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MULTIPHONON NONRADIATIVE TRANSITION OF RARE-EARTH IONS

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Abstract

Based on the general theory[2-4], the formula of RE^{3+} multiphonon nonradiative transition probability is derived by adopting simplified approximations involving single-frequency model. Satisfactory agreement is obtained through the comparison of theory and experiment.

The principal differences between the present paper and relevant literatures as well as the validity of simplified approximation are discussed.

I. Introduction

Nonradiative transition is a very important problem in the study and design of devices of solid-state luminescence and laser, because the competition between nonradiative transition and radiative transition decides the efficiency of luminescent centres.

The crystals that contain rare-earth (RE) active ions take an extremely important place in the solid-state luminescent and laser materials, therefore one is much interested in nonradiative transition of RE ions. The radiative transition probability of RE ions (or intensity of spectral lines) can be calculated by applying the Judd-Ofelt theory[5,6]. However, although the theory of nonradiative transition of RE ions has been studied (e.g., Refs.[7-9]), a proper theory has not yet been established because of its complexity. Up to now one still applies some phenomenological formulas to estimate nonradiative transition probability[10,11]. In addition, nonradiative transition probability can not be directly measured by experiment. Thus it is very meaningful to investigate the theory of nonradiative transition of RE ions.

The quantum theory of multiphonon transition has been developed first of all and developed further in recent years by K. HUANG and A. Rhys[1,2,3]. SU Zhao-bin and YU Lu have also developed the nonradiative transition theory in their works[4]. On the basis of the general theory of multiphonon nonradiative transition from Refs.[2-4], this paper has derived the formula of multiphonon nonradiative transition probability for RE ions by adopting simplified approximations involving the single-frequency model. A comparison of theory with experiments has been carried out.

By far the most common valence state of the RE ions in solids is the trivalent one, and we will discuss the trivalent RE ions (RE^{3+}) in this paper. For most practically important cases (e.g., laser crystals), owing to the low concentration of RE^{3+} in crystals the energy transfer arising from ion-ion interactions may be ignored. Therefore, it is the multiphonon nonradiative transition that makes the predominant contribution to nonradiative transition. That is what we will discuss in this paper.

II. Nonradiative Transition Probability

For the need of the discussions below, and being the foundation of the present paper, some main results from Refs.[2-4] are recapitulated as follows.

In earlier researches on nonradiative transition, the so-called Condon approximation has been adopted, that is, the nonadiabaticity operator obtained with the chosen wave function has included $\frac{\partial}{\partial Q_s}$, and has coefficients not dependent on the vibrational coordinates Q_s. Corresponding theoretical estimates for the transition probability, whenever subject to experimented comparison, have been found to be too small (differing by several orders of magnitude!). Hence the "non-Condon approximation" theory and the static coupling theory whose results agree with the experiments are developed later. It is shown in Refs.[2-3] that the Condon approximation involves an inconsistent and consequently impermissible application of the perturbation method. Having remedied this mistake, Refs.[2,3] gave the formula for calculating transition matrix element, which is much simpler than non-Condon approximation; it is proved also that the non-Condon approximation theory and static coupling theory have been unified in Refs.[2,3] within certain approximations. The nonradiative transition probability has been derived through careful calculations in Ref.[3] as follows:

$$W=\frac{1}{\hbar}\int_{-\infty}^{\infty}G(\mu)e^{F(\mu)}d\mu \ , \tag{1}$$

$$F(\mu)=-i\mu w_{ji}+\sum_l\left(\frac{\omega_l}{2\hbar}\right)\Delta_{jil}^2\left[\coth\frac{\beta\mathscr{E}_l}{2}(\cos\mu\mathscr{E}_l-1)+i\sin\mu\mathscr{E}_l\right], \tag{2}$$

