ELECTRONIC MATRIX ELEMENTS IN THE RADIATIONLESS RELAXATION THEORY OF RARE-EARTH IONS IN SOLIDS

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The first-order approximate expressions for the electronic matrix elements in the radiationless relaxation theory of rare-earth ions in solids are given. The non-radiative effects of ligand vibrations and the forbiddenness of non-radiative transitions in some special cases are described.

1. Introduction

Radiationless relaxation processes involving rare-earth ions in solids are directly related to the quantum efficiencies of many quantum electronic devices and luminescent materials. However, due to the well shielded nature of the 41^{71} states, the electron-phonon interaction of rare-earth ions is an example of weak coupling, and it is easier to work out approximate mathematical expressions for the radiationless transition rates. That is why there have been so many discussions on this subject. The theoretical models already established [1-7] can explain many experimental facts, such as the energy gap law and the special importance of effective cut-off phonon frequencies for the relaxation rates of rare-earth ions in solids.

However, the theory of radiationless relaxation is still in its formative stage and most of the theoretical papers concentrate on general schemes. Very little work has been done on the pre-exponential factor. However, in determining the decay rates and in discussing the selection rules, it is an important factor. Of other factors, the most important one is the electronic matrix element $\langle \alpha | \partial V / \partial R_m | \alpha' \rangle$ (or its square). In some of the theoretical methods [6.7], it is just left it as a parameter without further study. Actually, if we fully investigate these matrix elements, many different kinds of effects can be described, for example, the effect introduced by states of opposite parity, the effect of ligand internal vibrations, the forbiddenness of non-radiative transitions of rare-earth ions at centrosymmetric positions in solids, and so on. Ray and Chowdhury [8] discussed these effects using the method of hypersensitive transition theory. Some of their conclusions can be rederived by limiting the basis set only to metal orbitals.

In the present work we followed the Judd-Ofelt scheme [9] and used the formalism of Fong's theory of nonradiative relaxation to give detailed expressions for the electronic matrix elements, and some relevant problems are discussed.

2. Theoretical expressions

2.1. Approximation potential and wavefunctions

As is well known, in the weak-coupling limit the radiationless transition rate of the 4f electron transition from state α to state α' can be expressed as [6]

$$W_{\alpha\alpha'} = \sum_{m} (L_m |C_{\alpha\alpha'}^m|^2 / \hbar^2) \exp(-\sigma) \int_{-\infty}^{\infty} dt \exp[F(t + i\hbar\beta)]$$

where

$$C_{\alpha\alpha'}^{m} = \frac{\hbar^{3}\omega_{m}}{2M_{m}} \frac{\langle \alpha | \partial V / \partial R_{m} | \alpha \rangle|_{R=R_{0}}}{\epsilon_{\alpha'}(R_{0}) - \epsilon_{\alpha}(R_{0})}$$

Eq. (1) was derived by a time-correlation function method in the adiabatic approximation. If the generating-function method is used in the CBO scheme, it can be shown that the radiationless transition rate can be expressed as [7]

$$W_{\alpha\alpha'} = \hbar^2 \sum_p |C_{\alpha\alpha'}^p|^2 \int_{-\infty}^{\infty} dt \exp(-i\Delta Et/\hbar) \tilde{f}_p(t) \prod_u f_u(t),$$

where

$$C^{p}_{\alpha\alpha} = (i\hbar/\Delta E M_{p}^{1/2}) \langle \alpha | \partial V / \partial R_{p} | \alpha' \rangle$$

