A simple model for $f \rightarrow d$ transition of heavy lanthanide and actinide ions in crystals

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Abstract

The $f \rightarrow d$ transition model by Duan and co-workers [Phys. Rev. B 66, 155108 (2002); J. Solid State Chem. 171, 299 (2003)] has been very useful in interpreting the $f \rightarrow d$ absorption, emission and nonradiative relaxation of light lanthanide ions in crystals. However, based on the assumption that the $f^{N-1}$ core spin-orbit interaction is weak compared to $f \rightarrow d$ exchange interaction, this model, in the original form, is not applicable to interpretation of the $f \rightarrow d$ transitions of heavy lanthanide ions or actinide ions in crystals. In this work the model is extended to cover the cases of heavy lanthanides and actinides, where the spin-orbit interaction of $f$ orbitals may be stronger than the $f - d$ exchange interaction.

Keywords: lanthanide; f-d transition; model; spectrum; actinide; VUV;
I. INTRODUCTION

New luminescent phosphors for vacuum ultraviolet (VUV) excitation are required for plasma display panels and mercury-free fluorescent tubes, where the VUV emission from a noble gas xenon discharge is used to generate visible luminescence. Other applications where the VUV spectroscopy of lanthanides is involved are scintillator materials and VUV lasers. Due to these potential applications and availability of VUV excitation by synchrotron radiation, the VUV spectroscopy of lanthanide ions and actinide ions in crystal have recently become an important field of research.

The VUV spectroscopy of lanthanide and actinide ions mainly involves the parity allowed \( n_f^N \leftrightarrow n_f^{N-1}(n+1)d \) transitions \((n = 4\) for lanthanides and 5 for actinides), including ground and excited state excitations and emissions. It is well known that the \( 4f^N \rightarrow 4f^N \) spectra of lanthanide ions in noncentrosymmetric environments are dominated by many sharp zero-phonon lines. Interpretation of the energy levels and transition intensities may be modeled with a empirical crystal-field Hamiltonian \[1\] and Judd-Ofelt theory \[2, 3\] respectively. By contrast, the spectra of transitions between the \( 4f^N \) and \( 4f^N-15d \) configurations are feathered by broad-band structures, with some zero-phonon lines only resolvable at temperature below liquid nitrogen. This is due to great difference in vibrational equilibrium between \( 4f^{N-1}5d \) and \( 4f^N \) configurations, which makes the the transition intensities be dominant by vibronic broad bands. The phenomenological crystal-field Hamiltonian for \( 4f^N \) configuration has been extended to \( 4f^{N-1}5d \) configuration by adding the crystal-field and spin-orbit interactions for 5d orbitals, and Coulomb interactions between \( 4f^{N-1} \) core and 5d orbitals \[4\]. The \( 4f^N \leftrightarrow 4f^{N-1}5d \) transitions are electric dipole allowed, whose relative rates can be calculated straightforward. Actually, extensive calculations have been carried out for trivalent lanthanide ions in crystals \[4, 5\] which give satisfactory agreement with experimental \( 4f \rightarrow 5d \) spectra. However, the calculations give hundreds to thousands transition lines which convolve into several to a few dozen of broad bands after taking vibronic transitions into account to wash out the fine structures, making straightforward interpretations of the simulations and straightforward predictions of changing of broad-band numbers, their positions and relative intensities with ions and crystals quite difficult.

Recently Duan and co-workers \[6, 7, 8\] simplified the calculations by considering only the main interactions in the \( 4f^{N-1}5d \) configuration. The model gave quantum numbers char-
acterizing various groups of states, transition selection rules, and an expression of relative intensities with these quantum numbers. Application of the model to Eu$^{2+}$ and Sm$^{3+}$ in various crystals successfully explained the measured spectra. However, in the model there is an implicit assumption that the exchange Coulomb interaction between $f$ and $d$ orbitals is stronger than the spin-orbit interaction in the $f^{N-1}$ core. This assumption no long holds for heavy lanthanide ions or actinide ions in crystals.

In the present work, the original model is extended to the case where $f - d$ exchange Coulomb interaction may be weaker than that of the $f^{N-1}$ core spin-orbit interaction. The energy and transition line strengths for $f - d$ transitions directly applicable to actinides and heavy lanthanides are given analytically.