$$G(\mu)=\left\{\frac{1}{2}\sum_l\langle i|u_l|j\rangle\left[(\Delta_{jl}+\Delta_{il})+(\Delta_{jl}-\Delta_{il})\left(\cos\mu\mathscr{E}_l+i\coth\frac{\beta\mathscr{E}_l}{2}\sin\mu\mathscr{E}_l\right)\right]\right\}^2$$
$$+\frac{1}{2}\sum_l\langle i|u_l'|j\rangle^2\left(\frac{\hbar}{\omega_l}\right)\left(\coth\frac{\beta\mathscr{E}_l}{2}\cos\mu\mathscr{E}_l+i\sin\mu\mathscr{E}_l\right) \ , \tag{3}$$

where $\Delta_{jil}\equiv\Delta_{jl}-\Delta_{il}$, $\Delta_{jl}\equiv\frac{\langle j|u_l|j\rangle}{\omega_l^2}$, $\mathscr{E}_l\equiv\hbar\omega_l$, $\beta\equiv\frac{1}{kT}$,

w_{ji} is the energy difference between electronic states j and i, that is, energy gap ΔE.

By using the second quantization representation, Ref.[4] has further accounted for the multielectron background effects and the self-consistency of

the electron wave functions with the lattice relaxation, i.e., the initial and final states are multielectron states consistent with the different lattice symmetry breaking. The nonradiative transition probability has been obtained as follows:

$$W=\frac{1}{\hbar}\int_{-\infty}^{\infty}G(\tau)\exp\left(-\frac{F(\tau)}{\hbar}\right)d\tau\ , \tag{4}$$

$$F(\tau)=i\tau w_{if}+\frac{\rho}{2}\sum_{\nu}\omega_{\nu}|u_c^{\nu}-v_c^{\nu}|^2\left[\mathrm{cth}\frac{\beta\hbar\omega_{\nu}}{2}(1-\cos\omega_{\nu}\tau)-i\sin\omega_{\nu}\tau\right]\ ; \tag{5}$$

$$\begin{aligned}G(\tau)=&\frac{1}{4\hbar}\sum_{\nu,\mu}\langle e_f|K_{\nu}|e_i\rangle\langle e_i|K_{\mu}^{+}|e_f\rangle(u_c^{\nu}-v_c^{\nu})\cdot(u_c^{\tilde{\mu}}-v_c^{\tilde{\mu}})\\&\cdot\left[1-(\cos\omega_{\nu}\tau+i\mathrm{cth}\frac{\beta\hbar\omega_{\nu}}{2}\sin\omega_{\nu}\tau)\right]\left[1-\left(\cos\omega_{\mu}\tau+i\mathrm{cth}\frac{\beta\hbar\omega_{\mu}}{2}\sin\omega_{\mu}\tau\right)\right]\\&+\frac{1}{2}\sum_{\nu}\langle e_f|K_{\nu}|e_i\rangle\langle e_i|K_{\nu}^{+}|e_f\rangle\frac{1}{\rho\omega_{\nu}}\left(\mathrm{cth}\frac{\beta\hbar\omega_{\nu}}{2}\cos\omega_{\nu}\tau+i\sin\omega_{\nu}\tau\right)\ ,\end{aligned} \tag{6}$$

where for the symbols see Ref.[4].

If the self-consistency of the electronic states with the lattice relaxation and the non-orthogonality between initial and final electronic states are not accounted for, Eqs.(4)-(6) will reduce to Eqs.(1)-(3)

III. Derivation for RE^{3+} Multiphonon Nonradiative Transition Probability Formula

The 4f→4f transition for RE^{3+} will be discussed. The RE^{3+} in crystals possesses the following characteristic: the partially filled 4f shell behaves as an inner shell, which is deeply embedded within the RE^{3+} ion. (It is usually called lanthanide contraction). Furthermore, the 4f electrons are "shielded" by two electronic shells with larger radial extension ($5s^2$, $5p^6$). Thus the 4f electrons are only weakly perturbed by the crystal field, and the electron-phonon interaction is also very weak. Experiment shows that for the case of weak electron-phonon coupling multiphonon nonradiative transition probability W very rapidly decreases with increasing order p of the process. Hence, it can be thought that the phonon modes in the narrow range near the highest frequency (i.e. cutoff) of the phonon spectrum make the greatest contribution to W. Further, the contribution of these phonon modes can be considered equivalent to the contribution of the phonon modes whose frequencies are exactly ω_{eff}, that is, the simplified single-frequency model is adopted. Then, the analytic expression for W can be obtained by using the steepest descent method.

