their unique crystal-field [4], catalytic [5], electronic [6], irradiative [7], structural [8] and photoluminescence properties [9] when doped with V^{3+} and Cr^{4+} impurities. α-Al_2O_3 is also a model material for the investigations of defect structure and spectral properties for some doped transition-metal ions (e.g., Ni^{2+}, Cr^{3+}, Fe^{3+} and Mn^{4+}) by means of electron paramagnetic resonance (EPR) [10–12]. In particular, V^{3+} and Cr^{4+} can be regarded as typical systems in EPR investigations due to the fact that they only have two unpaired 3d electrons, associated with relatively simple energy levels [13]. The EPR experiments were carried out for V^{3+} and Cr^{4+} in α-Al_2O_3, and the spin Hamiltonian parameters (the zero-field splittings D, the anisotropic g factors $g_{//}$ and $g_{\perp}$, the hyperfine structure constants $A_{//}$ and $A_{\perp}$ and the spin–lattice coupling coefficients $|G_{-}|$, $|G_{15}|$, $|G_{51}|$ and $|G_{44}|$) were also measured for the two trigonal centers [14–20]. Although the zero-field splittings and the g factors have been theoretically interpreted on the basis of the static crystal-field model [21,22], the dynamical Jahn–Teller effect was not sufficiently analyzed for these typical Jahn–Teller systems. On the other hand, a systematic theoretical model was established for a trigonal $3d^2$ Jahn–Teller cluster in Refs. [14,15] by considering the first and second-order Jahn–Teller effect. However, there are some imperfections in their studies. First, the theoretical analysis was not correlated to the local structures of the impurity centers but treated by adopting some adjustable parameters (e.g., the trigonal field parameters and the related energy separations). Second, the configuration interactions between the ground $^3T_1(F)$ and the excited $^3T_1(P)$ states were taken into account by introducing the adjustable effective Lande factor α (=α'), with the anisotropy or difference between the configuration interactions parallel and perpendicular to the C_3 axis ignored. Third, only the central ion orbital and spin–orbit coupling contributions were included in the calculations, while those from the ligand orbital and spin–orbit coupling interactions were not taken into account. Fourth, the hyperfine structure constants have not been theoretically explained for α-Al_2O_3:V^{3+} up to now.

Therefore, the previous studies are largely inadequate, and this problem is worthy of further investigation. In this work, the improved perturbation formulas of the spin Hamiltonian parameters are established for a $3d^2$ ion under trigonally distorted octahedra by considering the dynamical Jahn–Teller effect. In the calculations, the configuration interactions, the ligand orbital and spin–orbit coupling contributions and the local angular variations of the dynamical Jahn–Teller nature are included uniformly from the ligand field model with much fewer adjustable parameters than the previous studies.

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* Corresponding author. Tel.: +86 2883202586; fax: +86 2883202009.
E-mail address: zhihongzhang723@163.com (Z.-H. Zhang).

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2. Theory and calculations

When a V^{3+} or Cr^{4+} ion is doped into the lattice of corundum, it may occupy substitutionally the Al^{3+} site and conserve the original trigonal symmetry. For a $3d^2$ ion under octahedra, its ground ^3F configuration may split into two orbital triplets $^3T_{1g}$ and $^3T_{2g}$ and a singlet $^3A_{2g}$ by the cubic part of the crystal fields. As a Jahn–Teller ion, V^{3+} or Cr^{4+} with the lowest threefold orbital degenerate $^3T_{1g}(F)$ state may experience the dynamical Jahn–Teller effect via vibrational interactions [14], e.g., the local impurity-ligand bond angles would suffer some variations via leaning the bonds towards or away from the C_3 axis. In addition, the size mismatching substitution of the smaller Al^{3+} by the larger impurities can also lead to some modifications of the immediate environments of the impurity centers. So, the local structures (i.e., the local impurity-ligand bond angles β'_1 and β'_2 of the upper and lower ligand triangles related to the C_3 axis) around the impurities V^{3+} and Cr^{4+} are usually dissimilar to those (i.e., the host bond angles β_1 and β_2) of the Al^{3+} site. Thus, the local structures of the impurity centers can be illustrated by the local angular variations.