From eqs. (1) and (2), it can be seen that either in the adiabatic approximation or in the CBO approximation, the radiationless transition rates are proportional to the square of $\langle \alpha | \partial V / \partial R_i | \alpha' \rangle$. It is necessary to study these matrix elements more carefully. V = V(r, R) includes the potential of electron-electron, electron-nuclear and nuclear-nuclear interaction, as shown in eq. (3) and in the diagram:

$$V(r, R) = V(LN, RF) + V(LE, RF) + V(LN, RN) + V(LE, RN) + V(RN, RF) + V(LN, LE)$$



It can be assumed, in the CBO scheme, that V(RN, RF) and V(LN, LE) are independent of R; on the other hand V(LN, RN) and V(LE, RN) are independent of the coordinate r of the 4f electrons in the rare-earth ions. Thus in the calculation of $\langle \alpha | \partial V / \partial R_i | \alpha' \rangle$, the potential V can be treated as V(LN, RF) + V(LE, RF):

$$V = -\sum_{i} \int \frac{e_{i}\rho(R)}{|R-r_{i}|} d\tau \equiv \sum_{k,q,i} B_{kq} C_{kq}(i), \qquad (4)$$

where B_{kq} is [10]

$$B_{kq} = -e \int (-1)^q \rho(R) C_{k-q}(\vartheta,\varphi) \left(r \overset{k+1}{\leq} \right) \, \mathrm{d}\tau \; .$$

If the charge distribution of the crystal does not enter that of the 4f electrons, i.e. if the overlap and exchange interaction can be omitted, after replacing r_{\leq}^{k} by r_{i}^{k} , then V can be expressed as

$$V = \sum_{k,q,i} A_{kq} r_i^k C_{kq}(i) \equiv \sum_{k,q} A_{kq}(R) D_{kq}(r), \qquad (5)$$

where

$$D_{kq} \equiv \sum_{i} r_i^k C_{kq}(i)$$

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(1)

(2)

(3)

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(8)

It should be noted that eq. (4) not only includes a point-charge contribution but also dipolar polarization and the quadrupolar contributions of the ligands. Actually, as Newman [11] pointed out, altogether ten different contributions can be incorporated into the crystal-field parameters, so that we can use eq. (4) or eq. (5) as a starting point to discuss the effect of ligand vibrations on the relaxation transition rates. The above parameters may also include both point-charge and multipole electric interactions and can be used to discuss both single ions and polyatomic charged groups.

2 2. Approximate wavefunctions

As is well known, the first-order wavefunctions of 4f electrons in rare-earth ions can be expressed as

$$\psi(\alpha) = \langle f^{n} \alpha SLJM | + \sum_{\alpha_{1}} \frac{\langle f^{n} \alpha SLJM | V_{e} | f^{n} \alpha_{1} S_{1} L_{1} J_{1} M_{1} \rangle}{E(f^{n} \alpha_{1}) - E(f^{n} \alpha)} \langle f^{n} \alpha_{1} S_{1} L_{1} J_{1} M_{1} |$$

$$+ \sum_{\alpha_{2}} \frac{\langle f^{n} \alpha SLJM | V_{o} | f^{n-1} I \alpha_{2} S_{2} L_{2} J_{2} M_{2} \rangle}{E(f^{n-1} I \alpha_{2}) - E(f^{n} \alpha)} \langle f^{n-1} I \alpha_{2} S_{2} L_{2} J_{2} M_{2} |, \qquad (6)$$

where the summation Σ_{α_1} is over the different $\langle f^n \alpha_1 S_1 L_1 J_1 M_1 |$ states and the summation Σ_{α_2} is over the different $\langle f^{n-1} I \alpha_2 S_2 L_2 J_2 M_2 |$ states. $E(f^n \alpha_1) \equiv E(f^n \alpha_1 S_1 L_1 J_1 M_1), E(f^{n-1} I \alpha_2) \equiv E(f^{n-1} I \alpha_2 S_2 L_2 J_2 M_2)$, and so on. On the other hand, V_e and V_o are respectively the even and odd components of the crystal field. The second term in eq. (6) is due to mixing within the same configuration. The third term expresses the mixing with $4f^{n-1}ml$ (*m* is an integer, m > 4), the most important configuration that mixes with $4f^n$ is $4f^{n-1}$ 5d. Thus