By applying Eqs.(1)-(3) (or Eqs.(4)-(6)), from equation determined saddle point

$$\left(\frac{\partial F}{\partial\mu}\right)_{\mu_0}=0\ , \tag{7}$$

we easily obtain

$$(i\mu_0+\frac{\beta}{2})\mathcal{E}_0=\sinh^{-1}\frac{P}{S\cdot\operatorname{csch}\frac{\beta\mathcal{E}_0}{2}} \quad , \tag{8}$$

where

$$\mathcal{E}_0=\hbar\omega_{eff}, \quad P=\frac{W_{ji}}{\mathcal{E}_0} \quad , \quad S\equiv\sum_l\frac{\omega_l}{2\hbar}\Delta_{jil}^2 \quad ,$$

i.e., K. HUANG-Rhys factor.

Thus, we have

$$\coth\frac{\beta\mathcal{E}_0}{2}\cos\mu_0\mathcal{E}_0+i\cdot\sin\mu_0\mathcal{E}_0=\left[\operatorname{csch}^2\frac{\beta\mathcal{E}_0}{2}+\left(\frac{P}{S}\right)^2\right]^{\frac{1}{2}}$$

$$=\left[4\bar{n}(\bar{n}+1)+\left(\frac{P}{S}\right)^2\right]^{\frac{1}{2}}\equiv H \quad , \tag{9}$$

$$\cos\mu_0\mathcal{E}_0+i\cdot\coth\frac{\beta\mathcal{E}_0}{2}\sin\mu_0\mathcal{E}_0=\frac{P}{S} \quad . \tag{10}$$

Substituting Eqs.(9), (10) into Eq.(3) gives

$$G(\mu_0)=\frac{1}{4}\left[\sum_l\langle i|u_l|j\rangle(\Delta_{jl}+\Delta_{il})+\frac{P}{S}\sum_l\langle i|u_l|j\rangle(\Delta_{jl}-\Delta_{il})\right]^2$$

$$+\frac{1}{2}\frac{\hbar^2}{\mathcal{E}_0}H\cdot\sum_l\langle i|u_l|j\rangle^2 \quad . \tag{11}$$

For the cases of weak electron-phonon coupling, S usually is much smaller than unity and we can assume

$$\frac{P}{S}>>1 \quad ; \qquad H\doteq\frac{P}{S} \quad .$$

Therefore, we have

$$G(\mu_0)\doteq\frac{1}{4}\frac{P^2}{S^2}\left[\sum_l\langle i|u_l|j\rangle(\Delta_{jl}-\Delta_{il})\right]^2+\frac{1}{2}\frac{\hbar^2}{\mathcal{E}_0}\frac{P}{S}\sum_l\langle i|u_l|j\rangle^2. \tag{12}$$

Here, the former term in the square brackets of the first term of Eq.(11) has been omitted. The validity of this approximation can be easily seen from Eq.(6), that is,

$$\frac{1}{4}\left(1-\frac{P}{S}\right)^2\left[\sum_\nu\langle e_f|K_\nu|e_i\rangle(u_c^\nu-v_c^\nu)\right]^2\doteq\frac{1}{4}\frac{P^2}{S^2}\left[\sum_\nu\langle e_f|K_\nu|e_i\rangle(u_c^\nu-v_c^\nu)\right]^2.$$

Compared with the second term in Eq.(11), the omitted part is also small, which can be seen from the ratio of the first term to the second term in Eq.(12). This ratio will soon be obtained.

