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Lattice Relaxation and Multiphonon Transitions

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ABSTRACT. The phenomenon of lattice relaxation, namely, that the atomic configuration surrounding a localized centre in solids changes with its change of electronic state, leads to various forms of multiphonon transitions. In optical emission or absorption spectra, such multiphonon transitions can cause shift and broadening of the spectral lines or give rise to distinct multiphonon peaks. Certain basic theoretical concepts relating to such multiphonon optical spectra are explained and a special discussion of the proper interpretation of the Franck–Condon principle in this connection is given. Lattice relaxation can also give rise to nonradiative transitions, which are important for carrier recombinations in semiconductors and quenching of luminescence.

1. Introduction

By the term 'lattice relaxation', used in the title, we refer specifically to the change of the equilibrium atomic configuration surrounding a localized centre (impurity or defect) in a crystal lattice, as the result of a quantum transition of the electronic state of the centre. From Franck's paper published in 1926, which led to the well-known Franck–Condon principle, it was apparently already common knowledge that the binding forces and hence the equilibrium atomic configuration in a molecule depend essentially on the electronic state. This essential fact relating to atomic systems was represented schematically by a 'configurational coordinate diagram' such as shown in fig. 1; the curves i and j represent the effective potential energy as functions of the atomic configuration, designated schematically by a coordinate Q, for two different electronic states i and j. During the thirties, the configurational coordinate diagram, together with the Franck–Condon principle was adapted to the discussion of various effects of lattice relaxation associated with localized centres in solids, including the difference between optical and thermal activation energies, peak shifts and broadening of emission and absorption spectra, nonradiative transitions between electronic states, etc (Mott and Gurney 1953). These developments, albeit very important and in concept and methodology still useful today, were essentially qualitative and semiclassical.

The first successful quantum-mechanical treatment of lattice relaxation effects was marked by two papers published respectively by Pekar (1950) and Huang and Rhys (1950), both on the most-studied localized centre at the time, namely, the F-centre in the alkali halides. Most importantly, lattice relaxation was explicitly related to the occurrence of multiphonon transitions, that is, electronic transitions accompanied by simultaneous emission or absorption of a number of phonons. Although various forms of multiphonon transitions are of common occurrence, the theoretical development was restricted for a number of years mainly to the solid state theoreticians. Now, after the developments of the intervening years, they have come to be accepted as a unified subject, which engages the interest of solid state spectroscopists, luminescence scientists, semiconductor physicists, etc. Particularly in the past few years, a greater degree of importance has been accorded to the subject

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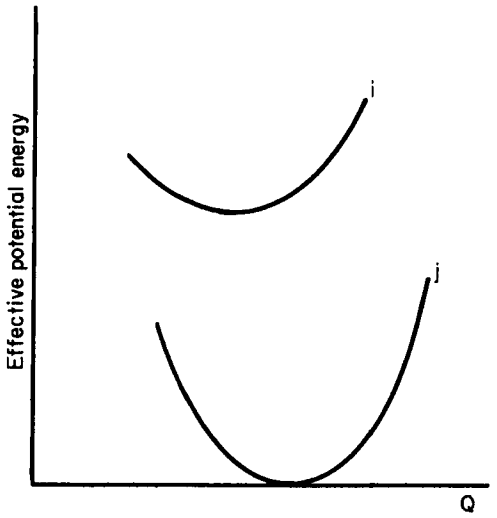

Fig. 1. Configurational coordinate diagram for two states i and j.

then ever before, so it seems worthwhile to present a brief survey of various aspects of the subject. The present article is written mainly for the general reader, but it is hoped that it may contain certain points of interest to scientists who are directly working on related subjects.

2. Multiphonon effects in optical emission and absorption

The present writer still remembers the occasion when his attention was first drawn to the problem at a seminar on luminescence held at Bristol University in 1947. A speaker, while commenting on the considerable width of the F-centre absorption band as being equivalent to a large number of phonons, remarked that a quantum-mechanical treatment would be difficult, for it would involve very high order of perturbation. When I was later working on the electron-LO (long optical wavelength) phonon interaction in ionic crystals, it became apparent, without having to resort to perturbation theory, that with lattice relaxation taken into account, an electronic transition is naturally accompanied by change in phonon numbers.

Thus for an allowed optical transition (emission or absorption), the transition probability is proportional to the square of the transition matrix element of the electric dipole moment er. For localized centres showing lattice relaxation, the atomic configuration changes with the transition, so in forming the transition matrix element, the atomic vibrational wave functions $\chi_{in}(Q)$, $\chi_{jn'}(Q)$ as well as the electronic wave functions $\varphi_i(r)$ and $\varphi_j(r)$ have to be taken into account. So one should write

$$\text{transition probability} \propto \left| \int \chi_{jn'}(Q) \left[\int \varphi_j er \varphi_i \, dr \right] \chi_{in}(Q) \, dQ \right|^2 .$$

As the integral over the electronic coordinates can be considered as approximately independent of the vibrational coordinates (the 'Condon approximation'), so one has approximately

$$\text{transition probability} \propto \left| \int \varphi_j er \varphi_i \, dr \right|^2 \left| \int \chi_{jn'}(Q) \chi_{in}(Q) \, dQ \right|^2 .$$