II. EIGENFUNCTIONS AND EIGENVALUES

A. $f^N$ configuration

The $f^N$ crystal-field splitting is well-understood both experimentally and theoretically via phenomenological crystal-field simulation. However, in $f^N \rightarrow f^{N-1}d$ transitions, the $f^N$ crystal-field energy levels are either hard to distinguish from vibronic lines in low temperature or unresolvable at all at temperature higher than 100K due to vibronic bands. In this work we are aimed to give an model which may interpret number of broad bands, their positions and relative intensities. We neglect $f^N$ Crystal-field splitting. In such a case, the highly degenerate eigenstates can be written as

$$||\eta SLJ⟩ = C_0 |\eta SLJ⟩ + \sum_{i \geq 1} c_i |\eta_i S_i L_i J⟩.$$  \hspace{1cm} (1)

Usually the states are denoted with the label of the main component $|\eta SLJ⟩$, whose coefficient is usually close to 1 for lanthanide ions.

B. $f^{N-1}d$ configuration

The general interactions for the $f^{N-1}d$ configuration can be written as

$$H(f^{N-1}d) = H_{\text{Coul}}(ff) + H_{\text{cf}}(d) + H_{\text{Coul}}(fd) + H_{\text{so}}(f) + H_{\text{so}}(d) + H_{\text{cl}}(f).$$  \hspace{1cm} (2)
The first two terms are the strongest terms of the following form

\[ H_0(f^{N-1}d) = \sum_{k=2,4,6} F_k(ff) \sum_{1 \leq i < j \leq N-1} C^k(i) \cdot C^k(j) + \sum_{k=2,4,6} \sum_{q=k} B^k_q C^q(d), \quad (3) \]

where \( F_k(ff) \) are Slater integrals, which are usually treated as adjustable parameters. \( B^k_q \) are crystal-field parameters for the \( d \) electron. Note that only those \( B^k_q \) with \( (k, q) \) allowed by the site symmetry are nonzero. \( H_0(f^{N-1}d) \) contribute to splitting of \( f^{N-1} \) core into energy levels characterized with spin and orbit angular momenta \( S \) and \( L \), and \( d \) orbital into strong crystal-field energy levels characterized with site-symmetry labels. The contribution to splitting from the third term of (2), i.e., the Coulomb interaction between \( f^{N-1} \) core and \( d \) orbitals, can be approximate with an isotropic exchange term

\[ H_{\text{exc}}(f^{N-1}d) = -J_{\text{exc}} S_f \cdot S_d, \quad \text{where} \]

\[ J_{\text{exc}} = \frac{6}{35} G_1(fd) + \frac{8}{105} G_3(fd) + \frac{20}{231} G_5(fd). \quad (4) \]

Here \( G_{1,3,5}(fd) \) are \( f - d \) Coulomb exchange radial integrals. It is straightforward to show that \( H_{\text{exc}} \) commutes with the total spin of \( f^{N-1}d \).

The following approximation is often used for \( f \)-electron spin-orbit interaction within a given zero-order \( f^{N-1} \) core energy level characterized by \( \eta SL \):

\[ H_{\text{so}}(f) = \sum_{i=1}^{N-1} \xi_{nl} S_i \cdot l_i \approx \lambda_{\eta SL} S \cdot L, \quad \text{where} \]

\[ \lambda_{\eta SL} = \sqrt{\frac{l(l+1)(2l+1)}{S(S+1)(2S+1)(L+1)(2L+1)} \langle l^{N\alpha SL} || V^{11} || l^{N\alpha SL} \rangle} \xi_{nl}. \quad (5) \]

In the case that \( S_f \) takes the largest possible value for the \( f^{N-1} \) configuration, \( \lambda_{\eta_s l_f} \) is simply \( \text{sign}(8-N)\xi_f/2S_f \). In general, \( H_{\text{so}}(f) \) commutes with the total angular momentum of \( f^{N-1} \) core, no matter the above approximation in Eq. (5) is used or not.

Other terms are not important in the interpretation of broad bands in \( f - d \) spectra and neglected. Therefore we have the effective Hamiltonian written as the sum of the above important terms as

\[ H_{\text{eff}} = H_0(f^{N-1}d) - H_{\text{exc}}(f^{N-1}d) + H_{\text{so}}(f). \quad (7) \]

It is straightforward to check that \( H_{\text{eff}} \) commutes with the following effective “angular momentum” operator

\[ \mathbf{J}_{\text{eff}} = \mathbf{S}_f + \mathbf{S}_d + \mathbf{L}_f. \quad (8) \]
Note that this operator is not the total angular momentum operator for \( f^{n-1}d \), since it does not contain the orbit angular momentum of \( d \) electron which is usually quenched in low symmetry sites.