$$\psi(\alpha') = |f^{n}\alpha'S'L'J'M'\rangle + \sum_{\alpha'_{1}} \frac{\langle f^{n}\alpha'_{1}S'_{1}L'_{1}J'_{1}M'_{1}|V_{e}|f^{n}\alpha'S'L'J'M'\rangle}{E(f^{n}\alpha'_{1}) - E(f^{n}\alpha')} |f^{n}\alpha'_{1}S'_{1}L'_{1}J'_{1}M_{1}\rangle + \sum_{\alpha_{2}} \frac{\langle f^{n-1}|\alpha'_{2}S'_{2}L'_{2}J'_{2}M'_{2}|V_{o}|f^{n}\alpha'S'LJ'M'\rangle}{E(f^{n-1}|\alpha'_{2}) - E(f^{n}\alpha')} |f^{n-1}|\alpha'_{2}S'_{2}L'_{2}J'_{2}M'_{2}\rangle.$$
(7)

In eq. (7), the summations $\Sigma_{\alpha'_1}$ and $\Sigma_{\alpha'_2}$, the energies $E(f^n \alpha')$, $E(f^{n-1} l \alpha'_2)$ and so on have the same meaning as in eq. (6).

2.3. Expressions for $\langle \alpha | \partial V / \partial R_m | \alpha' \rangle$

Obviously, up to first order, the electronic matrix elements can be expressed as

$$\langle \alpha | \partial V / \partial R_m | \alpha' \rangle = K_0 + K_1 + K_1'$$

where K_0 is the matrix element between the unperturbed 4f wavefunctions. The first-order terms K_1 and K'_1 are matrix elements between unperturbed wavefunctions and first-order wavefunctions corresponding respectively to mixing within the same configuration and mixing of different configurations. Following similar methods to those used in Judd-Ofelt theory [8,9], it is easy to work out all the expressions for K_0 , K_1 , and K'_1 :

$$K_{0} = \langle f^{n} \alpha SLJM | \partial V / \partial R_{m} | f^{n} \alpha' SL'J'M' \rangle = (-1)^{S+L+J+J'+k+M+1} \cdot 7(2J+1) \sum_{k=2,4,6} \sum_{q} \partial A_{kq} / \partial R_{m} \rangle \langle 4f | r^{k} | 4f \rangle$$

$$\times \left(\frac{3 \ k \ 3}{0 \ 0} \right) \left(\frac{J \ k \ J'}{-M \ q \ M} \right) \left\{ \frac{J \ J \ k}{L' \ L \ S} \left\{ f^{n} \alpha SL | | U^{(k)} | | f^{n} \alpha' SL' \rangle \right\}.$$

$$(9)$$

In deriving eq. (9) the following formulae have been used: 500

 $\langle l^n \alpha SLJM | D_{kg} | l^n \alpha' SL'J'M' \rangle = \langle l|r^k|l \rangle \langle l||C^{(k)}||l \rangle \langle l^n \alpha SLJM | U_a^{(k)}| l^n \alpha' SL'J'M' \rangle,$