In this formula, only the overlap integral between the initial and final state vibrational wave functions involves the phonon numbers. The vibrational wave functions are products of simple harmonic oscillator wave functions of the normal coordinates Q_s describing the various vibrational modes:

$$\chi_n(Q) = \prod_s \chi_{n_s}(Q_s).$$

Lattice relaxation is represented by appropriate displacements of the origins of these normal coordinates. Thus two different electronic states i and j of a localized centre will have respectively vibrational wave functions:

$$\chi_{in}(Q) = \prod_s \chi_{n_s}(Q_s - \Delta_{is}); \quad \chi_{jn'}(Q) = \prod_s \chi_{n_s'}(Q_s - \Delta_{js})$$

characterized by different lattice relaxation parameters Δ_{is} and Δ_{js} ($s = 1 \ldots N$). The optical transition probability, which was seen to be proportional to

$$\left| \int \chi_{jn'}(Q)\chi_{in}(Q)\,dQ \right|^2 = \prod_s \left| \int \chi_{n_s'}(Q_s - \Delta_{js})\chi_{n_s}(Q_s - \Delta_{is})\,dQ_s \right|^2$$

depends essentially on the lattice relaxation. Thus, without lattice relaxation (i.e., $\Delta_s = 0$), the oscillator wave functions with different quantum numbers would be mutually orthogonal, so the transition probability is non-zero only if the vibrational quantum numbers n_s and n_s' before and after the transition are unchanged. But with the presence of the lattice relaxation Δ_{is}, Δ_{js} in the arguments, the orthogonality between the oscillator wave functions no longer holds. This means that transitions with changes in the phonon numbers n_s, n_s' can occur with finite probability. The first quantitative calculation on this basis for the F-centre absorption assumed only interaction with long optical vibrational modes (LO modes), all having the same frequency ω_0 and gave a series of equally spaced spectral lines, corresponding to the emission of different numbers of phonons. As represented schematically in fig. 2, they were smoothed into a continuous intensity distribution, which adequately accounted for the experimentally observed absorption band.

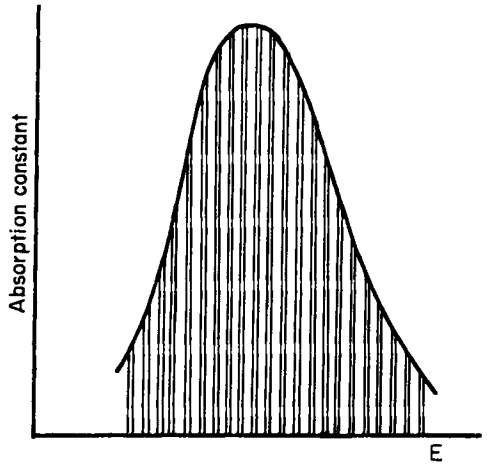

Fig. 2. Multiphonon lines reproducing absorption band.

Figure 3 shows the edge emission from CdS, which was the first case of distinct multiphonon peaks accurately interpreted in terms of the quantum mechanical theory (Hopfield 1959). The integrated peak intensities conform well with the theoretically predicted intensity distribution:

$$n\text{th peak} \propto S^n/n!$$

where S is a parameter characterizing the lattice relaxation and n represents the number of phonons emitted. The first line, corresponding to $n=0$, is usually known as the zero-phonon line and represents the undisplaced spectral line with photon energy equal to the electronic energy level difference. The above formula is a much used basic formula, applicable to multiphonon structures characterized by a single phonon frequency ω_0 (phonon energy $=\hbar\omega_0$) at low temperatures such that the thermal average phonon number $\ll 1$. It can be understood quite simply as follows. Suppose there are N modes of the same frequency interacting with the emission centre and let $\bar{s}$ be an average value of the squared overlap integral for a single mode emitting a phonon:

$$\bar{s}=\mathrm{Av}\left|\int \chi_{n_s+1}(Q_s-\Delta_{fs})\chi_{n_s}(Q_s-\Delta_{is})\,\mathrm{d}Q_s\right|^2$$

So for an n-phonon transition, the n-modes concerned will contribute

$$\bar{s}^n$$

Out of the N modes, the total number of all such n-mode transitions will be

$$C_n^N \cong \frac{N^n}{n!}$$

and they contribute in all:

$$\frac{N^n}{n!}\bar{s}^n=\frac{S^n}{n!}$$

where $S=N\bar{s}$ clearly represents the sum of the above squared overlap integral over all the N modes.

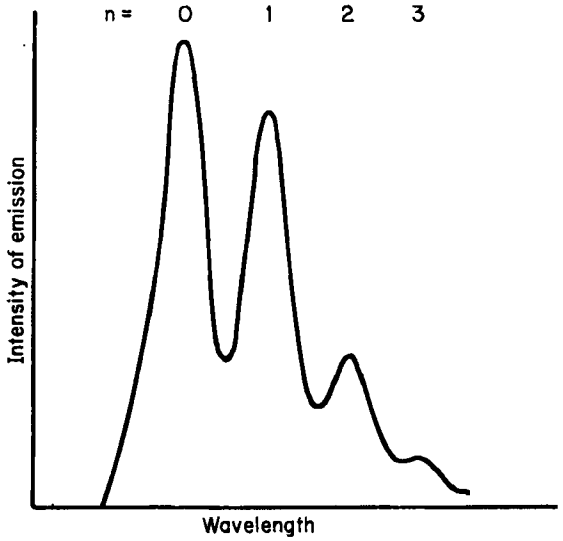

Fig. 3. Multiphonon emission peaks.

In practice, such multiphonon structures characterized by a distinct frequency are commonly attributed to either the LO lattice modes or a single local mode at the emission centre; it can be proved that the above intensity distribution formula applies in fact to both cases. As different vibrational modes contribute to the transition probability through their respective overlap integrals, which are multiplicative, for observed multiphonon structures involving more than one distinct phonon energy, the spectrum can be analysed by corresponding multiplication of the above intensity formula.