Former work used an implicit assumption that \( fd \) exchange interaction is stronger than \( f^{N-1} \) spin-orbit interaction. In that case the energy levels were written as

\[
E \left( |l^{N-1} \eta S_f L_f, 2d_i; SJ \rangle \right) = E_0(\eta S_f L_f) + \epsilon_{d_i} - J_{\text{exc}} \left[ S(S + 1 - S_f(S_f + 1) - \frac{3}{4} \right] \\
+ \left( 2 - \frac{2S + 1}{2S_f + 1} \right) \lambda_{\eta S_f L_f} \frac{J(J + 1) - S(S + 1) - L_f(L_f + 1)}{2}.
\] (9)

However, the strength of the exchange interaction decreases as the nucleus charge increase, while at the same time the spin-orbit interaction increases. It happens that for heavy lanthanide and actinide ions, the cases where spin-orbit interaction is comparable or even stronger than exchange interaction need to be considered. In the case \( H_{\text{so}}(f) \) is much stronger than \( H_{\text{exc}}(fd) \), opposite to the one considered by Duan et al., The coupling \((SO_f^d \times SO_L) \times SO_e^d \) may be preferred and the approximate eigenstates can be written as \( |(l^{N-1} \eta S_f L_f, J_f), 2d_i; J \rangle \) and the eigenvalues can be written as

\[
E(\eta S_f L_f J_f, 2d_i; J) = E_0(\eta S_f L_f, 2d_i) + \lambda_{\eta S_f L_f} \left[ \frac{(J_f(J_f + 1) - S_f(S_f + 1) - L_f(L_f + 1)}{2} \right] \\
- J_{\text{exc}} \frac{J_f(J_f + 1) + S_f(S_f + 1) - L_f(L_f + 1)}{2J_f(J_f + 1)} [J(J + 1) - J_f(J_f + 1) - S_d(S_d + 1)].
\] (10)

In the medium case where \( H_{\text{so}}(f) \) and \( H_{\text{exc}}(d) \) are comparable, The effective of \( H_{\text{eff}} \) can be calculated with either \( |l^{N-1} \eta S_f L_f J_f, 2d_i J \rangle \) or \( |l^{N-1} \eta S_f L_f, 2d_i S J \rangle \)as bases. Eigenvalue and wave-function of each eigenstate can then be obtained by diagonalizing the matrix. Here we give the matrix element of effective Hamiltonian under the bases \( |l^{N-1} \eta S_f L_f, 2d_i S J \rangle \) as

\[
\langle l^{N-1} \eta S_f L_f, 2d_i; SJ \rangle H_{\text{eff}} \langle l^{N-1} \eta S_f L_f, 2d_i; S'J' \rangle = \\
\delta_{d_i,d_i'} \delta_{S_f,S_f'} \delta_{L_f,L_f'} \delta_{S,J,S',J'} \left[ \langle f^{N-1} \eta S_f L_f \rangle + \epsilon_{d_i} - J_{\text{exc}} \frac{S(S + 1) - S_f(S_f + 1) - s_d(s_d + 1)}{2} \right] \\
+ \xi_n(-1)^{J + L_f + S_f} \left\{ \begin{array}{ccc}
L_f & L_f' & 1 \\
S & S' & J
\end{array} \right\} \sqrt{l(l + 1)} \langle \eta S_f L_f S J \rangle \langle V_{11} | \eta S_f'L_f'S J \rangle
\] (11)

Under the approximation in Eq. (5), the matrix for \( H_{\text{eff}} \) reduces into many \( 2 \times 2 \) blocks and the diagonalization become straightforward.
III. ONE-PHOTON TRANSITION LINE STRENGTH BETWEEN $f^N$ AND $f^{N-1}d$

The $f^N$ to $f^{N-1}d$ transitions are electric dipole allowed. Here we consider only this mechanism. The electric dipole moment is a spin independent rank 1 tensor in both total orbital angular momentum and total angular momentum spaces. It can be written as

$$D = \sum_q \epsilon_q \sum_{i=1}^N r_q(i),$$

where $\epsilon_q$ is the $q$ component of the polarization vector and $r_q(i)$ is the $q$ component of the position of $i$th electron.

Using the second quantization techniques, the electric dipole moment can be written as

$$D^{(0,1)1}_q = \sqrt{2} \langle f | r | d \rangle \left\{ (a^+)(1/2\cdot3) \tilde{a}^{(1/2\cdot2)}(0\cdot1)^1q - [(a^+)(1/2\cdot2) \tilde{a}^{(1/2\cdot3)}](0\cdot1)^1q \right\},$$

where

$$(\tilde{a})^{sm,lm} = (-1)^{s-m_s+l-m_l} a^{sm,lm},$$

and $(a^+)^{(sm,lm)}$ are components of tensors that transform under symmetry operator the same way as basis $|sm,lm\rangle$, and $\langle f | r | d \rangle$ is radial integral. The coupling of two creation-annihilation operators are just coupling of two tensors to give a new tensor. In Eq. (13), $a^+$ and $\tilde{a}$ couples to give a rank $(0 \cdot 1)$ tensor of spin and orbital angular moments.

