Theory of light absorption and non-radiative transitions in F-centres

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A quantitative theory for the shapes of the absorption bands of F-centres is given on the basis of the Franck-Condon principle. Underlying the treatment are two simplifying assumptions: namely, (*a*) that the lattice can be approximately treated as a dielectric continuum; (*b*) that in obtaining the vibrational wave functions for the lattice, the effect of the F-centre can be considered as that of a static charge distribution. Under these assumptions, it is shown that the absorption constant as a function of frequency and temperature can be expressed in terms of the Bessel functions with imaginary arguments. The theoretical curves for the absorption constant compare very favourably with the experimental curves for all temperatures.

Also considered in the paper are the probabilities of non-radiative transitions, which are important in connexion with the photo-conductivity observed following light absorption by F-centres. The treatment given differs from the qualitative considerations hitherto in one important aspect, namely, the strength of the coupling between the electron and the lattice is taken into account. The adiabatic wave functions for the F-centre electron required for the discussion are obtained by perturbation methods. The probability for an excited F-centre to return to its ground state by non-radiative transitions is shown to be negligible; similar transitions to the conduction band are, however, important if the excited state is separated from the conduction band by not much more than 0·1 eV. The temperature dependence of such transitions is complicated, but, for a wide range of temperatures, resembles $e^{-W/kT}$. Tentative estimates show that the result is consistent with the observed steep drop of the photo-conductive current with temperature.

1. Introduction

It has long been recognized that the considerable widths of the characteristic absorption curves of F-centres (Pohl 1937) are caused by the coupling of the electronic motion in the F-centre to the ionic lattice. Owing to the coupling, while an F-centre electron is making a transition, a number of lattice vibration quanta can be created or annihilated. Thus for the same electronic transition a certain latitude in the absorption frequency results, corresponding to a greater or lesser number of vibrational quanta being annihilated or created during the absorption act.

Although the basic mechanism underlying the absorption is clear, no quantitative theory of the absorption curves has hitherto been given. The usual interpretation of the optical properties of F-centres is based upon a schematic application of the Franck-Condon principle, whereby a single parameter is used to specify schematically the lattice configuration (von Hipple 1936; Seitz 1939; Mott & Gurney 1948). Apart from the natural limitations of the procedure, the principle is often indifferently interpreted so that important features could well be missed (no account, for instance, is usually taken of the detailed nature of the vibrational wave functions, which are, however, well known to be important for an understanding of the intensity distributions of the absorption spectra of molecules (cf. Finkelnburg 1938)). In a recent paper Muto (1949) has attempted to give a quantitative treatment of the problem.

He has, however, proceeded no further than giving the general expressions for the transition probabilities. His results remain so formal that no actual comparison with experiments can be made. The only concrete conclusion he has drawn from the theory, namely, that the maximum of absorption corresponds to no change in the vibrational quanta, is in fact, as we shall see, incorrect.

General references in this connexion have not infrequently been made to the works of Frenkel (1936) and Peierls (1932), which are mainly concerned with a different problem, namely, the absorption by pure crystals. An important difference, however, exists between an impurity centre such as an F-centre and an exciton which is responsible for absorption in pure crystals. Owing to the high mobility of the latter and its internal motion shared by both the positive hole and the electron, an exciton cannot polarize the lattice to an appreciable extent. An impurity centre, on the other hand, is practically immobile; purely as a static charge distribution, it can polarize strongly the lattice in its neighbourhood. It is our belief that such a polarizing effect of the F-centre is mainly responsible for the observed course of absorption.

In this paper we shall give a quantitative theory of the absorption constant on the basis of the Franck-Condon principle, the effect of the F-centres on the lattice being considered as that of static charge distributions. It is found that if the lattice is treated approximately as a dielectric continuum, the result contains but few constants that cannot be reliably calculated on purely theoretical ground. Once the values of these constants are assigned, the absorption constant can be calculated for all temperatures and frequencies. The theoretical absorption curves are found to be in good agreement with the experimental curves (Pohl 1937).

The light absorption by F-centres is known experimentally to be associated with photoconductivity (Pohl 1937). But below a certain temperature in the liquid-air region, the photo-current is observed to drop very steeply with temperature. The problem has been discussed by Mott and Gurney (Gurney & Mott 1938; Mott 1938), who suggest that an F-centre electron raised to the excited state by light absorption can be thrown into the conduction band by lattice vibrations before it has the opportunity to return to the ground state. These authors have tentatively assumed that such non-radiative transitions vary with temperature as $\exp(-W/kT)$. By an extension of the above theory, the transition probabilities can be calculated. It will be seen that for a wide range of temperatures the probabilities follow closely the exponential form. The results in general are in agreement with the experiments on photoconductivity.