The spectral intensity distribution $I(E)$ can be expressed generally as

$$I(E) \propto \sum_{n_s'} \prod_s \left| \int \chi_{n_s'}(Q_s - \Delta_{js}) \chi_{n_s}(Q_s - \Delta_{is}) \, \mathrm{d}Q_s \right|^2 \delta(E - (E_i - E_j) + \sum_s (n_s' - n_s)\hbar\omega_s)$$

for the case of emission due to a transition from state i (energy E_i) to state j(energy E_j), E in the δ-function being energy of the emitted photon (for absorption due to the reverse transition $j \rightarrow i$, one has only to change the sign of the phonon term in the δ-function). The δ-function expresses that the energy of the emitted photon is equal to the electronic energy level difference $E_i - E_j$ minus the net emitted phonon energy. In actual calculations, one has also to take a thermal average over the initial vibrational quantum numbers n_s. For a general distribution of the lattice mode frequencies, it is not possible to express $I(E)$ in explicit analytical form. However a simple general result can be proved, namely, the first moment of the spectral distribution (i.e. the weighted mean photon energy) is given by

$$\frac{\int I(E) E \, \mathrm{d}E}{\int I(E) \, \mathrm{d}E} = E_i - E_j - \sum_s \tfrac{1}{2}\omega_s^2 (\Delta_{is} - \Delta_{js})^2$$

We note that $\Delta_{is} - \Delta_{js}$ represents the lattice relaxation in a transition from state i to state j, so the second term in the above expression is just the elastic energy associated with the relaxation. This relaxation energy can be represented schematically in the configurational coordinate diagram, as shown in fig. 4. The significance of the above result is clearest in the case of a continuous spectral distribution of an approximately symmetric shape (e.g. Gaussian), such as shown in fig. 5. In this case the first moment should give directly the position of the peak. As indicated in the figure, $E_i - E_j$ marks the position of the zero-phonon line; so the above result signifies that the spectral peak is shifted from the zero-phonon line by an energy equal to the lattice relaxation energy. The lattice relaxation energy is usually expressed as a parameter S multiplying into an average phonon energy:

$$S\overline{\hbar\omega} = \sum_s \tfrac{1}{2}\omega_s^2 (\Delta_{is} - \Delta_{js})^2$$

Referring to fig. 4, we note that this peak position corresponds exactly to what one would obtain by an application of the Franck–Condon principle.

As lattice relaxation effects on optical spectra are widely discussed in the context of the Franck–Condon principle, it is of interest to relate the discussion of multiphonon transitions to the interpretation of the principle. In this connection, the Franck–Condon principle is commonly represented as stating that the electronic transition is such a fast process that the atoms can be considered as stationary. It seems to the present writer that stating the Franck–Condon principle in this way is inaccurate. In fact, in a way such a statement would put the Franck–Condon

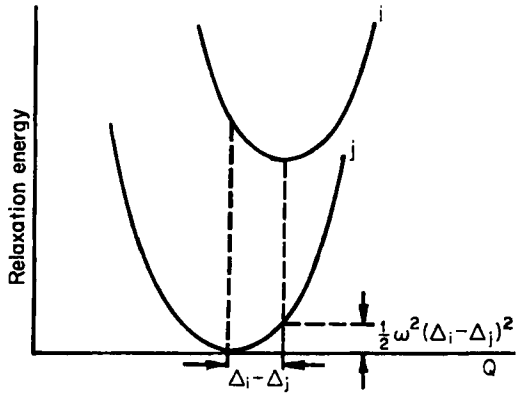

Fig. 4. Relaxation energy for an electronic transition.

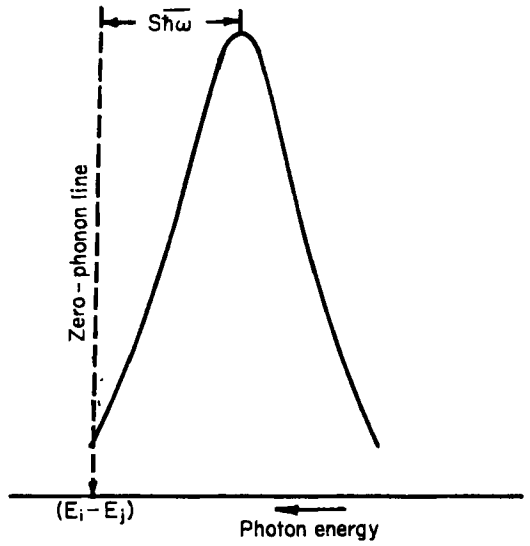

Fig. 5. Peak shift of a symmetric band.

principle in direct conflict with the observation of multiphonon structures. For instance, one could then ask the question: if the electron makes the transition so fast, how can it 'know' with what frequencies the atoms vibrate? If it is without the time to gauge the vibrational frequencies, how can it make the transition with just such energies as to produce the observed multiphonon structures, which are characterized by these vibrational frequencies?