In order to simplify further the results, the following assumption is introduced on the basis of the aforementioned single-frequency model. Since the

phonon modes in the narrow range near the cut-off frequency make the dominant contribution to W, we may include only these modes in the summation $\sum_l$ for calculating W.

We introduce the ratio

$$R \equiv \frac{\langle i|u_l|j\rangle}{\langle j|u_l|j\rangle - \langle i|u_l|i\rangle} = \frac{\langle i|u_l|j\rangle}{\omega_l^2 \Delta_{jil}} \quad . \tag{13}$$

Having noted that the numerator and denominator of Eq.(13) both depend on the strength of electron-phonon coupling of l-th mode, it is easily understood that through evaluating ratio, even if the dependence on l-th mode does not completely cancel out, R must vary only slightly with mode l. Therefore we may assume that R is a constant in the narrow range for summation $\sum_l$ mentioned above. Thus we have

$$\frac{1}{4}\frac{P^2}{S^2}\Big[\sum_l \langle i|u_l|j\rangle \Delta_{jil}\Big]^2 = \frac{P^2}{4S^2}\Big(\sum_l R\omega_l^2 \Delta_{jil}^2\Big)^2$$

$$\doteq \frac{P^2}{4S^2} R^2 \omega_{eff}^2 \Big(\sum_l \frac{\omega_l}{2\hbar}\Delta_{jil}^2 \cdot 2\hbar\Big)^2 = P^2 R^2 \hbar^2 \omega_{eff}^2$$

and

$$\frac{\hbar^2 P}{2\mathcal{E}_0 S}\sum_l \langle i|u_l|j\rangle^2 = \frac{\hbar P}{2\omega_{eff} S}\sum_l (R\omega_l^2 \Delta_{jil})^2 \doteq P R^2 \hbar^2 \omega_{eff}^2 \quad .$$

That is, the first term is exactly P times the second term for $G(\mu_0)$ of Eq.(12). Then we obtain

$$G(\mu_0) \doteq (P+1) P R^2 \hbar^2 \omega_{eff}^2 . \tag{14}$$

Furthermore, $F(\mu_0)$ has been easily obtained from Ref.[3]. Hence we have

$$W \doteq \frac{1}{\hbar} G(\mu_0)\Big(\frac{2\pi}{|F''(\mu_0)|}\Big)^{\frac{1}{2}} e^{F(\mu_0)} = \frac{1}{\hbar}(P+1) P R^2 \hbar^2 \omega_{eff}^2 \frac{\sqrt{2\pi}}{\hbar\omega_{eff}\sqrt{SH}}$$

$$\cdot \exp\Big\{-S\coth\frac{\beta\mathcal{E}_0}{2} + \frac{P\beta\mathcal{E}_0}{2} + SH - P\cdot \sinh^{-1}\frac{P}{S\operatorname{csch}\frac{\beta\mathcal{E}_0}{2}}\Big\} \quad .$$

By rewriting and using $H \doteq \frac{P}{S}$ to simplify this expression, we finally obtain the multiphonon nonradiative transition probability for RE^{3+} as follows:

$$W = B\omega_{eff} e^{-S}\sqrt{P}(P+1) e^{-(\ln\frac{P}{S} - 1)P} \cdot (\bar{n}+1)^P e^{-2S\bar{n}} \quad , \tag{15}$$

where

$$B \equiv \sqrt{2\pi} R^2 = \sqrt{2\pi}\Big(\frac{\langle i|u_l|i\rangle}{\langle j|u_l|j\rangle - \langle i|u_l|i\rangle}\Big)^2 \quad . \tag{16}$$

IV. Comparison of Theory with Experiment

1. Temperature Dependence

Eq. (15) can be written as

$$W_p=W_{po}(\bar{n}+1)^P e^{-2S\bar{n}} \tag{17}$$

and

$$W_{po}=B\omega_{eff}e^{-S}\sqrt{P}(P+1)e^{-(1n\frac{P}{S}-1)P} , \tag{18}$$

where W_{po} is p-phonon nonradiative transition probability at T=0.