2. General expression for the absorption constant

Consider generally an absorption centre in vacuum, upon which falls a nearly homogeneous beam of radiation of unit cross-section, with $\rho(\nu)$ practically uniform in the frequency range $\nu \to \nu + \Delta\nu$ and vanishing at other frequencies ($\rho(\nu)$ denotes as usual the energy density per unit frequency range). The rate of energy absorption is then given by

$$\frac{8\pi^3}{3h}\nu\rho(\nu)\sum_{f}^{\nu<\nu_{fi}<\nu+\Delta\nu}|<i|\mathbf{M}|f>|^2, \tag{2·1}$$

where $<i\,|\,\mathbf{M}\,|f>$ is the matrix element of the electric moment between the initial state i and a final state f of the absorption centre; as indicated, the summation is over such final states that the transition frequency ν_{fi} lies within the relevant range. However, if the absorption is imbedded in a refractive medium, $\rho(\nu)$ should be identified with $(\mathbf{E}^2/4\pi)$ rather than the energy density. In a medium with refractive index n, the intensity of radiation is given by

$$I = \frac{nc\mathbf{E}^2}{4\pi}.$$

(2·1) can thus be written as

$$\frac{8\pi^3\nu I}{3hnc}\left\{\frac{1}{\Delta\nu}\sum_{f}^{\nu<\nu_{fi}<\nu+\Delta\nu}|<i\,|\,\mathbf{M}\,|f>|^2\right\}. \tag{2·2}$$

Let us consider a single F-centre in the lattice. A state of the whole system is specified by two quantum numbers: μ for the electronic states of the F-centre and n for the vibrational states of the lattice. The energy of a state will thus be written as $E_{\mu n}$. Following the usual approximation in the quantum-mechanical application of the Franck-Condon principle (Condon & Morse 1929), we write

$$<i\,|\,\mathbf{M}\,|f>\rightarrow<\mu'\,|\,e\mathbf{x}\,|\,\mu''>\int \mathrm{X}^*_{\mu'n'}(X)\,\mathrm{X}_{\mu''n''}(X)\,dX, \tag{2·3}$$

where $<\mu'\,|\,e\mathbf{x}\,|\,\mu''>$ is the matrix element of the electric moment of the F-centre electron between the two electronic states μ', μ'' of the F-centre which are assumed responsible for the observed absorption. X in the formula stands symbolically for the nuclear co-ordinates specifying the lattice configurations, and $\mathrm{X}_{\mu'n'}$, $\mathrm{X}_{\mu''n''}$ are the vibrational wave functions of the lattice, when the F-centre is respectively in its initial and final states. If there are a number of F-centres present, their energy absorptions can clearly be considered additively. Let C be the number of centres per unit volume and x the direction of the incident beam. On combining (2·3) and (2·2), one obtains the rate of absorption in a layer of thickness dx in the following form:

$$-dI = \frac{8\pi^3 C}{3hnc}|<\mu'\,|\,e\mathbf{x}\,|\,\mu''>|^2\,\nu F(\nu)\,I dx, \tag{2·4}$$

where $F(\nu)$ is the function of frequency defined by

$$F(\nu) = \frac{1}{\Delta\nu}\sum_{n''}^{(\nu-\nu+\Delta\nu)}\left|\int \mathrm{X}^*_{\mu'n'}(X)\,\mathrm{X}_{\mu''n''}(X)\,dX\right|^2. \tag{2·5}$$

n'' is summed over final vibrational states with frequencies $h^{-1}(E_{\mu''n''}-E_{\mu'n'})$ within a range $\Delta\nu$ about ν. The absorption constant is thus given by

$$k(\nu) = \frac{8\pi^3 C}{3hnc}|<\mu'\,|\,e\mathbf{x}\,|\,\mu''>|^2\,\nu F(\nu). \tag{2·6}$$

The absorption curves depend essentially on $F(\nu)$, which, we notice, depend in turn on the overlap integrals between vibrational wave functions of the lattice for two different states of the F-centre.

3. Continuum approximation for the lattice and the vibrational wave functions

We shall assume that the effect of the F-centre on the lattice is due purely to the Coulomb field $\mathscr{E}_{\mu'}$(or $\mathscr{E}_{\mu''}$) of the average charge distribution in the F-centre; the suffix to the field indicates the state of the F-centre. To avoid introducing many unknown parameters into the theory, we shall consider the lattice essentially as a dielectric continuum. The behaviour of such a continuum lattice is completely described by a pair of equations given by Huang (1950). In the continuum approximation, apart from purely elastic deformations which are irrelevant here, the lattice configuration is specified by giving over all positions $\mathbf{r}$ in the lattice the displacement vector $\mathbf{u}(\mathbf{r})$ of the positive ions relative to the negative ions. Using Huang's equations and following the method exemplified in his paper, it is not difficult to show that the total energy of the lattice (potential energy counted from the configuration $\mathbf{u}(\mathbf{r}) \equiv 0$) in the presence of an external electric field $\mathscr{E}_{\mu'}(\mathbf{r})$ is given by

$$\frac{\bar{M}}{2}\int\{\dot{\mathbf{u}}_l^2+\omega_l^2\mathbf{u}_l^2+\dot{\mathbf{u}}_t^2+\omega_0^2\mathbf{u}_t^2\}\frac{dv}{v_a}-\omega_l\left[\frac{\bar{M}}{4\pi v_a}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\right]^{\frac{1}{2}}\int\mathbf{u}_l.\mathscr{E}_{\mu'}dv, \tag{3·1}$$