It seems that the Franck–Condon principle should be interpreted along the following lines. To describe the electronic transition as a process fast compared with the atomic vibrations is inaccurate; one cannot assign any time constant for the transition other than the lifetime of the electronic state (that is, the inverse of the transition probability). This latter must in fact be greater than the vibrational periods, if multiphonon structures are not to be completely obliterated by line broadening owing to the uncertainty principle. It is the orbital motion of the electron

in its stationary states that is fast compared to the atomic vibrations; it is on this ground that the electronic states can be regarded as functions of the vibrational coordinates Q, as in the adiabatic approximation theory. On this premise, one can consider the electron making a transition at given positions of the vibrational coordinates; however, it is subject to the uncertainty principle. For instance, one is certainly allowed to consider the electron making the transition with the vibrational coordinates Q limited to a certain small neighbourhood ΔQ. But this implies a time interval for observation equal to the time required to traverse ΔQ, which is naturally much smaller than the vibrational periods. A moment's reflection will show that owing to the uncertainty principle such an analysis will be subject to an energy uncertainty greater than the phonon energy, that is, consideration of finer details such as multiphonon structures is ruled out in principle. Or speaking more generally, one can consider the electronic transition to be as fast as one chooses, in the sense that one can specify a ΔQ as small as one chooses (i.e. a time interval as short as one chooses) and there is always a certain probability for the electron making the transition. However, it will be subject to an energy uncertainty proportionately greater.

To sum up, it is legitimate to make the usual Franck–Condon type of analysis for optical transitions, on the ground that the electronic orbital motions are fast compared to the atomic motion. But such an analysis is always subject to an energy uncertainty large enough to obliterate all multiphonon structures. This is of course to be expected, as the vibrational coordinate Q is treated as a variable parameter, which implies a classical treatment of the vibrational motion and is thus incompatible with the quantized phonon energies.

3. Multiphonon nonradiative transitions

With the application of the configurational coordinate diagram to localized centres in solids, it was early realized that lattice relaxation makes it possible for electrons at localized centres to make nonradiative transitions, whereby the transition energy is provided by or dissipated into thermal vibrational energy of the lattice. In quantum-mechanical theory, the possibility of such transitions is in fact even more readily evident, for multiphonon emission or absorption, made possible by lattice relaxation, are just the processes required for energy balance in nonradiative transitions.

In quantum-mechanical theory, the adiabatic approximation, which assumes the electronic state to follow the atomic motion adiabatically, forms the natural basis for representing the lattice relaxation effects. Transitions will occur between the adiabatic electronic states, as though caused by a perturbation represented by the following transition matrix element (Huang and Rhys 1950):

$$\int \chi_{jn'}(Q) L_{ji}(Q) \chi_{in}(Q)\, \mathrm{d}Q$$

where the χs represent the initial and final vibrational wave functions and the 'nonadiabaticity operator':

$$L_{ji}(Q) = \int \left\{ \varphi_j \left[-\frac{\hbar}{2} \sum_s \frac{\partial^2}{\partial Q_s^2} \varphi_i \right] + \varphi_j \left[-\hbar^2 \sum_s \frac{\partial \varphi_i}{\partial Q_s} \frac{\partial}{\partial Q_s} \right] \right\} \mathrm{d}\boldsymbol{r}$$

where φ_i, φ_j are the initial and final adiabatic electronic wave functions.

The nonradiative transitions are sometimes called thermal transitions, to be distinguished from the optical transitions associated with the absorption or emission of electromagnetic radiation. They are of general importance as one of the basic processes underlying the kinetics of electrons (and holes) in solids. In particular, they are responsible for recombination of carriers in semiconducting materials and quenching of luminescence in luminescent materials. Although the basic theory was formulated in the early fifties, its further development and application were for many years beset with inconsistencies and uncertainties.

During the early developments, theoretical calculations of the transition probabilities yielded results which were apparently too small when compared with the experimental results. So these early attempts tended in a way to discredit the interpretation of nonradiative transitions in terms of multiphonon processes and led people to look for alternative mechanisms. However, some scientists thought that the discrepancy might be due to inappropriate approximations introduced in the actual calculations. The major approximation used in these calculations related to the way adiabatic electronic wave functions depend on the atomic vibrational coordinates Q and this played a decisive role in the evaluation of the nonadiabaticity operator. It became known as the Condon approximation, which just means using adiabatic electronic wave functions obtained by usual first order perturbation procedure regarding the electron–lattice interaction as the perturbation. Therefore attempts were made to replace the Condon approximation by improved 'non-Condon' approximations. Thus Kovarskii (1962) and co-workers adopted a 'non-Condon' wave function of the following form:

$$\varphi_i(rQ) = \varphi_i^0(r) + \sum_k \frac{\langle k|H_{el}|i\rangle}{W_i(Q) - \bar{W}_k(Q)} \varphi_k^0(r)$$

(H_{el} represents the electron–lattice interaction), which resembles usual first-order perturbation wave functions, but with the exact adiabatic eigenvalue $W_i(Q)$ and the first-order perturbation eigenvalue $\bar{W}_k(Q)$ replacing the usual zeroth-order eigenvalues. This wave function was proposed on the ground that it should hold for wider ranges of the Qs than the Condon approximation. They obtained transition probabilities 3–4 orders of magnitudes higher than Condon approximation results and generally in agreement with the experimental results.

During the seventies, Pässler, apparently thinking the problem still unsolved, sought to find another way out (Pässler 1974). He gave up the adiabatic approximation in the belief that it could not give the right result and used simple electronic wave functions not dependent on the atomic coordinates. So in his version of the theory, the electron–lattice interaction is left over to act as the perturbation inducing the nonradiative transitions. With this very much simpler and apparently basically different approach, Pässler obtained estimates of the transition probabilities which turned out to be very similar to the results given by Kovarskii.