$$\begin{split} &\langle l^n \alpha SLJM | U_q^{(k)} | l^n \alpha' SL'J'M' \rangle = (-1)^{J-M} \begin{pmatrix} J & k & J' \\ -M & q & M \end{pmatrix} \langle l^n \alpha SLJ | | U^{(k)} | | l^n \alpha' SL'J' \rangle , \\ &\langle l^n \alpha SLJ | | U^{(k)} | | l^n \alpha' SL'J' \rangle = (-1)^{S+L+J'+k} \left([J,J'] \right)^{1/2} \begin{pmatrix} J & J' & k \\ L' & L & S \end{pmatrix}, \langle l^n \alpha SL | | U^{(k)} | | l^n \alpha' SL'J' \rangle , \\ &\langle l^n \alpha SLJ | | U^{(k)} | | l^n \alpha' SL'J' \rangle = (-1)^{S+L+J'+k} \left([J,J'] \right)^{1/2} \begin{pmatrix} J & J' & k \\ L' & L & S \end{pmatrix}, \langle l^n \alpha SL | | U^{(k)} | | l^n \alpha' SL'J' \rangle , \\ &\langle l^n \alpha SLJ | | U^{(k)} | | l^n \alpha' SL'J' \rangle = (-1)^{S+L+J'+k} \left([J,J'] \right)^{1/2} \begin{pmatrix} J & J' & k \\ L' & L & S \end{pmatrix}, \langle l^n \alpha SL | | U^{(k)} | | l^n \alpha' SL'J' \rangle , \\ &\langle l^n \alpha SLJ | | U^{(k)} | | l^n \alpha' SL'J' \rangle = (-1)^{S+L+J'+k} \left([J,J'] \right)^{1/2} \begin{pmatrix} J & J' & k \\ L' & L & S \end{pmatrix}, \langle l^n \alpha SL | | U^{(k)} | | l^n \alpha' SL'J' \rangle . \end{split}$$

Similarly

$$K_{1} = \sum_{\alpha_{1}} \left(\frac{1}{E(f^{n}\alpha) - E(f^{n}\alpha_{1})} + \frac{1}{E(f^{n}\alpha') - E(f^{n}\alpha_{1})} \right) \sum_{\substack{k,k'=2,4,6 \\ q,q'}} A_{k'q'} (\partial A_{kq}/\partial R_{m}) \langle 4f|r^{k}|4f\rangle \langle 4f|r^{k'}|4f\rangle \\ \times 49(2J+1)^{2} (-1)^{J+J'+L+L'+M+M'} \left(\frac{J}{-M} + \frac{J'_{1}}{q} \right) \left(\frac{J'_{1}}{-M'_{1}} + \frac{J'}{q'} \right) \left(\frac{3}{0} + \frac{3}{0} \right) \left(\frac{3}{0} + \frac{3}{0} \right) \\ \times \left\{ \int_{L'_{1}} \frac{J'_{1}}{L} + \frac{k}{S} \right\} \left\{ \int_{L'} \frac{J'_{1}}{L} + \frac{J'_{1}}{S} \right\} \langle f^{n} \alpha SL ||U^{(k)}|| f^{n} \alpha'_{1} SL'_{1} \rangle \langle f^{n} \alpha'_{1} SL'_{1} ||U^{(k')}|| f^{n} \alpha' SL' \rangle.$$
(10)

In deriving the expression for K'_1 , it should be noted that there are three odd crystal-field components contributing to the mixing of configurations with opposite parity. As in Judd-Ofelt theory [9], it can be assumed that

$$E(f^{n-1}l\alpha'_2) - E(f^n\alpha') = E(f^{n-1}l\alpha_2) - E(f^n\alpha) \equiv \Delta(fl).$$
(11)

 $\Delta(fl)$ is the average separation between the 4fⁿ configuration and the 4fⁿ⁻¹ ml configuration.

As in Judd-Ofelt theory, it is easy to show that

$$K_{1}' = \sum_{\substack{v=1,3 \ s}} \frac{\partial A_{vq}}{\partial R_{m}} \sum_{\substack{t=1,3,5 \\ \lambda=2,4,6 \\ p}} (2\lambda + 1) (-1)^{p+q} A_{Ip} \begin{pmatrix} v & \lambda & t \\ q & -p-q & p \end{pmatrix} \begin{pmatrix} J & J' & \lambda \\ L' & L & S \end{pmatrix}$$

 $\times \langle f^n \alpha SL \| U^{(\lambda)} \| f^n \alpha' SL' \rangle \Xi_{\nu}(t, \lambda),$

where

$$\Xi_{\nu}(t,\lambda) = -14 \sum_{l'} (-1)^{3+l'} (2l'+1) \begin{cases} \nu & \lambda & t \\ 3 & l & 3 \end{cases} \binom{3 & \nu & l}{0 & 0 & 0} \binom{l}{0} \begin{pmatrix} t & 3 \\ 0 & 0 & 0 \end{cases}$$

 $\times \langle 4f|r^{\nu}|ml\rangle \langle 4f|r^{t}|ml\rangle / \Delta(fl) .$

 $\Xi_1(t, \lambda)$ here corresponds to $\Xi(t, \lambda)$ in Judd-Ofelt theory.

