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d-orbital theory for an O_h -site-symmetry crystal and its application to plumbogjarosite

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Abstract. A d orbital in an octahedral (O_h)-site-symmetry crystal is proposed by considering the ligand charge penetration. The quantitative relationship between the reduction in the Racah parameters B and C and crystalline parameters is established by using a simple point-charge model. The d orbital is applied to calculation of the spectrum of Fe^{3+} ions in plumbogjarosite. The calculated results are in good agreement with experiment.

As is well known, when a transition-metal ion ($3d^n$) is located in an octahedral (O_h)-site-symmetry crystal, the Racah parameters B and C and spin-orbit-coupling parameter ξ_d are reduced with respect to their free-ion values, which is usually called the nephelauxetic effect [1–3]. In some cases, the reductions in B , C and ξ_d have a considerable effect on the d–d transitions in the crystal. In order to explain the nephelauxetic effect, there have been a variety of methods which can be grouped as follows. Firstly, the reduction in B , C and ξ_d is attributed to the decrease in the effective nuclear charge Z_{eff} [2, 3]. Secondly, the parameter reduction in the crystal is considered to be a result of the orbital mixing of the central ion and ligands. A number of simplified LCAO models have been proposed by introducing some parameters, such as ϵ , β [4–7] or N_σ and N_π [8]. In practical calculations of the d–d transitions, Z_{eff} , ϵ , β , N_σ and N_π in these models are often taken as fitting parameters. However, when the calculations of B , C and ξ_d in the crystal are required to be related to the corresponding crystalline parameters, some complicated calculations such as overlap integrals have to be used [2, 8]. There is therefore a need for a simple model, but one in which the nephelauxetic effect can be described in relation to the crystalline parameters. In this work, we propose such a model in the framework of crystal-field (CF) theory.

In an O_h -site-symmetry crystal, the CF potential for a single d electron is written as

$$V(r_i) = \sum_{k=0,4} \sum_{q=0,\pm 4} B_{kq}(r_i) C_q^{(k)}(\theta_i, \varphi_i) \quad (1)$$

with

$$B_{kq}(r_i) = - \int e\rho(R, \Theta, \Phi) (r_{<}^k / r_{>}^{k+1}) (-1)^q C_{-q}^{(k)}(\Theta, \Phi) d\tau$$

$$C_q^{(k)}(\theta_i, \varphi_i) = \sqrt{4\pi / (2k + 1)} Y_{kq}(\theta_i, \varphi_i) \quad i = 1, 2, \dots, n$$

where $\rho(R, \Theta, \Phi)$ is the ligand charge (LC) distribution, (R, Θ, Φ) is the coordinate of LC, $r_{>}$ and $r_{<}$ are the greater and lesser values of r_i and R , respectively, and $Y_{kq}(\theta_i, \varphi_i)$

denotes the spherical harmonic function. In fact, the nephelauxetic effect is dominated by the covalency effect. This implies that the LC can be allowed to penetrate into the region where the d electrons are distributed. For a more complete description of the d-electron state in the crystal, the LC penetration may be taken into account. On the basis of this idea and using a point-charge model [1-3], we have

$$V(r_i) = -6eq(1/r_>) - \frac{7}{2}eq(r_<^4/r_>^5)C_0^{(4)}(\theta_i, \varphi_i) + (\sqrt{70}/4)eq(r_<^4/r_>^5)[C_{-4}^{(4)}(\theta_i, \varphi_i) + C_4^{(4)}(\theta_i, \varphi_i)] \quad (2)$$

where q is the effective charge of a ligand. Here $r_>$ and $r_<$ are the greater and lesser values of r_i and L , respectively, where L is bond length (the distance between the central ion and the ligand). In the treatment of the conventional CF theory [1-3], r_i^k/L^{k+1} is substituted for $r_<^k/r_>^{k+1}$ in equation (2), which implies that the LCs are always assumed to be outside the region of the d-electron distribution and the LC penetration is neglected. By considering the LC penetration, the free-ion radial function $R_d(r)$ and conventional expression for the CF parameter D_q will be modified.