To resolve this paradoxical situation, the present writer has pointed out in a recent paper (Huang 1981) that the Condon approximation actually involves an inconsistent application of the perturbation method with respect to the electron–lattice interaction responsible for the lattice relaxation. Thus in forming the matrix element

$$\int \chi_{jn'}(Q) L_{ji}(Q) \chi_{in}(Q)\, \mathrm{d}Q$$

the vibrational wave functions $\chi_{jn'}, \chi_{in}$ contain effectively all order terms in the lattice relaxation, whereas the use of the Condon approximation wave function in the non-adiabaticity operator $L_{ji}(Q)$ means cutting off the perturbation expansion after the first-order term. It was shown that an electron wave function, which takes proper account of the part of the electron–lattice interaction responsible for lattice relaxation without having recourse to perturbation expansion can in fact be constructed, namely:

$$\varphi_i(rQ) = \varphi_i^0(r) + \sum_k \frac{\langle k|H_{el}|i\rangle}{\bar{W}_i(Q) - \bar{W}_k(Q)} \varphi_k^0(r)$$

This wave function is seen to be very close to the 'non-Condon' wave function adopted by Kovarskii. Moreover, it was proved that using this corrected wave function, the matrix element of the nonadiabaticity operator in the adiabatic approximation theory, namely:

$$\int \chi_{jn'}(Q) L_{ji}(Q) \chi_{in}(Q)\, \mathrm{d}Q$$

is exactly equal to the transition matrix element:

$$\int \chi_{jn'}(Q) \left[\int \varphi_j^0(r) H_{el} \varphi_i^0(r)\, \mathrm{d}r \right] \chi_{in}(Q)\, \mathrm{d}Q$$

due to electron–lattice interaction in Pässler's theory. Thus the apparently incompatible developments of the basic theory are reconciled in an unexpectedly simple way.

Working out explicitly the nonradiative transition probability is quite an involved task and results in an expression too unwieldly to reproduce here. However, in a practically important limiting case, which may be called the strong-coupling high-temperature limit, the theory yields a simple result for the nonradiative transition probability, which may be represented as follows:

$$W \cong C T^{1/2} \exp(-\Delta E/kT)$$

where ΔE represents the minimum energy required to reach a configuration where the two adiabatic electronic levels coincide. On a configurational coordinate diagram, the energy ΔE can be very simply represented as shown in fig. 6. A formula of this form was proposed by Mott long before the advent of the quantum mechanical theory. It has a very simple interpretation in the semiclassical theory, which treats the atomic motion classically. For in such a semiclassical theory, energy conservation requires that electronic transitions occur only at configurations where the two electronic levels cross. The point C in fig. 6 is just such a configuration and the exponential factor in the above formula represents the thermal probability of reaching this configuration. Of course only the quantum mechanical theory prescribes a definite mechanism and permits quantitative evaluation of W in terms of the actual interaction. Moreover, in the semiclassical theory, the formula was considered to be valid only for temperatures high enough for the vibrational motion of the atoms to be considered classically; this would mean that the average vibrational quantum number

$$\bar{n}(T) = \{\exp(\hbar\omega_0/kT) - 1\}^{-1} \gg 1$$

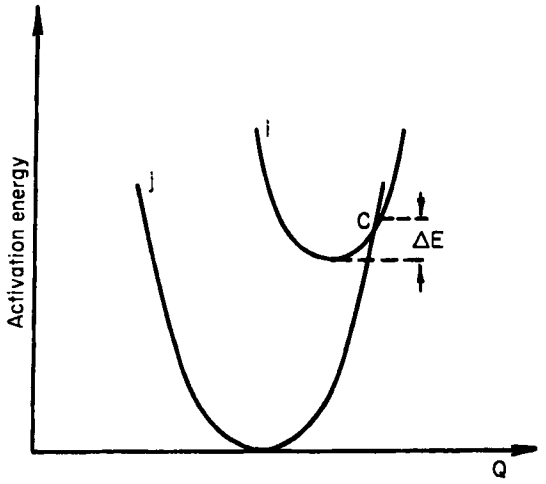

Fig. 6. Activation energy for nonradiative transition.

Taking this criterion seriously, it would appear dubious whether the formula could ever be used in practical circumstances.

The quantum-mechanical derivation of the above formula depends on the assumption of strong joint effect of coupling and temperature. Actual calculations show that so long as

$$\bar{n}(T)S \geqslant p = \frac{E_i - E_j}{\hbar\omega_0}$$

the formula is accurately usable. We notice that $p=(E_i-E_j)/\hbar\omega_0$ is just the electronic transition energy expressed as number of phonons. So for strong coupling such that the lattice relaxation energy $S\hbar\omega_0$ is comparable to the transition energy E_i-E_j, $\bar{n}(T)$ need not be large. The adjoining table, based on simplified calculations, compares the accurately calculated values with values calculated from the above formula; they are given in pairs with the accurate value on top (all values given are relative values), for various values of $\bar{n}(T)$, S and p. The values below the solid partition lines represent cases conforming to the requirement that $\bar{n}(T)S \geqslant p$; the approximate and accurate values are seen to be in close agreement.

The tabulated values are instructive in another way. Certain early calculations of the nonradiative transition probability had left one with the impression that the theoretically calculated transition probabilities were excessively sensitive to changes in the transition energy. Values given in the table show that this actually depends essentially on the strength of coupling relative to the transition energy. Thus for coupling strong enough for the strong-coupling high-temperature formula to be valid, the variation with either the transition energy or the coupling is relatively slight. Only in the case of weak coupling with lattice relaxation energy very much smaller compared with the electronic transition energy, the transition probability varies sharply with the transition energy.