where $\mathbf{u}_l(\mathbf{r})$ and $\mathbf{u}_t(\mathbf{r})$ are respectively the irrotational and solenoidal parts of $\mathbf{u}(\mathbf{r})$, and

$$\left.\begin{aligned}
&\epsilon_0 = \text{static dielectric constant},\\
&\epsilon_\infty = \text{high frequency dielectric constant},\\
&\omega_0 = \text{infra-red dispersion frequency (circular)},\\
&\bar{M} = \text{reduced mass of the ions in the cell } M_+M_-/(M_++M_-),\\
&v_a = \text{volume of unit cell},\\
&\omega_l = (\epsilon_0/\epsilon_\infty)^{\frac{1}{2}}\omega_0.
\end{aligned}\right\} \tag{3·2}$$

We observe that $\mathbf{u}_t(\mathbf{r})$ is not coupled to the F-centre field; this part of $\mathbf{u}(\mathbf{r})$ gives rise to independent modes of vibrations (transverse waves) irrelevant for our discussion, and will henceforth be ignored.

The energy expression (3·1) can be normalized to a finite volume by imposing the Born-Kármán boundary conditions on a region containing $L\times L\times L = N$ cells and restricting the volume integrations in (3·1) to the same. Thus it is convenient to write

$$\sqrt{N}\,\mathbf{u}_l(\mathbf{r}) = \left(\frac{1}{\bar{M}}\right)^{\frac{1}{2}}\sum_{\mathbf{y}} Q(\mathbf{y})\,(\mathbf{y}/|\,\mathbf{y}\,|)\exp\left[2\pi i\mathbf{y}.\mathbf{r}\right], \tag{3·3}$$

where we have resolved $\mathbf{u}_l(r)$ into longitudinal waves; this is possible because of the irrotational character of $\mathbf{u}_l(\mathbf{r})$. The condition of reality permits us to write

$$Q(\mathbf{y}) = \frac{1}{\sqrt{2}}(q_{\mathbf{y}1}+iq_{\mathbf{y}2}) = -Q^*(-\mathbf{y}). \tag{3·4}$$

The Born-Kármán conditions can be expressed by restricting the values of $\mathbf{y}$ as follows:

$$\mathbf{y} = L^{-1}(h^1\mathbf{b}_1+h^2\mathbf{b}_2+h^3\mathbf{b}_3) \quad |\,h^i\,| = \text{integers} < \tfrac{1}{2}L, \tag{3·5}$$

where $\mathbf{b}^1, \mathbf{b}^2, \mathbf{b}^3$ are the reciprocal basic vectors of the lattice (only in a genuine continuum does $|\,h^i\,| > \frac{1}{2}L$ lead to further distinct modes of displacements). On

substituting (3·3) in (3·1), ignoring $\mathbf{u}_l(\mathbf{r})$, and carrying out the volume integration over the region of N cells, one obtains

$$H = \tfrac{1}{2}\sum_{\lambda=1,2}\sum_{\mathbf{y}}(\dot{q}^2_{\mathbf{y}\lambda}+\omega_l^2 q^2_{\mathbf{y}\lambda}) - \frac{1}{\sqrt{N}}\sum_{\mathbf{y}\lambda} A'_{\mathbf{y}\lambda} q_{\mathbf{y}\lambda}, \tag{3·6}$$

where

$$\left.\begin{aligned} A'_{\mathbf{y}1} &= \omega_l\left[\frac{1}{2\pi v_a}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\right]^{\frac{1}{2}}\int(\mathbf{y}/|\,\mathbf{y}\,|).\mathscr{E}_{\mu'}(\mathbf{r})\cos 2\pi\mathbf{y}.\mathbf{r}\,dv,\\ A'_{\mathbf{y}2} &= -\omega_l\left[\frac{1}{2\pi v_a}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\right]^{\frac{1}{2}}\int(\mathbf{y}/|\,\mathbf{y}\,|).\mathscr{E}_{\mu'}(\mathbf{r})\sin 2\pi\mathbf{y}.\mathbf{r}\,dv. \end{aligned}\right\} \tag{3·7}$$

Owing to the combination of terms arising from $Q(\mathbf{y})$ and $Q(-\mathbf{y})$, the summation over $\mathbf{y}$ now extends over the values of $\mathbf{y}$ lying on one side of an arbitrary plane through the origin of the $\mathbf{y}$-space; in this way only one of a pair $\mathbf{y}$, $-\mathbf{y}$ is counted. For simplicity, we introduce a single index j for $\mathbf{y}\lambda$; (3·6), for instance, becomes

$$H = \tfrac{1}{2}\sum_j(\dot{q}_j^2+\omega_l^2 q_j^2) - \frac{1}{\sqrt{N}}\sum_j A'_j q_j. \tag{3·8}$$

In the absence of the F-centre, the linear term in (3·8) drops out. The Hamiltonian describes then a system of independent oscillators, all having the same frequency ω_l (circular). q_j are thus the normal co-ordinates of the perfect lattice; the corresponding modes have the form of longitudinal waves.