The doubly reduced matrix elements of $U^{(k)}$ can be found from the tables of Nielson and Koster [12] and the 3j and 6j symbols can be found from the tables of Rotenberg [13]. Eqs. (9), (10), and (12) can be used to study

(12)

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the contribution of various effects and the selection rules for relaxation transitions.

There is another perturbation, the vibrations of ligands, which will modify the wavefunctions of 4f electron in rare-earth ions. After taking account of this effect, $A_{k'q'}$ in eq. (10), A_{tp} in eq. (12) should be replaced by $A'_{k'q'}$ and A'_{tp} respectively:

$$A'_{i\tau} = A_{i\tau} + \sum_{j,\eta,\eta} (\partial A_{i\tau}/\partial R_j) \langle \eta | R_j | \eta' \rangle \psi(\eta) , \qquad (13)$$

where R_j denotes the normal coordinates of the vibrating complex and η , η' are vibrational quantum numbers. The $\psi(\eta)$ introduced here is the probability amplitude of a certain vibrating state η ; we define

$$|\psi(\eta)|^2 = \rho(\eta) , \qquad (14)$$

where $\rho(\eta)$ is as in Judd–Ofelt theory, viz. the probability of the vibrating complex in the state.

3. Discussion

3.1. The ligand vibration contribution

From eqs. (9), (10) and (12), it is easy to see that all the ligand vibration contributions to the radiationless transition can be induded in the crystal-field theory scheme. These contributions not only appear as K'_1 but also as K_0 and K_1 . Actually A_{kq} can be expressed as

$$A_{kq} = \sum_{L} \sum_{l,p} T_{q,p}^{(k,l)}(L) D_{l,p}(L), \qquad (15)$$

where Σ_L represents the summation over all the ligands, when we refer to the rare-earth-ligands vibration. Let R_L be the instantaneous distance between a rare-earth ion and its ligand L,

$$\frac{\partial A_{kq}}{\partial R_m} = \frac{\partial A_{kq}}{\partial R_L} = \sum_L \sum_{l,p} \frac{\partial T_{q,p}^{(K,l)}}{\partial R_L} D_{l,p}(L).$$
(16)

• On the other hand, when we discuss the effect of internal vibrations of the ligand group, let R_{1L} represent the normal-mode amplitude of the internal vibration of ligand L, then

$$\frac{\partial A_{kq}}{\partial R_m} = \sum_{L} \sum_{l,p} T_{q,p}^{(k,l)}(L) \frac{\partial D_{l,p}(L)}{\partial R_{1L}}$$
(17)

In eqs. (16) and (17), l = 0 corresponds to the point-charge contribution of the ligands, l = 1 to the dipole contribution, l = 2 to the quadrupole contribution, and so on. If the ligands are composed of single ions, $\partial A_{kq}/\partial R_m$ will only come from eq. (16), but when the ligands are composed of multiatomic groups, both eqs. (16) and (17) have contributions to $\partial A_{kq}/\partial R_m$. Clearly, $\partial A_{kq}/\partial R_m$ appear at the same time in eqs. (7), (8) and (9). This means that the internal and external vibrations of ligand groups both have contributions to K_0 , as well as to K_1 , K'_1 and other higher-order terms.