The strong variation of the nonradiative transition probability with the electronic transition energy in the case of rare-earth luminescent centres (coupling parameter S estimated to be of the order of 0·1!) underlies one of the most successful

$\bar{n}(T)$	S	p	10	15	20	25	30
2	1		$1{\cdot}86\times10^{-4}$ $4{\cdot}88\times10^{-5}$	$1{\cdot}07\times10^{-7}$ $4{\cdot}23\times10^{-10}$	$1{\cdot}28\times10^{-11}$ $2{\cdot}30\times10^{-17}$	$4{\cdot}63\times10^{-16}$ $7{\cdot}79\times10^{-27}$	$6{\cdot}37\times10^{-21}$ $1{\cdot}70\times10^{-28}$
	3		$1{\cdot}99\times10^{-2}$ $1{\cdot}98\times10^{-2}$	$1{\cdot}07\times10^{-3}$ $7{\cdot}99\times10^{-4}$	$1{\cdot}75\times10^{-5}$ $5{\cdot}96\times10^{-6}$	$1{\cdot}05\times10^{-7}$ $8{\cdot}19\times10^{-9}$	$2{\cdot}67\times10^{-10}$ $2{\cdot}08\times10^{-12}$
	5		$4{\cdot}78\times10^{-2}$ $4{\cdot}84\times10^{-2}$	$1{\cdot}08\times10^{-2}$ $1{\cdot}06\times10^{-2}$	$1{\cdot}03\times10^{-3}$ $8{\cdot}39\times10^{-4}$	$4{\cdot}43\times10^{-5}$ $2{\cdot}42\times10^{-5}$	$9{\cdot}31\times10^{-7}$ $2{\cdot}52\times10^{-7}$
	10		$5{\cdot}65\times10^{-2}$ $5{\cdot}68\times10^{-2}$	$4{\cdot}36\times10^{-2}$ $4{\cdot}41\times10^{-2}$	$2{\cdot}05\times10^{-2}$ $2{\cdot}06\times10^{-2}$	$6{\cdot}02\times10^{-3}$ $5{\cdot}81\times10^{-3}$	$1{\cdot}12\times10^{-3}$ $9{\cdot}85\times10^{-4}$
	15		$3{\cdot}92\times10^{-2}$ $3{\cdot}92\times10^{-2}$	$4{\cdot}61\times10^{-2}$ $4{\cdot}63\times10^{-2}$	$3{\cdot}88\times10^{-2}$ $3{\cdot}91\times10^{-2}$	$2{\cdot}34\times10^{-2}$ $2{\cdot}36\times10^{-2}$	$1{\cdot}02\times10^{-2}$ $1{\cdot}01\times10$
1·5	1		$6{\cdot}73\times10^{-5}$ $6{\cdot}49\times10^{-6}$	$1{\cdot}64\times10^{-8}$ $2{\cdot}72\times10^{-12}$	$8{\cdot}18\times10^{-13}$ $1{\cdot}92\times10^{-21}$	$1{\cdot}21\times10^{-17}$ $2{\cdot}28\times10^{-33}$	$6{\cdot}76\times10^{-33}$ $4{\cdot}58\times10^{-48}$
	3		$1{\cdot}59\times10^{-2}$ $1{\cdot}45\times10^{-2}$	$4{\cdot}60\times10^{-4}$ $2{\cdot}53\times10^{-4}$	$8{\cdot}01\times10^{-7}$ $5{\cdot}29\times10^{-7}$	$1{\cdot}06\times10^{-8}$ $1{\cdot}31\times10^{-10}$	$1{\cdot}21\times10^{-11}$ $3{\cdot}88\times10^{-15}$
	5		$4{\cdot}66\times10^{-2}$ $4{\cdot}76\times10^{-2}$	$7{\cdot}59\times10^{-3}$ $7{\cdot}0\times10^{-3}$	$4{\cdot}43\times10^{-4}$ $2{\cdot}88\times10^{-4}$	$3{\cdot}01\times10^{-5}$ $3{\cdot}30\times10^{-6}$	$2{\cdot}90\times10^{-7}$ $1{\cdot}05\times10^{-8}$
	10		$6{\cdot}33\times10^{-2}$ $6{\cdot}37\times10^{-2}$	$4{\cdot}55\times10^{-2}$ $4{\cdot}63\times10^{-2}$	$1{\cdot}79\times10^{-2}$ $1{\cdot}78\times10^{-2}$	$3{\cdot}94\times10^{-3}$ $3{\cdot}60\times10^{-3}$	$5{\cdot}04\times10^{-4}$ $3{\cdot}86\times10^{-4}$
	15		$4{\cdot}22\times10^{-2}$ $4{\cdot}21\times10^{-2}$	$5{\cdot}16\times10^{-2}$ $5{\cdot}21\times10^{-2}$	$4{\cdot}15\times10^{-2}$ $4{\cdot}21\times10^{-2}$	$2{\cdot}21\times10^{-2}$ $2{\cdot}22\times10^{-2}$	$7{\cdot}93\times10^{-3}$ $7{\cdot}66\times10^{-3}$
1	1		$1{\cdot}67\times10^{-5}$ $1{\cdot}88\times10^{-5}$	$1{\cdot}41\times10^{-9}$ $4{\cdot}17\times10^{-16}$	$2{\cdot}36\times10^{-14}$ $1{\cdot}60\times10^{-28}$	$1{\cdot}16\times10^{-19}$ $1{\cdot}05\times10^{-44}$	$2{\cdot}15\times10^{-25}$ $1{\cdot}20\times10^{-64}$
	3		$9{\cdot}59\times10^{-3}$ $8{\cdot}00\times10^{-3}$	$1{\cdot}32\times10^{-4}$ $3{\cdot}31\times10^{-5}$	$4{\cdot}29\times10^{-7}$ $7{\cdot}62\times10^{-9}$	$4{\cdot}48\times10^{-10}$ $9{\cdot}79\times10^{-14}$	$1{\cdot}83\times10^{-13}$ $6{\cdot}99\times10^{-20}$
	5		$4{\cdot}33\times10^{-2}$ $4{\cdot}41\times10^{-2}$	$4{\cdot}20\times10^{-3}$ $3{\cdot}38\times10^{-3}$	$1{\cdot}21\times10^{-4}$ $4{\cdot}31\times10^{-5}$	$1{\cdot}27\times10^{-6}$ $1{\cdot}00\times10^{-7}$	$5{\cdot}57\times10^{-9}$ $4{\cdot}11\times10^{-11}$
	10		$7{\cdot}31\times10^{-2}$ $7{\cdot}43\times10^{-2}$	$4{\cdot}70\times10^{-2}$ $4{\cdot}82\times10^{-2}$	$1{\cdot}37\times10^{-2}$ $1{\cdot}31\times10^{-3}$	$1{\cdot}95\times10^{-3}$ $1{\cdot}50\times10^{-3}$	$1{\cdot}42\times10^{-4}$ $7{\cdot}25\times10^{-5}$
	15		$4{\cdot}57\times10^{-2}$ $4{\cdot}54\times10^{-2}$	$5{\cdot}96\times10^{-2}$ $6{\cdot}06\times10^{-2}$	$4{\cdot}44\times10^{-2}$ $4{\cdot}54\times10^{-2}$	$1{\cdot}93\times10^{-2}$ $1{\cdot}91\times10^{-2}$	$5{\cdot}05\times10^{-3}$ $4{\cdot}50\times10^{-3}$