We notice that the linear terms in (3·8) represent the coupling between the F-centre and the lattice and are proportional to $1/\sqrt{N}$. It is thus mathematically important to have normalized the lattice to a finite volume. In the result, we can, of course, let $N\to\infty$, as we are not concerned with surface effects.

When the F-centre is present and in the state μ', the following modified normal co-ordinates can be introduced:

$$q'_j = q_j - \frac{1}{\sqrt{N}}\frac{A'_j}{\omega_l^2}. \tag{3·9}$$

For on substituting (3·9) in (3·8), one finds

$$H = \tfrac{1}{2}\sum_j(\dot{q}'^2_j+\omega_l^2 q'^2_j) - \frac{1}{2N}\Sigma\frac{A'^2_j}{\omega_l^2}. \tag{3·10}$$

The Hamiltonian is again that of a system of simple oscillators, apart from the last term, which represents the equilibrium potential energy between the F-centre and the lattice. It is usual to include the latter as part of the electronic energy of the state μ' of the F-centre. Thus the first part alone in (3·10) will be considered as the lattice vibration energy.

$\dot{q}'_j$ is classically the canonical conjugate momentum of q'_j; thus on going over to quantum mechanics, the vibrational Hamiltonian of the lattice becomes

$$H_{\text{vib.}} = \tfrac{1}{2}\sum_j\left(-\hbar^2\frac{\partial^2}{\partial q'^2_j}+\omega_l^2 q'^2_j\right). \tag{3·11}$$

The corresponding wave functions are the products of the oscillator wave functions

$$\prod_j \mathrm{X}_{n'_j}(q'_j), \tag{3·12}$$

where n'_j is the quantum number for the oscillator j; the corresponding vibrational energy is the sum

$$\hbar\omega_l\sum_j(n'_j+\tfrac{1}{2}). \tag{3·13}$$

4. Calculation of $F(\nu)$

Consider the overlap integrals required for constructing the function $F(\nu)$:

$$\int X^*_{\mu' n'} X_{\mu'' n''} dX = \prod_j \int X_{n'_j}(q'_j) X_{n''_j}(q''_j) dq_j, \tag{4·1}$$

where the vibrational wave functions (3·12) have been substituted and q'_j, q''_j refer respectively to the modified normal co-ordinates of the lattice when the F-centre is in state μ' and state μ''.

Remembering that

$$q'_j = q_j - \frac{1}{\sqrt{N}} \frac{A'_j}{\omega_l^2}, \quad q''_j = q_j - \frac{1}{\sqrt{N}} \frac{A''_j}{\omega_l^2},$$

we expand the oscillator wave functions in (4·1) about q_j, thus

$$\begin{aligned} &\int X_{n'_j}(q'_j) X_{n''_j}(q''_j) dq_j \\ &\quad = \int \left\{ \left[X_{n'_j}(q_j) - \frac{1}{\sqrt{N}} \frac{A'_j}{\omega_l^2} X'_{n'_j}(q_j) + \frac{1}{2} \left(\frac{1}{\sqrt{N}} \frac{A'_j}{\omega_l^2} \right)^2 X''_{n'_j}(q_j) + \dots \right] \right. \\ &\qquad \left. \times \left[X_{n''_j}(q_j) - \frac{1}{\sqrt{N}} \frac{A''_j}{\omega_l^2} X'_{n''_j}(q_j) + \frac{1}{2} \left(\frac{1}{\sqrt{N}} \frac{A''_j}{\omega_l^2} \right)^2 X''_{n''_j}(q_j) + \dots \right] \right\} dq_j. \end{aligned} \tag{4·2}$$

When the multiplication of the two series is carried out, one observes that the terms of order $(1/\sqrt{N})^s$ are associated with integrals of the form

$$\int X^{(t)}_{n'_j} X^{(s-t)}_{n''_j} dq_j$$

(superscripts indicate the order of derivative), all of which can, by integration by parts, be expressed in terms of

$$\int X_{n'_j} X^{(s)}_{n''_j} dq_j.$$

This integral vanishes, whenever the difference between n'_j and n''_j is numerically greater than s. Thus if $|\, n'_j - n''_j \,| = s$, the leading term of the integral (4·2) is of the order $(1/\sqrt{N})^s$. As we shall later see, it follows from this fact that all transitions in which any of the vibrational quantum numbers changes by more than one can be ignored.