Using coupling and recoupling techniques, we can rewrite the electric dipole momentum into the following two forms.

$$D = \sum_{q_1,q_2} C_{q_1,q_2}^1 [(a^+)(1/2\cdot3) \tilde{a}^{(1/2\cdot2)}(0\cdot3\cdot2)(3q_1,2q_2) + \ldots$$

$$= \sum_{j_1,j_2,q_1,q_2} C_{j_1,j_2,q_1,q_2}^2 [(a^+)(1/2\cdot3) \tilde{a}^{(1/2\cdot2)}(j_1\cdot1/2\cdot2)(3q_1,2q_2) + \ldots,$$

where the neglected terms ($\cdots$) will not contribute when $f^N$ states are on the left and $f^{N-1}d$ are on the right and hence are not written out explicitly. $C_{q_1,q_2}^1$ and $C_{j_1,j_2,q_1,q_2}^2$ are appropriate coefficients that depend on $(q_1, q_2)$ and $(j_1, q_1, q_2)$ respectively. The matrix elements of $D$ between initial states $|f^N d^J L S \rangle$ and final states $|(f^{N-1} d^J (SfLd) SLf)J', d_i\rangle$ (or final states $|(f^{N-1} d^J (SfLf) J_f s_d)J', d_i\rangle$) can then be obtained via Wigner-Ekwart theorem [10].
Transition line strength $S$ between initial states $|I_i\rangle$ and $|F_f\rangle$, where $i$ and $f$ are indexes to distinguish degenerate states, are defined as follows

$$S(I, F) = \sum_{i,f} |\langle I_i | D | F_f \rangle|^2. \quad (17)$$

Using orthonormal relations of coupling and recoupling coefficients, after a lengthy but straightforward analytic calculation, we finally get the line strength for isotropic absorption or emission. For the case I of strong $H_{\text{exc}}(f^{N-1}d)$ which is applicable to light lanthanides, the line strength is:

$$S_{\text{iso}}(|f^N\eta S L J\rangle \leftrightarrow |(f^{N-1}\eta f S_f L_f, \ 2d_i; S'J')\rangle)$$

$$= N \langle f | r | d \rangle^2 \frac{35}{\delta_{SS'}[d_i][L, J, J']\langle f^N\eta S L | f^{N-1}\eta f S_f L_f \rangle^2} \left\{ \begin{array}{ccc} L & L_f & 3 \\ J' & J & S' \end{array} \right\}^2. \quad (18)$$

where the $[d_i]$ is the degeneracy of $d_i$ crystal field levels, and $[S]$ etc. are short for $(2S + 1)$ etc., respectively.

For the case II of stronger $H_{\text{so}}(f)$ than $H_{\text{exc}}(f^{N-1}d)$, the line strength is:

$$S_{\text{iso}}(|f^N\eta S L J\rangle \leftrightarrow |(f^{N-1}\eta f S_f L_f)J_f, \ 2d_i; J'\rangle) = N \langle f | r | d \rangle^2 [d_i][S, L, J_f, J, J']$$

$$\times \langle f^N\eta S L | f^{N-1}\eta f S_f L_f \rangle^2 \left\{ \begin{array}{ccc} 7/2 \\ j_f = 5/2 \end{array} \right\} \left( \begin{array}{ccc} 1/2 & S_f & S \\ 3 & L_f & L \\ j_f & J_f & J \end{array} \right) \left\{ \begin{array}{ccc} j_f & 3 & 1/2 \\ J_f & J & J \end{array} \right\}^2. \quad (19)$$

IV. CONCLUSION

The model for $f^N \rightarrow f^{N-1}d$ transitions proposed earlier has been extended to the case II where spin-orbit interaction in $f^{N-1}$ is stronger than the isotropic exchange interaction between $f^{N-1}$ and $d$ by utilizing Racah-Wigner algebra and second quantization techniques. The result is expected to be useful for actinide ions where the effect of $f$ spin-orbit interaction is stronger than the exchange interaction. Heavy lanthanides fall into the medium case where the effect of spin-orbit interaction is comparable or slightly stronger than the exchange interaction, where the case II may serve as an approximation.
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