If the internal vibration contribution to K_0 is forbidden, then the contribution to K_1 will be more important than that to K'_1 (it is pointed out in the following paragraph that K'_1 has the same selection rules as K_0). So we cannot associate any particular term with the special effect induced by ligand internal vibrations. On the other hand, the appearance of the effects of opposite parity states does not necessarily relate to the existence of ligand

internal vibrations. Actually, most of the examples cited in ref. [8] to support the effect represented by K'_1 are rare-earth ions in simple ionic crystals.

3.2. The selection rules

Clearly, K_0 and K'_1 will not be equal to zero only if

$$\begin{pmatrix} J & J' & k \\ L' & L & S \end{pmatrix} \langle f^n \alpha SL \| U^{(k)} \| f^n \alpha' SL' \rangle \neq 0 ,$$

so K_0 has the same selection rules as K'_1 , i.e. $\Delta S = 0$; $\Delta L \leq 6$; $\Delta J \leq 6$. If the initial or final state has J = 0, then ΔJ can only be 2, 4, or 6. Because of the spin—orbit interaction and J-mixing, it will lead to a relaxation or even breakdown of these selection rules. Obviously, it is exactly the same as that of the electric dipole transition. Talking about parallelism between radiative and non-radiative transition rates, we should first take account of the effect of K_0 . It should also be noted that there are three terms in K'_1 , v = 1 corresponding to the "electric dipole" term. Unlike the formula for electric multipole transition rates, the factor $(2\pi r_0/\lambda)^2$ does not appear here (r_0 is the atomic dimension, λ is the wavelength of light). On the other hand $\langle 4f|r|^{5}d\rangle$, $\langle 4f|r^{5}|5d\rangle$ increase in order of magnitude [9], so the importance of the terms corresponding to v = 3 and v = 5 in eq. (12) should be considered.

3 3. Discussion of some examples

(A) Clearly, from the selection rules given previously, for the ${}^{5}D_{1} \rightarrow {}^{5}D_{0}$ radiationless transition, both K_{0} and K'_{1} are equal to zero. In the case of the rare-earth ions M^{3+} , the low non-radiative decay rate comes mainly from K_{1} , as briefly mentioned by Weber [14]. It should be pointed out that the ${}^{5}D_{1} \rightarrow {}^{5}D_{0}$ non-radiative transition in Eu³⁺ is a very special case. In this case, not only is $K_{0} = K'_{1} = 0$, but also K_{1} is very small. This situation occurs because the only intermediate level lying near ${}^{5}D_{1}$ and which can provide a non-zero K_{1} , is ${}^{5}D_{2}$, but ${}^{5}D_{2}$ itself has only a very low non-radiative decay rate. In more usual cases, even if $K_{0} = 0$, K_{1} will provide the non-radiative decay rates demanded by the exponential law, for example, the ${}^{4}S_{3/2} \rightarrow {}^{4}F_{9/2}$ transition of Er³⁺ ions in $Y_{2}O_{3}$. LaCl₃, LaBr₃ and LaF₃ [14,15]. In this case $U_{\lambda} = \langle \alpha SL || U^{(\lambda)} || \alpha' SL' \rangle$ for $\lambda = 2$, 4, 6 are all equal to zero [12], so $K_{0} = K'_{1} = 0$. But the non-radiative decay rate is only a little lower than expected by the exponential law.

In the case of rare-earth ions M^{2+} , for example the ${}^5D_1 \rightarrow {}^5D_0$ transition of Sm²⁺ in BaCl₂, BaF₂ and BaFCl crystals [16], the separations between these levels and the $4f^{n-1}$ 5d states are narrow. The second-order term, i.e. the matrix elements between the third term of eq. (6) and the third term of eq. (7), become non-zero. In this circumstance, because the $4f^{n-1}$ 5d states are sensitive to changes in the host crystals, so the lifetime-temperature curves of the 5D_1 state of Sm²⁺ are quite different from host to host. Of course, in this case the K_1 term still has its effect.