The first term in equation (2), a spherical shell potential, is different from the constant potential in usual treatments [1, 2]. It can affect the d-d transition energies in the crystal. By adding it to the effective core potential for the one d electron of the free ion, expansion of the radial d orbital $R_d(r)$ will occur because $q < 0$. Then reduction in B , C and ξ_d will follow from this. Despite the difficulty in solving the expanded $R_d(r)$ exactly, for simplicity we can make the assumption that the expansion of $R_d(r)$ is represented as a partial scaling transformation of the $R_d(r)$ of the free ion, i.e. replacing r by $\delta_1 r$ in the free ion $R_d(r)$ when $r > L$ (physically, $\delta_1 < 1$). Using the double-zeta-type $R_d(r)$ for the free ion [8], we obtain the radial d orbital in the O_h -site-symmetry crystal:

$$R_d(r) = \begin{cases} \delta_0[a_1 N_1 r^2 \exp(-\xi_1 r) + a_2 N_2 r^2 \exp(-\xi_2 r)] & r < L \\ \delta_0[a_1 N_1 (\delta_1 r)^2 \exp(-\xi_1 \delta_1 r) + a_2 N_2 (\delta_1 r)^2 \exp(-\xi_2 \delta_1 r)] & r > L \end{cases} \quad (3)$$

with

$$N_i = [(2\xi_i)^7/6!]^{1/2} \quad i = 1, 2$$

$$\delta_0 = \{1 + a_1^2 N_1^2 [\delta_1^4 \Gamma^{(0)}(L, 2\delta_1 \xi_1) - \Gamma^{(0)}(L, 2\xi_1)] + a_2^2 N_2^2 [\delta_1^4 \Gamma^{(0)}(L, 2\delta_1 \xi_2) - \Gamma^{(0)}(L, 2\xi_2)] + 2a_1 a_2 N_1 N_2 [\delta_1^4 \Gamma^{(0)}(L, \delta_1 \xi_1 + \delta_1 \xi_2) - \Gamma^{(0)}(L, \xi_1 + \xi_2)]\}^{-1/2}$$

$$\Gamma^{(k)}(L, \xi) = \int_L^\infty r^{6+k} \exp(-\xi r) dr \quad (4)$$

where δ_0 is the renormalized factor. The Racah parameters B and C in the crystal can be calculated from the Slater-Condon parameter F^k ($k = 2, 4$) [1-3] which is given by

$$F^k = e^2 \int_0^\infty \int_0^\infty R_d^2(r_1) (r_<^k/r_>^{k+1}) R_d^2(r_2) r_1^2 r_2^2 dr_1 dr_2 \quad (5)$$

with the help of the following auxiliary formulae:

$$\begin{aligned} J_a^{(k)}(L, \alpha, \beta) &= \int_0^L \int_0^{r_1} r_1^6 r_2^6 (r_<^k/r_>^{k+1}) \exp(-\alpha r_1) \exp(-\beta r_2) dr_2 dr_1 \\ &= \frac{(6+k)!}{\beta^{7+k}} \left[\frac{(5-k)!}{\alpha^{6-k}} - \Gamma^{(-k-1)}(L, \alpha) \right. \\ &\quad \left. - \sum_{i=0}^{6+k} \frac{\beta^i}{i!} \left(\frac{(5-k+i)!}{(\alpha+\beta)^{6-k+i}} - \Gamma^{(-k-1+i)}(L, \alpha+\beta) \right) \right] \end{aligned} \quad (6a)$$

Table 1. The d-d transitions of Fe^{3+} in plumbojarosite.

Transitions from ${}^6A_{1g}(S)$	Theoretical values ^a (cm^{-1})	Experimental values [12] (cm^{-1})
${}^4T_{1g}(G)$	15 007.7	12 500, 15 385
${}^4T_{2g}(G)$	19 357.9	19 045
${}^4A_{1g}(G), {}^4E_g(G)$	22 707.5	22 730
${}^4T_{2g}(D)$	24 856.2	24 390
${}^4E_g(D)$	26 541.4	25 975
${}^4T_{1g}(P)$	30 469.9	30 300
${}^4T_{1g}(F)$	37 758.8	37 735
${}^4T_{2g}(F)$	41 206.8	41 665

^a The Trees correction $\alpha = 90\text{ cm}^{-1}$ [13].

$$\begin{aligned}
 J_b^{(k)}(L, \alpha, \beta, \delta_1) &= \delta_1^4 \int_L^\infty \int_0^\infty r_1^6 r_2^6 (r_<^k / r_>^{k+1}) \exp(-\alpha \delta_1 r_1) \exp(-\beta r_2) dr_2 dr_1 \\
 &= \delta_1^4 \left(\frac{(6+k)!}{\beta^{7+k}} - \Gamma^{(k)}(L, \beta) \right) \Gamma^{(-k-1)}(L, \delta_1 \alpha) \tag{6b}
 \end{aligned}$$

$$\begin{aligned}
 J_c^{(k)}(L, \alpha, \beta, \delta_1) &= \delta_1^8 \int_L^\infty \int_{r_1}^\infty r_1^6 r_2^6 (r_<^k / r_>^{k+1}) \exp(-\alpha \delta_1 r_1) \exp(-\beta \delta_1 r_2) dr_2 dr_1 \\
 &= \delta_1^8 \frac{(5-k)!}{(\delta_1 \beta)^{6-k}} \sum_{i=0}^{5-k} \frac{(\delta_1 \beta)^i}{i!} \Gamma^{(k+i)}(L, \delta_1 \alpha + \delta_1 \beta) \tag{6c}
 \end{aligned}$$