Refs.[8,9] have also given the same dependence on $\bar{n}$ (hence on T) as Eq.(17), and have shown that this is in good agreement with experiments.

If the temperature is not very high and S is very small, we have $e^{-2S\bar{n}}\doteq 1$. Thus

$$W_p=W_{po}(\bar{n}+1)^P .$$

This is the commonly applied phenomenological temperature dependence[10,11]. Although better fits to the experimental data for temperature dependence are obtained in Refs.[8,9], it is also shown in these references that the dependence of its W_{po} on energy gap does not exhibit a good fit to the experiments. In fact this implies that the W_{po} given in Refs.[8,9] is doubtful (cf. later discussion).

Therefore we will put emphasize discussion on the dependence of W_{po} on energy gap.

2. Energy-Gap Dependence

The above-mentioned $P=\frac{W_{ji}}{\omega_0}=\frac{\Delta E}{\hbar\omega_{eff}}$, namely, the order of multiphonon nonradiative transition process, is usually called "Normalized energy gap". The dependence of W_{po} on P (hence on ΔE, i.e., the energy gap to the next-lower level) has been given by Eq.(18).

Up to now, although there are some experimental data on W_{po}, their accuracies are generally not high enough. As far as we know, only the data on $YA1O_3$ in Ref.[13] are relatively systematic and accurate. Seventeen excited states of five different RE^{3+} ions have been studied in Ref.[13].

In order to carry out the meaningfully quantitative comparison of theory with experiment, according to the error and statement given in Ref.[13] we mainly use eleven comparatively accurate data to compare and fit with Eq.(18), while six data with serious error have been ignored (they have been used for reference in later discussion).

We have chosen the following values of parameters $\hbar\omega_{eff}=600cm^{-1}$, S=0.19, $B\omega_{eff}e^{-S}=3.18\times10^7S^{-1}$, and have used Eq.(18) to calculate W_{po}, which have been

compared with the data taken from Ref.[13] and listed in Table 1, then Fig.1 has been plotted.

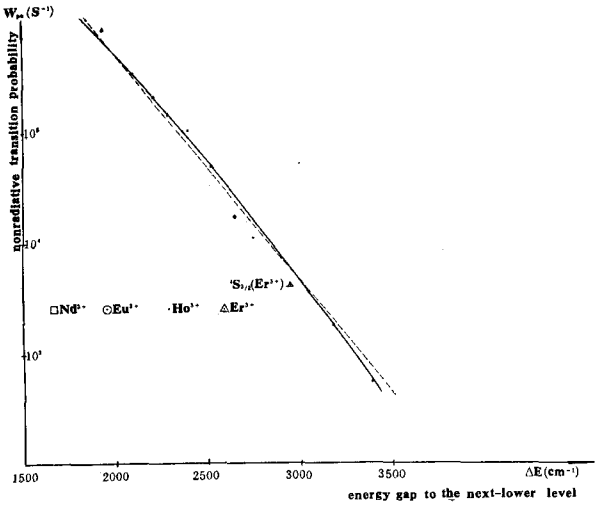

Fig.1. Dependence of the nonradiative transition probability on energy gap to the next-lower level for excited state of rare-earth ions in $YAlO_3$ at T=0. The solid curve is calculated from Eq.(18); the broken curve shows the straight line of fit given in Ref.[13] using Eq.(20), ($c=5\times10^9 s^{-1}$, $\alpha=4.6\times10^{-3}cm$); the data of experimental points are taken from Ref.[13]. (see Table 1.)

It is shown from Table 1 that all results calculated are in agreement with the experimental data within experimental error. We can also see from Fig.1 that the theoretical curve is in good agreement with the experimental points.