Accurate (upper figure) and approximate (lower figure) relative values of nonradiative transition probabilities for various values of $\bar{n}(T)$, the average vibrational quantum number; S, the electron–lattice coupling that provides lattice relaxation; and p, the electronic transition energy expressed as the number of phonons. Below the solid lines $\bar{n}(T)S \geqslant p$.

lines of research on multiphonon nonradiative transitions, notably by Weber (1967), and Moos (1970) and collaborators. The rare-earth luminescent centres are characterized by possessing a large number of electronic levels. The remarkable rule was discovered that the levels showing observable luminescence are those separated

by a wider energy gap from the next level below. This was correctly surmised to be a manifestation of the fact that with the other levels having a lesser energy gap below, nonradiative transitions to the level below will dominate and quench the luminescence. This sharply marked division of the levels is just the consequence of the strong variation of the nonradiative transition probability with the transition energy. Subsequent accurate measurements of the nonradiative transition probabilities led to the exponential gap law, which states that the nonradiative transition probabilities from different levels are proportional to the function $\exp(-\alpha\Delta E)$ of the energy gap ΔE from the next level beneath and has been adequately explained by the non radiative transition theory.

4. Resonance energy transfer—another form of multiphonon transitions

The transfer of excitation energy between different localized centres is an important subject for research in luminescence. Notably, it is the basic process underlying the phenomenon of sensitization, whereby the luminescent centres are excited indirectly through energy transfer from sensitizer centres, which can absorb energy effectively from the primary radiation. There are various mechanisms for such energy transfer. The direct transfer of excitation energy between non-overlapping centres owing to their Coulomb interaction is known as resonance energy transfer. As the excitation energies of the centres concerned do not generally match, the resonance energy transfer has to be accompanied by multiphonon emission or absorption to conserve energy. So it is a multiphonon process and nonradiative, but, as we shall presently see, it is quite distinct from the thermal transitions discussed in the previous section.

For a theoretical treatment of the process, the energy donor centre A and the energy acceptor B are to be considered as forming a single system. Thus if $\varphi_{Ag}(r_1)$, $\varphi_{Ae}(r_1)$, $\varphi_{Bg}(r_2)$, $\varphi_{Be}(r_2)$ represent respectively the ground(g) and excited(e) states of A and B, the energy transfer process is represented as a quantum transition from the initial state $\varphi_{Ae}(r_1)\,\varphi_{Bg}(r_2)$ of the system to the final state $\varphi_{Ag}(r_1)\varphi_{Be}(r_2)$, as illustrated in fig. 7.

Formally the transition is similar to the nonradiative transition process discussed in the previous sections; thus, it involves a change of electronic state from (Ae, Bg) to (Ag, Be) with its transition energy to be compensated by multiphonon emission or absorption. However, the nature of the transition is basically different; it is caused by the Coulomb interaction between the two centres. Thus the transition matrix element may be represented as

$$\int \chi_{jn'}(Q)\left[\int \varphi_{Ag}(r_1)\varphi_{Be}(r_2)\frac{e^2}{|r_1-r_2|}\varphi_{Ae}(r_1)\varphi_{Bg}(r_2)\mathrm{d}r_1\mathrm{d}r_2\right]\chi_{in}(Q)\,\mathrm{d}Q$$

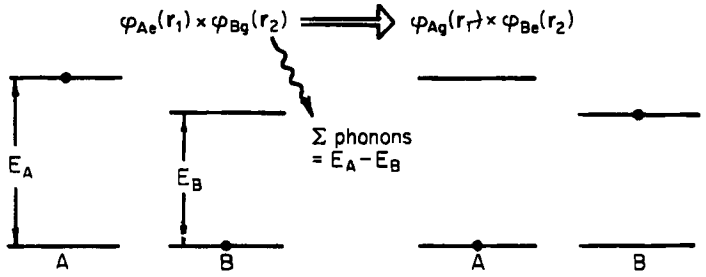

Fig. 7. Resonance energy transfer between two centres.