where equation (4) is used. For calculation of the d-d transition energies, the terms in equation (2), other than the spherical shell term, are treated as a perturbation. The CF parameter D_q is of the form

$$D_q = -\frac{1}{6} e q \langle r_<^4 / r_>^5 \rangle = -e q \langle r^4 \rangle / 6L^5 \tag{7}$$

where $\langle r^4 \rangle$ is defined as

$$\langle r^4 \rangle = \int_0^L R_d^2(r) r^6 dr + \int_L^\infty R_d^2(r) (L^9 / r^3) dr. \tag{8}$$

It should be pointed out that $\langle r^4 \rangle$ differs from the usual expression of the point-charge model [1-3]. Here $\langle r^4 \rangle$ can be considered as a correct expression [9]. In addition to B , C and D_q , ξ_d in the crystal can also be obtained in the same way as in [8]. In the above treatment of B , C , D_q and ξ_d , the free-ion $R_d(r)$ and bond length L are assumed to have been given. The remaining parameters δ_1 and q can be taken as two fitting parameters and varied to obtain a set of the d-d transition energies calculated in good agreement with experimental data. To illustrate the application of the above method, we take plumbojarosite ($Pb[Fe_3(SO_4)_2(OH)_6]_2$) as an example, since at present there is no calculation which relates its spectra to its structural data. In plumbojarosite the Fe^{3+} is surrounded by four hydroxyl groups and two oxygen ligands [10]. The average bond length $L = 2.008\text{ \AA}$. In order to calculate the d-d transitions, we make an approximation that the point group for the Fe^{3+} site is O_h . Using the double-zeta type of radial function for free Fe^{3+} , i.e. $a_1 = 0.667$, $a_2 = 0.55237$, $\xi_1 = 5.6$ and $\xi_2 = 1.732$ [11], and taking the scaling factor $\delta_1 = 0.647$ and the LC $q = -0.67786e$, we calculate the values of B , C and D_q from equations (3)-(8): $B = 727.775\text{ cm}^{-1}$, $C = 2726.131\text{ cm}^{-1}$ and $D_q = 900.161\text{ cm}^{-1}$. Then, by solving the energy matrices for the d^5 configuration [1], the d-d transition energies are obtained. The comparison between the calculated results and experimental data [12] is shown in table 1. The theoretical values are in good agreement with experiment.

In the preceding calculation of the d-d transitions for Fe^{3+} in plumbojarosite, δ_1 and q were determined with the help of a least-squares fitting routine. The scaling factor $\delta_1 = 0.647$ is found to be smaller than unity. This implies that a considerable covalency effect exists between the central ion and ligands. The effective LC $|q| = 0.67786e$ is smaller than the value of the O^{2-} ion charge. This result can be attributed to the covalency effect and the existence of the H^+ ion associated with the O^{2-} ion in hydroxyl group. If we neglect the LC penetration in equation (7) and therefore use the conventional expression for $\langle r^4 \rangle$ in equation (7), $\langle r^4 \rangle$ will be calculated to be much larger with the same $R_d(r)$ and q . In this case, the effective charge $|q|$ is fitted as $|q| = 0.150e$ which is much smaller than the physically expected value. Hence, the expression given for $\langle r^4 \rangle$ in equation (8) is reasonable. Furthermore, the spin-orbit-coupling parameter ξ_d can also be calculated from equation (3) in the same way as in [8]. Like B and C , the calculated value $\xi_d = 460.181 \text{ cm}^{-1}$ is reduced from its free-ion value [11].

In conclusion, the extra core potential obtained from consideration of the LC penetration in the O_h -site-symmetry crystal is found to give rise to nephelauxetic decreases in B , C and ξ_d . Based on this mechanism, an empirical d orbital in an O_h -site-symmetry crystal has been proposed by using a simple point-charge model. The method for calculation of the d-d transitions is in the framework of the CF theory and contains two fitting parameters δ_1 and q . This model has been used to calculate the d-d transition energies of Fe^{3+} in plumbojarosite. Although the symmetry-dependent covalency effect [2] and the exchange interactions between the central ion and ligands are neglected in the model, the calculated results agree well with experiment. This shows that the radial d orbital in the crystal is a good approximation of its exact solution. Therefore the model obtained by considering the LC penetration can be regarded as a starting point for more sophisticated theoretical calculations.

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