In the following, let us briefly discuss the remaining six data given in Ref.[13]. Although the measured errors of $^5D_1$ and $^5D_2$ data of Eu^{3+} are not large, Ref.[13] (for $YAlO_3$) and Ref.[14](for Y_2O_3) both point out that for these data similar serious systematic deviations are found, because they are subject to selection-rule restrictions, which should not be discussed here. It is shown by Refs.[13,14] that the $^4S_{3/2}(Er^{3+})$ is also subject to selection-rule restriction, which seems to explain the larger deviation of $^4S_{3/2}(Er^{3+})$ in Table 1 and Fig.1. As for the remaining four data, they cannot be adopted in quantitative investigation because of serious errors. But these experimental values are still roughly in agreement with values calculated by Eq.(18) within experimental uncertainties. For example, $\Delta E=4700cm^{-1}$ for $^4F_{3/2}(Nd^{3+})$ and $^5I_7(Ho^{3+})$, and we obtain $W_{Po}=0.44\ S^{-1}$ by using Eq.(18), and the experiments show that for $^4F_{3/2}(Nd^{3+})$ and $^5I_7(Ho^{3+})$ with such large energy gap the W_{Po} is indeed small enough to be neglected.

To sum up, Eq.(18) is in satisfactory agreement with eleven experimental data of W_{Po} over a range of four orders of magnitude.

Of course, up to now, comparatively reliable data are limited to $YAlO_3$. Therefore it is necessary to test the theory by using more extensive experimental data.

We have analyzed the experimental results for another five kinds of crystal (Y_2O_3, $Y_3Al_5O_{12}$, $LaCl_3$, $LaBr_3$, LaF_3), all of which can be fitted and explained by using Eq.(18). However, these data are not be quantitatively useful because

of their large uncertainties. Hence more accurate experimental measurements are necessary for obtaining meaningful quantitative results.

Table 1. Comparison between Experimental Values† and Calculated Values of W_{Po} for $YAlO_3:RE^{3+}$
(parameters: $\hbar\omega_{eff}=600cm^{-1}$, S=0.19, $B\omega_{eff}e^{-S}=3.18\times10^7s^{-1}$)

Excited State	$\Delta E(cm^{-1})$	$W_{Po}(s^{-1})$	
		experimental	calculated
$^2P_{3/2}(Nd^{3+})$	2220	$\sim2\times10^5$	2.0×10^5
$^5F_5(Ho^{3+})$	2100	$\cong3.3\times10^5$	3.3×10^5
$^3P_1,^3D_3(Ho^{3+})$	~2400	$\sim1\times10^5$	0.9×10^5
$^3F_3(Ho^{3+})$	1850	$\sim1\times10^6$	0.92×10^6
$^5S_2(Ho^{3+})$	2800	1.1×10^4	1.3×10^4
$^5I_6(Ho^{3+})$	3200	1.8×10^3	1.8×10^3
$^5D_3(Eu^{3+})$	2700	1.7×10^4	2.2×10^4
$^2H_{9/2}(Er^{3+})$	~1940	$\sim8\times10^5$	6.4×10^5
$^4F_{9/2}(Er^{3+})$	2530	4.9×10^4	4.9×10^4
$^4S_{3/2}(Er^{3+})$	2950	$\sim4\times10^3$	6×10^3
$^4I_{11/2}(Er^{3+})$	3425	5.9×10^2	5.6×10^2

V. Discussion

1. Some Discussions Related to References

Ref.[3] has clearly indicated and remedied the mistake Condon approximation, and hence has obtained the formula which can unify "non-Condon approximation" theory with static coupling theory. On the basis of these results, Eqs.(17) and (18) in this paper have been derived. It appears that Ref.[7] and Refs.[8,9] have still used Condon approximation (i.e., the nonadiabaticity operator includes $\frac{\partial}{\partial Q_s}$ and has coefficients not dependent on Q_s). Correspondingly, the results obtained are different.