For the case $\Delta n_j = n''_j - n'_j = \pm 1$, one finds on multiplying out the series in (4·2) that

$$\begin{aligned} &\int X_{n'_j}(q'_j) X_{n'_j \pm 1}(q''_j) dq_j \\ &\quad = -\frac{1}{\sqrt{N}\,\omega_l^2} \left[A'_j \int X'_{n'_j}(q_j) X_{n' \pm 1}(q_j) dq_j + A''_j \int X_{n'_j}(q_j) X'_{n' \pm 1}(q_j) dq_j \right] + O\frac{1}{N}, \quad \text{etc.} \\ &\quad = \frac{A''_j - A'_j}{\sqrt{N}} \left(\frac{\hbar}{2\omega_l^3} \right)^{\frac{1}{2}} \begin{cases} \sqrt{(n'_j + 1)} \\ -\sqrt{n'_j} \end{cases} + O\frac{1}{N}, \quad \text{etc.} \end{aligned} \tag{4·3}$$

The leading term is the only one that we shall require.

Let $E_{\mu'' \mu'}$ be the difference of electronic energies between the states μ'' and μ'. The transition frequency for a particular transition $\mu' n' \to \mu'' n''$ is given by (cf. (3·13))

$$h\nu = E_{\mu'' \mu'} + \hbar \omega_l \sum_j \Delta n_j, \quad \text{where} \quad \Delta n_j = n''_j - n'_j. \tag{4·4}$$

In our simplified model, thus ν depends only on the change in the total number of vibrational quanta, and, moreover, ν does not cover a continuum when n'' goes through all possible final vibrational states, but only takes on the discrete values

$$\nu = \frac{E_{\mu''\mu'}}{h^*} + p\left(\frac{\omega_l}{2\pi}\right), \tag{4·5}$$

where p is an integer, equal to $\sum_j \Delta n_j$. The function $F(\nu)$ as defined in (2·6) can obviously be rewritten in this case as

$$F(\nu) = \frac{2\pi}{\omega_l}\left\{\sum_{n''}\left|\int \mathrm{X}^*_{\mu'n'}\,\mathrm{X}_{\mu''n''}\,dX\right|^2\right\}_{\sum_j \Delta n_j = p} \tag{4·6}$$

As indicated, the summation over n'' is restricted by the condition $\sum_j \Delta n_j = p$, where p and the absorption frequency ν are related by (4·5).

Consider first transitions in which no $|\Delta n_j|$ is greater than one. Transitions of this type that contribute to (4·6) are made up of s oscillators going down by one quantum and $s+p$ oscillators going up by one quantum. Let us consider a particular transition of this type, where the oscillators going up and down are respectively $l', l'', \ldots, l^{(s+p)}$ and $k', k'', \ldots, k^{(s)}$. The square of the overlap integral (4·1) for this transition can be written as

$$\begin{aligned}\left|\int \mathrm{X}^*_{\mu'n'}\,\mathrm{X}_{\mu''n''}\,dX\right|^2 &= \left\{\prod_j \left|\int \mathrm{X}_{n'_j}(q'_j)\,\mathrm{X}_{n'_j}(q''_j)\,dq_j\right|^2\right\} \\ &\times \left\{\prod_l \frac{\left|\int \mathrm{X}_{n'_l}(q'_l)\,\mathrm{X}_{n'_l+1}(q''_l)\,dq_l\right|^2}{\left|\int \mathrm{X}_{n'_l}(q'_l)\,\mathrm{X}_{n'_l}(q''_l)\,dq_l\right|^2}\right\}\left\{\prod_k \frac{\left|\int \mathrm{X}_{n'_k}(q'_k)\,\mathrm{X}_{n'_k-1}(q''_k)\,dq_k\right|^2}{\left|\int \mathrm{X}_{n'_k}(q'_k)\,\mathrm{X}_{n'_k}(q''_k)\,dq_k\right|^2}\right\},\end{aligned} \tag{4·7}$$

where the products range respectively over all the oscillators, and the oscillators $l', l'', \ldots$ and $k', k'', \ldots$. For given p and s, there are a large number of distinct transitions, corresponding to different choices of the oscillators $l', l'', \ldots$ and $k', k'' \ldots$. Their total contribution can be obtained by summing (4·7) over all the indices $l', l'', \ldots$ and $k', k'', \ldots$ and dividing afterwards by $s!(s+p)!$; the latter division takes account of the repetition of each distinct transition implied in the straightforward summation. The summation obtained in this way formally also includes terms corresponding to some of the indices $l', l'', \ldots, k', k'', \ldots$ being equal, which is meaningless. But it will become evident that these terms can make no finite difference to the result. Thus we find that the total contribution to $F(\nu)$ by transitions in which $s+p$ oscillators go up by one quantum and s oscillators go down by one quantum can be written as

$$\begin{aligned}&\frac{2\pi}{\omega_l}\frac{1}{s!(s+p)!}\left\{\prod_j \left|\int \mathrm{X}_{n'_j}(q'_j)\,\mathrm{X}_{n'_j}(q''_j)\,dq_j\right|^2\right\} \\ &\times \left\{\sum_l \frac{\left|\int \mathrm{X}_{n'_l}(q'_l)\,\mathrm{X}_{n'_l+1}(q''_l)\,dq_l\right|^2}{\left|\int \mathrm{X}_{n'_l}(q'_l)\,\mathrm{X}_{n'_l}(q''_l)\,dq_l\right|^2}\right\}^{s+p}\left\{\sum_k \frac{\left|\int \mathrm{X}_{n'_k}(q'_k)\,\mathrm{X}_{n'_k-1}(q''_k)\,dq_k\right|^2}{\left|\int \mathrm{X}_{n'_k}(q'_k)\,\mathrm{X}_{n'_k}(q''_k)\,dq_k\right|^2}\right\}^{s}\end{aligned} \tag{4·8}$$