As in the case of the optical transitions, the electronic matrix element within the square brackets may be considered as approximately independent of the atomic coordinates Q. So calculation of the transition probability involves essentially only the overlap integrals between the initial and final vibrational wave functions, entirely similar to the case of optical transitions discussed earlier:

$$\text{transition probability} = \text{const} \times \sum_{n_s'} \prod_s |\chi_{n_s'}(Q_s - \Delta_{\mathrm{Bes}})\chi_{n_s}(Q_s - \Delta_{\mathrm{Aes}})\,\mathrm{d}Q_s|^2 \delta(E_{\mathrm{A}} - E_{\mathrm{B}} - \sum_s (n_s' - n_s)\hbar\omega_s)$$

In the above overlap integrals, Δ_{Aes} and Δ_{Bes} represent respectively the lattice relaxations with A or B in the excited state.

A comparison with the optical transition probability shows that the above transition probability varies with the energy discrepancy E_{A}–E_{B} in exactly the same way as the intensity of optical emission spectrum varies with the energy separation from the zero-phonon line position. As we noted before, lattice relaxation causes a shift of the spectral peak from the zero-phonon line equal to the lattice relaxation energy associated with the transition, so it follows here that the maximum probability for resonance energy transfer does not occur for exact coincidence of E_{A} and E_{B}, but corresponds to a level difference $E_{\mathrm{A}} - E_{\mathrm{B}}$ equal to the lattice relaxation energy accompanying the transition. This conclusion is just an instance which we cite to indicate the close relationship with multiphonon optical transitions. In fact it follows from a more general theorem which states that the probability of resonance energy transfer depends on the product of the emission spectrum of the energy donor and the absorption spectrum of the energy acceptor (Fonger and Struck 1978).

5. Relaxation effect relating to virtual states—multiphonon Raman scattering

In usual phonon Raman scattering in solids, the incident light is scattered inelastically with emission (Stokes component) or absorption (anti-Stokes component) of one (first-order scattering) or two (second-order scattering) phonons. As with optical emission or absorption processes, Raman scattering can also be directly related to localized centres. On first thought, one might think that Raman scattering from localized centres should not be affected by lattice relaxation in the way that optical emission and absorption are. For in Raman scattering, before and after the event, the electronic state remains unchanged, so it would seem that lattice relaxation does not come into the question. This is however not true.

In terms of the interaction of the scattering centre with the photon field, Raman scattering must be a second-order process, so as to achieve the elementary acts of annihilating the incident photon and creating the scattered photon. This is realized by the intervention of a virtual intermediate state. Thus typically the second-order process can occur first by a virtual transition of the electron to the intermediate state with the annihilation of the incident photon, then followed by the transition of the electron back to the initial state with the creation of the scattered photon. Now with an additional intermediate state taking part, lattice relaxation may conceivably play a role through the intermediate state, much as in the case of optical transitions. For instance, the second-order process will depend on the product of the matrix elements corresponding to the two virtual transitions and these matrix elements can lead to multiphonon emission or absorption during the scattering, owing to lattice relaxation. However, as the intermediate states are virtual states, whether they can

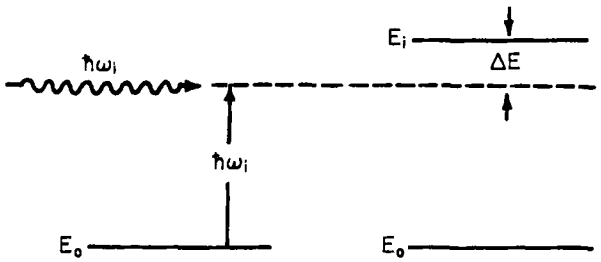

Fig. 8. Intermediate state energy relation.

show lattice relaxation effects requires special consideration. By virtual state is meant one that departs from the real energy of the system. As illustrated in fig. 8, the energy of the system is represented by the dashed horizontal line, which is equal to the energy E_0 of the initial state of the scattering centre plus the incident photon energy $\hbar\omega_i$, whereas the intermediate state energy E_i departs from it by a certain energy ΔE.

By virtue of the uncertainty principle, such a virtual state can exist only as a transitory state with a time duration of $\Delta t \approx \hbar/\Delta E$. Physically, $\Delta\tau$ must clearly be larger than the phonon vibration period for lattice relaxation to take effect. As one readily sees, this means that the energy departure of the virtual intermediate state must be smaller than the phonon energy in order to show lattice relaxation effects. From fig. 8, it is seen that a small ΔE means that the incident photon is close to resonance with the intermediate state. And in actual fact, multiphonon structures were discovered early in resonance Raman scattering research. However, as Raman scattering is a second-order process, the observed multiphonon structures and their theoretical interpretation are much more involved than in the case of emission or absorption spectra. Moreover, with scattering experiments in proper resonance, absorption can occur and other complicated processes also give rise to secondary radiations with structures related to the phonon frequencies. Therefore for the purpose of studying multiphonon structures associated with lattice relaxation effects, it should be most advantageous to investigate near-resonance scattering.

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