If we leave out the nonadiabaticity operator in the formula for calculating multiphonon nonradiative transition probability, the rest part is the so-called transition overlap integral[3], namely, the part left after leaving out $G(\mu)$ in Eq.(1) mentioned above. As for this part, the results of the present paper and Refs.[7-9] are identical; but as for the other part $G(\mu)$ related to the nonadiabaticity operator, the results of the present paper and Refs.[7-9] are

† *Ref.[13] determine W_p by using $W_p=\frac{1}{\tau_i}-\sum_j A_{ij}$, where the total decay probability $\frac{1}{\tau_i}$ is measured by experiment, the radiative decay probabilities A_{ij} are calculated by using Judd-Ofelt intensity parameters for RE ions in $YAlO_3$. (the rms deviation between measured line strengths and line strengths calculated by using the Judd-Ofelt approach is typically about 10-15%).*

different. Since both experiments and theory have proved that Condon approximation implies a serious mistake, the G(μ) given in Refs.[7-9] are not proper, and it is easily understood that the dependences of their W_{Po} corresponding to G(μ) on energy gap cannot quantitatively agree with the experiments.

By using Kiel's approach, Refs.[10,15] etc., it is considered that it was necessary to carry the first-order term for Q_s in the expansion of H_{eL} to Pth-order perturbation,..., until the Pth-order term for Q_s in H_{eL} is carried to first-order perturbation theory, and then by the summation of all these contributions to find P-phonon nonradiative transition probability. Thus these authors consider that *ab initio* calculations of such transition rates are quite intractable. It appears that they have not recognized an essential idea that lattice relaxation can lead to multiphonon transition. Refs.[3,4] show that since the initial and final states of transition are states with different lattice relaxations, they embrace all high-orders of perturbation and therefore will lead to multiphonon transition! Thus even by carrying the linear electron-phonon interaction H_{eL} to first-order perturbation, the necessary results can be obtained. It is based on such an idea and approach that the formula of multiphonon nonradiative transition probability has been derived.

So far, the following simple empirical formula is usually adopted in practice[10-15]

$$W=W_0(\bar{n}+1)^P , \tag{19}$$

where

$$W_0=Ce^{-\alpha\Delta E} . \tag{20}$$

In Eq.(19), phenomenological parameters C and α are found to be the constants dependent on the host crystal and strength of electron-phonon coupling but, with rare exceptions, independent of the specific rare-earth ion or electronic states involved[10,13]. Eqs.(19) and (20) are in rough agreement with experiments.

If S is very small and T is not very high, Eq.(17) will agree with Eq.(19); if S is very small and P is rather large, within not a wide range of variation for P, $\log W_{Po}\sim\Delta E$ curve given by Eq.(18) is almost a straight line, i.e., Eq.(18) will approach Eq.(20). But, for example, if the range of variation for P is large, especially when S is not very small, relatively great difference between Eq.(18) and Eq.(20) will be exhibited.

It appears from Fig.1 and related discussions that Eq.(18) of this paper is in better agreement with the experiments than Eq.(20). Of course, in order to examine further the agreeable degree between theory and experiment, it is yet necessary to perform more accurate experiments within a large range of variation for P. It is worthwhile to indicate that if P is small, the formula of this paper and the above-mentioned empirical formula will become inaccurate, thus measurements should mainly extend towards large P values. But, if P is fairly large, $\frac{1}{\tau_i}$ and $\sum_j A_{ij}$ are very close, and their difference i.e., W_{Po}, is very small. In order that W_{Po} has certain accuracy, it is necessary that τ_i, A_{ij}

have very high accuracies!