Under the influences of the trigonal part of the crystal fields, the lowest $^3T_1(F)$ state can further be separated into one singlet $^3A_{2g}$ and one doublet ^3E_g. Importantly, the $^3T_1(F)$ state also has configuration interactions with the excited $^3T_1(P)$ state of the same irreducible representation. In order to establish the formulas of the spin Hamiltonian parameters, the effective Hamiltonian of the fiction orbital angular momentum $l' = 1$ and spin $S = 1$ for the $^3T_1(F)$ ground state (the 9 × 9 matrix) may be expressed as [14]:

$$\begin{aligned}\vec{H} = {} & \gamma\left[\frac{\delta}{3} - \frac{|E_{JT}|\Delta_1}{\sqrt{2}\Delta_2}\right](3l_z^2 - 2) + \frac{\gamma}{2}[\alpha\zeta l_z S_z + \alpha'\zeta'(l_x S_x + l_y S_y)] \\ & + \mu_B H_z(\gamma k\alpha l_z + 2S_z) + \mu_B H_x(\gamma k'\alpha' l_x + 2S_x) + P \\ & \times \sum_i \left\{\frac{(l_i - s_i)\cdot I}{r_i^3} + \frac{3(r_i\cdot s_i)(r_i\cdot I)}{r_i^5} + \frac{8\pi\delta(r_i)(s_i\cdot I)}{3}\right\}\end{aligned} \tag{1}$$

Here δ denotes the trigonal splitting (i.e., the energy separation between $^3A_{2g}$ and ^3E_g levels) of the ground $^3T_1(F)$ state. γ is the first-order Jahn–Teller reduction factor. α and α' are the effective Lande factors parallel with and perpendicular to the C_3 axis. ζ (and ζ'), k (and k') and P (and P') are, respectively, the spin–orbit coupling coefficients, the orbital reduction factors and the dipolar hyperfine structure parameters for the $3d^2$ ions in crystals. E_{JT} is the Jahn–Teller stabilization energy. Δ_1 and Δ_2 are the constants describing the coupling of the orbital triplets (i.e., $^3T_2(t_2e)$ and $^3T_1(t_2e)$) to the E-type vibration modes under trigonal and cubic symmetries, respectively, which are relevant to the energy separations (e.g., E_{T2}) with regard to the ground $^3T_1(F)$ state. Using the energy matrices for a $3d^2$ ion under trigonally distorted octahedra, the energy separations δ and E_{T2} as well as the effective trigonal splitting δ' between ^3E_g and $^3A_{2g}$ levels in view of the Jahn–Teller effect can be obtained from the strong field scheme [15]:

$$\begin{aligned}&\delta \approx v + 2v'/3, \\ &\delta' = (2/\zeta)\{\gamma[\delta - 3\sqrt{10}\,E_{JT}v'/(4E_{T2})] + v^2F_a/3\}, \\ &E_{T2} \approx 2Dq - \{(15B - 6Dq) - [(15B + 6Dq)^2 + 64Dq^2]^{1/2}\}/2.\end{aligned} \tag{2}$$

Here v and v' are the trigonal field parameters. F_a (and F_b) are the second-order Jahn–Teller reduction factors. Dq is the cubic field parameter, and B is the Racah parameter for the $3d^2$ ions in crystals. Then the eigenvectors $|S, M_s>$ of the ground $^3T_1(F)$ state are expressed in terms of the bases $|m_l, m_s>$ [14]:

$$\begin{aligned}&|1, 0\ >= |0, 0> +\epsilon|1, -1> +\epsilon|-1, 1>, \\ &|1, \pm1\ >= |0, \pm1> +\Psi|\pm1, 0> \pm\Phi|\mp1, \mp1>\end{aligned} \tag{3}$$

Here the admixture coefficients of these bases can be obtained from the perturbation method by considering the first- and second-order Jahn–Teller effects:

$$\begin{aligned}&\epsilon = -[k\alpha\gamma + \alpha F_a v/3 + \alpha'^2\zeta F_a/2 + \alpha'^2\zeta(F_b - F_a)/6]/(\delta' - k\alpha\gamma \\ &\qquad + 2\alpha F_a v/3), \\ &\Psi = -[k'\alpha'\gamma + \alpha F_a v/3 - \alpha'^2\zeta(F_b - F_a)/6]/\delta', \\ &\Phi = (1/6)\alpha'^2\zeta(F_b - F_a)/(\delta' + k'\alpha'\gamma + 2\alpha F_a v/3).\end{aligned} \tag{4}$$