(B) The forbiddenness of the non-radiation transition in the presence of inversion symmetry. There are many examples of forbiddenness of non-radiative transitions when rare-earth ions are sited at positions of inversion symmetry in solids. In these cases, not only is K'_1 , the term corresponding to electric multipole transitions, equal to zero, but also, and more importantly, K_0 and K_1 are equal to zero. The higher-order terms provide the low non-radiative decay rates.

It is easy to see that A_{kq} and $\partial A_{kq}/\partial R_m$ should have different parity. In the case of inversion symmetry, when t is odd, $A_{tp} = 0$, and when t is even $\partial A_{tp}/\partial R_m = 0$, then from eqs. (9), (10) and (12), it can be seen that $K_0 = K_1 = K'_1 = 0$. Classically, when V(R) = V(-R), $\partial V/\partial R|_{R=R_0} = 0$.

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4. Conclusion

The non-radiative effects of ligand vibrations, including the introduction of the same-parity intermediate states (represented by K_1) and the introduction of opposite-parity intermediate states (represented by K_1), the forbiddenness of non-radiative transitions in some special cases, and so on, can be described by the generating-function method (or correlation-function method) and crystal-field theory. For promoting radiationless transitions, any effects that contribute to crystal-field parameter changes $\partial A_{kq}/\partial R_m$ should be considered. It is clear that the ligand internal vibration as well as ligand—metal vibrations contribute to the zeroth-order term K_0 , which appears to be the most important term in non-radiative decay. Because K_0 and K'_1 have the same selection rules as electric dipole transitions, there is a parallelism of radiative and non-radiative transitions. It seems unnecessary to associate ligand-induced non-radiative effects with any one special term only. In the case of rare-earth ions M^{3+} , in addition to the zeroth-order term K_0 , usually the same-parity mixing term K_1 is important, especially when the terms K_0 and K'_1 are forbidden. When the energy levels are close, the configuration with opposity parity (for example, some higher-energy levels in M^{2+} ions) K'_1 and the second-order terms (representing mixing with opposite-parity states) have their effects. There are altogether three terms that represent the first-order effects of vibration through the introduction of opposite-parity states.

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References

- [1] Yu.E. Perlin, Soviet Phys. Uspekhi 6 (1964) 542.
- [2] R. Orbach, Phys. Rev. 133A (1964) 34.
- [3] S.H. Lin, J. Chem. Phys. 44 (1966) 3759.
- [4] L.A. Riseberg and H.W. Moos, Phys. Rev. 174 (1968) 429.
- [5] T. Miyakawa and D.L. Dexter, Phys. Rev. B1 (1970) 2961.
- [6] F.K. Fong. Theory of molecular relaxation: applications in chemistry and biology (Wiley, New York, 1975).
- [7] R. Englman, Non-radiative decay of ions and molecules in solids (North-Holland, Amsterdam, 1979).
- [8] D.R. Ray and M. Chowdhury, Chem. Phys. 61 (1981) 157.
- [9] B.R. Judd, Phys. Rev. 127 (1962) 750;
 - G.S. Ofelt, J. Chem. Phys. 37 (1962) 511.
- [10] B.G. Wybourne, Spectroscopic properties of rare earths (Wiley, New York, 1965).
- [11] D.J. Newman, Advan. Phys. 20 (1971) 197.
- [12] C.W. Nielson and G.F. Koster. Spectroscopic coefficients for pⁿ, dⁿ and fⁿ configurations (MIT Press, Cambridge, Massachusetts, 1964).
- [13] M. Rotenberg et al., The 3-j and 6-j symbols (MIT Press, Cambridge, Massachusetts, 1959).
- [14] M.J. Weber, Phys. Rev. 171 (1968) 283.
- [15] M.J. Weber, Phys. Rev. 157 (1967) 262.
- [16] H.V. Lauer and F.K. Fong, J. Chem. Phys. 65 (1976) 3108.