The summations over l and k are both extended over all the lattice oscillators; if we return to the indices $\mathbf{y}$, λ for the lattice oscillators the summations can be replaced by the integrations

$$\sum_{\mathbf{y}\lambda} \to \sum_{\lambda} \int dh^1 dh^2 dh^3 = N v_a \sum_{\lambda} \int d\mathbf{y}. \tag{4·9}$$

The leading term of the corresponding integrand

$$\frac{\left| \int \mathrm{X}_{n_l'}(q_l') \, \mathrm{X}_{n_l'\pm 1}(q_l'') \, dq_l \right|^2}{\left| \int \mathrm{X}_{n_l'}(q_l') \, \mathrm{X}_{n_l}(q_l'') \, dq_l \right|^2},$$

is, according to (4·2), (4·3), given by

$$\frac{(A_l'' - A_l')^2}{N} \left(\frac{\hbar}{2\omega_l^3} \right) \begin{Bmatrix} n_l' + 1 \\ n_l' \end{Bmatrix}. \tag{4·10}$$

N in the denominator cancels the factor outside the $\mathbf{y}$-integral (4·9) and leads thus to a finite contribution; besides the leading term the rest of the expansion contributes only by terms of order $(1/\sqrt{N})$ or higher, and may thus be ignored. Therefore (4·8) can be written as

$$\frac{2\pi}{\omega_l} \frac{1}{s\,!(s+p)\,!} \prod_j \left| \int \mathrm{X}_{n_j'}(q_j') \, \mathrm{X}_{n_j'}(q_j'') \, dq_j \right|^2 S_+^{s+p} S_-^s, \tag{4·11}$$

where $S_\pm$ are the following integrals:

$$S_\pm = \frac{\hbar v_a}{2\omega_l^3} \sum_{\lambda} \int (A_{\mathbf{y}\lambda}'' - A_{\mathbf{y}\lambda}')^2 \begin{Bmatrix} n_{\mathbf{y}\lambda}' + 1 \\ n_{\mathbf{y}\lambda}' \end{Bmatrix} d\mathbf{y}. \tag{4·12}$$

As regards transitions involving certain oscillators changing by more than one quantum, let us consider, for instance, transitions in which certain s' oscillators go up by two quanta. Corresponding to (4·8), we would obtain an expression in which appears the factor

$$\left\{ N \sum_{\lambda} \int d\mathbf{y} \, \frac{|\, \mathrm{X}_{n_{\mathbf{y}\lambda}'}(q_{\mathbf{y}\lambda}') \, \mathrm{X}_{n_{\mathbf{y}\lambda}'+2}(q_{\mathbf{y}\lambda}'') \, dq_{\mathbf{y}\lambda} \,|^2}{|\, \mathrm{X}_{n_{\mathbf{y}\lambda}'}(q_{\mathbf{y}\lambda}') \, \mathrm{X}_{n_{\mathbf{y}\lambda}'}(q_{\mathbf{y}\lambda}'') \, dq_{\mathbf{y}\lambda} \,|^2} \right\}.$$

It follows from our earlier explanations that the integrand of the $\mathbf{y}$-integration will be of the order $(1/N)^2$; thus the integral will be of order $(1/N)$. Results of even higher orders will be obtained, if one considers some oscillators changing by more than two quanta. Hence no finite contributions arise from such transitions.

All relevant contributions to $F(\nu)$ are thus included, if we sum (4·11) over various values of s:

$$F(\nu) = \frac{2\pi}{\omega_l} \prod_j \left| \int \mathrm{X}_{n_j'}(q_j') \, \mathrm{X}_{n_j'}(q_j'') \, dq_j \right|^2 \sum_{s=0}^{\infty} \frac{S_+^{s+p} S_-^s}{s\,!(s+p)\,!}. \tag{4·13}$$

where, we remember, ν and p are related by (4·5). The sum can be expressed in terms of the Bessel function with imaginary argument of order p (Whittaker & Watson 1946), for

$$\sum_{s=0}^{\infty} \frac{S_+^{s+p} S_-^s}{s\,!(s+p)\,!} = \left(\frac{S_+}{S_-} \right)^{\frac{1}{2}p} \sum_{s=0}^{\infty} \frac{(S_+ S_-)^{s+\frac{1}{2}p}}{s\,!(s+p)\,!} = \left(\frac{S_+}{S_-} \right)^{\frac{1}{2}p} I_p(2\sqrt{(S_+ S_-)}). \tag{4·14}$$