2.Discussion for Adopted Approximation

First, the "single-frequency model" approximation is adopted. In fact, Refs.[7-15] related to RE^{3+} nonradiative transition have both adopted some single-frequency approximations, and have indicated that the results which were in agreement with the experiments could be obtained hereby. Physically, on one hand, W rapidly decreases basically exponentially with increasing P for weak electron-phonon coupling, therefore the predominant contributions to W come from the phonon modes in a narrow range near cut-off frequency; on the other hand, the strong peak of optical branch in high-frequency region of phonon spectrum more clearly emphasizes the contribution from these phonon modes near the peak. The results of determining the parameter ω_{eff} by experiment indicate that in most instances the vibronic spectrum shows strong peaks near the phonon cut-off frequency, and ω_{eff} is taken to be a value very near the cut-off frequency. In some cases (for example, $Y_3Al_5O_{12}$ and $YAlO_3$), the highest energy phonons appear as weak peaks in the vibronic spectra, and the more prominent peaks in the high-energy region correspond to lower energy phonons. Therefore, in obtaining the value of parameter ω_{eff}, both cut-off and the shape of the vibronic spectrum should be considered[10]. It is clear that the weaker the electron-phonon coupling, the smaller the S, the more rapidly the decrease of W with P, and therefore the better the "single-frequency model" approximation.

Secondly, it is assumed that the ratio R (see Eq.(13)) is a constant in the narrow range of phonon modes for summation in W. We take S, ω_{eff}, B (thus R^2) as the constants determined only by host crystals, the results obtained were in agreement with the experiments. It has been shown above that C in Eq.(20) (corresponding to $B\,\omega_{eff}e^{-S}$) is a constant determined basically by host crystals. Hence the above assumption is reasonable and practical.

Thirdly, for solid-state luminescence and laser, it is invariably desirable to gain strong radiation. For this reason, larger energy gaps are required (for example, >1000 cm^{-1})[8,11]. Thus for the cases of practical interest, P is large (for example, >3), and S for RE^{3+} is usually very small. Therefore, in the derivation given above we assume $\frac{P}{S}>>1$ and then adopt some approximate simplification and approximation of the steepest descent method, which will not bring about large errors.

Although the theory has been compared with some experimental results, it is yet necessary to test further the theory by more extensive experiments. And it is also meaningful, through specific models, to analyze and estimate the parameters S and R. It is worthwhile to notice that $S\equiv\sum_l \frac{\omega_l}{2\hbar}\Delta_{jil}^2$, in which the summation is taken only over the phonon modes in the narrow range near cut-off frequency, is different from the S appearing in radiative transitions.

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References

[1] K. HUANG and A. Rhys, Proc. Roy. Soc., A204(1950)406.

[2] Kun HUANG,Scientia sinica, 24(1981)27.

[3] Kun HUANG, Progr. in Phys. (Nanjing, China), 1(1981)31.

[4] SU Zhao-bin and YU Lu, Commun. in Theor. Phys. (Beijing, China)2(1983)1203.

[5] B. R. Judd, Phys. Rev., 127(1962)750.

[6] G.S. Ofelt, J. Chem. Phys., 37(1962)511.

[7] T. Miyakawa and D.L. Dexter, Phys. Rev., B1(1970)2961.

[8] F.K. FONG, S.L. Naberhuis and M.M. Miller, J. Chem. Phys., 56(1972)4020.

[9] F.K. FONG and W.A. Wassam, J. Chem. Phys., 58(1973)956.

[10] L.A. Riseberg, M.J. Weber: Relaxation phenomena in rare earth luminescence, in:"Progress in Optics" (ed. E. Wolf), Vol.14, (1976), p.89.

[11] S. Hüfner:"Optical Spectra of Transparent Rare Earth Compounds". Academic Press, (1978).

[12] B. Lal and D.R. Rao, J. Phys. Chem. Solids, 40(1979)97.

[13] M.J. Weber, Phys. Rev., B8(1973)54.

[14] M.J. Weber, Phys. Rev., 171(1968)283.

[15] L.A. Riseberg and H.W. Moos, Phys. Rev., 174(1968)429.

[16] S. Fisher, J. Chem. Phys., 53(1970)3195.