In the above formulas, α and α' are determined from the perturbation method in terms of the related configuration interaction coefficients:

$$\begin{aligned}&\alpha = \sqrt{5}\varepsilon\rho + \tau^2 - 3/2\varepsilon^2 - \rho^2/2, \\ &\alpha' = \sqrt{5}/2\varepsilon'\rho + \tau\tau' - 3/2\varepsilon\varepsilon' - 2\rho\sigma.\end{aligned} \tag{5}$$

The related configuration interaction coefficients ε, ε', τ, τ', ρ and σ are acquired from the perturbation method. The basis $|m_l, m_s>$ can be expanded as linear combinations of the corresponding components of the ground state $^3T_1(F)$ under trigonal symmetry (similar to the treatments of the ground $^4T_1(F)$ orbital triplet for a $3d^7$ ion in trigonally distorted octahedra [13]):

$$\begin{aligned}&|1\ >= -\tfrac{1}{\sqrt{2}}(\phi'_x + i\phi'_y), \\ &|-1\ >= \tfrac{1}{\sqrt{2}}(\phi'_x - i\phi'_y), \\ &|0\ >= \phi'_z,\end{aligned} \tag{6}$$

Here ϕ'_x, ϕ'_y and ϕ'_z stand for the corresponding components of $^3T_1(F)$ state in view of the configuration interactions between the ground $^3T_1(F)$ and the excited $^3T_1(P)$, $^3T_2(F)$ and $^3A_2(F)$ states. Thus, we have

$$\begin{aligned}&\phi'_x = \varepsilon\phi_x - \tau\pi_x - \rho\psi_y, \\ &\phi'_y = \varepsilon\phi_y - \tau\pi_y - \rho\psi_x, \\ &\phi'_z = \varepsilon'\phi_z - \tau'\pi_z - \sigma\chi,\end{aligned} \tag{7}$$

Here φ_j ($j = x$, y and z), π_j, ψ_i ($i = x$ and y) and χ denote the corresponding components of the pure $^3T_1(F)$, $^3T_1(P)$, $^3T_2(F)$ and $^3A_2(F)$ states, respectively. The configuration interaction coefficients can be calculated from the energy matrices for a $3d^2$ ion under trigonal symmetry in terms of the cubic and trigonal field parameters and the Racah parameter:

$$\begin{aligned}&\varepsilon^2 + \tau^2 + \rho^2 = 1, \\ &\varepsilon'[1 + (\tau'/\varepsilon')^2 + (\sigma/\varepsilon')^2]^{1/2} = 1, \\ &\tau/\varepsilon = (\sqrt{6}/2v' + 4Dq)/(15B + 6Dq), \\ &\tau'/\varepsilon' = (\sqrt{2}v'/3 - 4Dq)/[7\sqrt{6}v/72 + 2v/(3\sqrt{3}) - 15B - 6Dq], \\ &\rho/\varepsilon = v/(16\sqrt{3}Dq), \\ &\sigma/\varepsilon' = (-\sqrt{2}v')/(7\sqrt{6}v/72 - 8Dq)\end{aligned} \tag{8}$$

Using the above effective Hamiltonian and the bases of the ground state, the improved perturbation formulas of the spin Hamiltonian parameters (zero-field splitting D, g factors $g_{//}$ and $g_\perp$, the hyperfine structure constants $A_{//}$ and $A_\perp$ and the spin–lattice coupling coefficients G_-, G_{15}, G_{51} and G_{44}) for a $3d^2$ ion in trigonally distorted octahedra are derived as follows:

$$\begin{aligned}D = {} & (\zeta/2)\{-\zeta\alpha^2F_a(\psi^2 + \Phi^2 - 6\epsilon - 1)/2 + 2\alpha F_a v(3\Phi^2 + 4\Phi^2\psi \\ & - 6\epsilon^2)/3 + \epsilon^2\zeta\alpha^2(F_b - F_a)/3 - \alpha\gamma(3\Phi^2 + 4\Phi^2\psi + 6\epsilon^2) \\ & + \delta'[(11/3)(\psi^2 + \Phi^2 - 2\epsilon^2) - 4\Phi^2\psi]\},\end{aligned}$$