Hence (4·13) may be written alternatively as

$$F(\nu) = \frac{2\pi}{\omega_l}\left\{\prod_j \left|\int \mathrm{X}_{n_j'}(q_j')\,\mathrm{X}_{n_j'}(q_j'')\,dq_j\right|^2\right\}\left(\frac{S_+}{S_-}\right)^{\frac{1}{2}p} I_p(2\sqrt{(S_+S_-)}). \tag{4·15}$$

We have tacitly assumed that $p \geqslant 0$, i.e. the number of oscillators going up equals or exceeds the number going down. For $p < 0$, i.e. the number of oscillators going down exceeds the number going up by $|p| = -p$, the previous arguments apply, if we interchange the roles of the two sets of oscillators; the net effect on the result is equivalent to interchanging S_+ and S_-. Thus for $p < 0$, we would obtain

$$F(\nu) = \frac{2\pi}{\omega_l}\left\{\prod_j \left|\int \mathrm{X}_{n_j'}(q_j')\,\mathrm{X}_{n_j'}(q_j'')\,dq_j\right|^2\right\}\left(\frac{S_-}{S_+}\right)^{-\frac{1}{2}p} I_{-p}(2\sqrt{(S_+S_-)})$$

However as $I_{-p} = I_p$ (Whittaker & Watson 1946), this formula is identical with (4·15) which holds thus equally for positive and negative values of p.

The value of the product

$$\prod_j \left|\int \mathrm{X}_{n_j'}(q_j')\,\mathrm{X}_{n_j'}(q_j'')\,dq_j\right|^2 \tag{4·16}$$

remains to be evaluated. With the help of (4·2), one can express

$$\int \mathrm{X}_{n_j'}(q_j')\,\mathrm{X}_{n_j'}(q_j'')\,dq_j$$

in a series in $(1/N)$:

$$1 - \frac{1}{2N}(A_j'' - A_j')^2\left(\frac{\hbar}{2\omega_l^3}\right)(2n_j'+1) + O\frac{1}{N^2}, \quad \text{etc.}$$

On squaring the series, one finds

$$\left|\int \mathrm{X}_{n_j'}(q_j')\,\mathrm{X}_{n_j'}(q_j'')\,dq_j\right|^2 = 1 - \frac{1}{N}(A_j'' - A_j')^2\left(\frac{\hbar}{2\omega_l^3}\right)(2n_j'+1) + O\frac{1}{N^2}, \quad \text{etc.} \tag{4·17}$$

When the factors in (4·16) are expanded in this way, it is readily seen on multiplying out the factors that terms of order $(1/N)^2$ or higher in the factors can be ignored without making any finite difference to the result. Thus retaining in each factor only the two terms, which are explicitly given in (4·17), one finds that the considerations required for working out the product in (4·16) reduce to essentially the same as that used earlier in this section. It is easily verified that the result is

$$\prod_j \left|\int \mathrm{X}_{n_j'}(q_j')\,\mathrm{X}_{n_j'}(q_j'')\,dq_j\right|^2 = \sum_{t=0}^{\infty} \frac{(-S_+ - S_-)^t}{t!} = \exp[-(S_+ + S_-)]. \tag{4·18}$$

When (4·18) is substituted, (4·15) becomes

$$F(\nu) = \frac{2\pi}{\omega_l}\left(\frac{S_+}{S_-}\right)^{\frac{1}{2}p} \exp[-(S_+ + S_-)]\, I_p(2\sqrt{(S_+S_-)}). \tag{4·19}$$

When we average the initial state over the thermal distribution, the quantities S_+, S_- defined in (4·12) become

$$S_\pm = S\begin{matrix}\overline{n}(T)+1 \\ \overline{n}(T)\end{matrix}, \tag{4·20}$$

where S is the constant integral

$$S = \frac{\hbar v_a}{2\omega_l^3} \sum_{\lambda} \int (A''_{\mathbf{y}\lambda} - A'_{\mathbf{y}\lambda})^2 d\mathbf{y}, \tag{4·21}$$

and $\bar{n}(T)$ is the thermal average of the vibrational quantum number which is the same for all oscillators in our case:

$$\bar{n}(T) = \{\exp[\hbar\omega_l/kT] - 1\}^{-1}. \tag{4·22}$$

When the expression (4·19) for $F(\nu)$ is substituted in (2·6) and $S_{\pm}$ are expressed in terms of S and $\bar{n}(T)$ by (4·20), we obtain eventually the following expression for the absorption constant as a function of frequency and temperature:

$$k(\nu) = A\nu \exp[-S(2\bar{n}+1)] \left(\frac{\bar{n}+1}{\bar{n}}\right)^{\frac{1}{2}p} I_p(2S\sqrt{[\bar{n}(\bar{n}+1)]}). \tag{4·23}$$

$$A = \frac{16\pi^4 C}{3\hbar n c \omega_l} |<\mu' | e\mathbf{x} | \mu''>|^2.$$

5. Comparison with experimental results

We can disregard for a moment the absolute frequency scale, if we divide the absorption constant k by ν:

$$k/\nu = A \exp[-S(2\bar{n}+1)] \left(\frac{\bar{n}+1}{\bar{n}}\right)^{\frac{1}{2}p} I_p(2S\sqrt{[\bar{n}(\bar{n}+1)]}), \tag{5·1}$$

and plot k/ν against $p\hbar\omega_l$. For the large arguments of I_p, with which we shall be concerned ($S \sim 20$), no tabulated values or satisfactory asymptotic formulae for the function are available for the whole desired range for p. The values of the function have thus to be obtained by laborious computations; and we have confined our comparisons to the often-quoted absorption curves for KBr due to Pohl (1937).

As Pohl's curves are plotted on an arbitrary scale, for the comparison the constant A in (5·1) serves merely as an arbitrary scale factor. It is found that with the value of S suitably chosen ($S = 22{\cdot}4$) the theoretical curves for k/ν can be fitted on to Pohl's curves (reduced by ν) with excellent agreement for all temperatures. The arbitrary scale constant A is of course kept at the same value for the theoretical curves corresponding to different temperatures.

I_p, as a function of its order (for fixed argument), has a maximum at $p = 0$. The maximum is shifted towards positive values of p, after the multiplication by $[(\bar{n}(T)+1)/\bar{n}(T)]^{\frac{1}{2}p}$. When the value of $\bar{n}(T)$ is raised by temperature, the latter factor approaches nearer to unity; however, owing to the raised value of the argument $2S[\bar{n}(\bar{n}+1)]^{\frac{1}{2}}$, I_p itself has a flatter maximum, and one finds in fact that the maximum of the curve $k/\nu \sim p\hbar\omega_l$ occurs practically at the same value of $p(\simeq 22)$ for all the temperatures considered. Since the maxima of Pohl's curves shift with temperature, it becomes evident that no choice of the difference $E_{\mu''\mu'}$ of electronic energies (cf. (4·5)) will bring agreement between the absolute positions of the theoretical and experimental curves on the frequency scale. Owing to the otherwise satisfactory agreement between the two sets of curves, one expects that the dis

crepancy must be due to circumstances not affecting the substance of the above theory.

The maxima of k and k/ν as function of ν do not greatly differ; thus it follows from our result that the maximum of absorption corresponds to the net creation of about 20 vibrational quanta for all temperatures. This, as we have mentioned, directly contradicts Muto's conclusion that the maximum of absorption corresponds to no change in the vibrational quanta; the nature of his argument is not clear to us, however, it appears that it must amount to ignoring the difference between $\overline{n}+1$

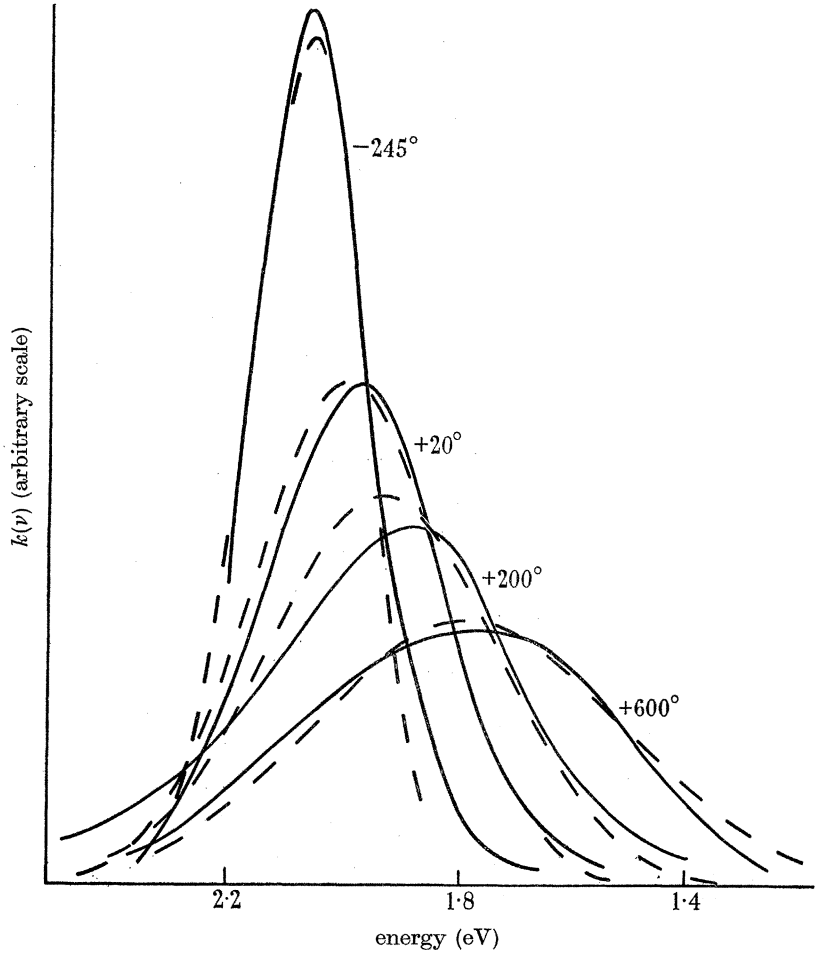

FIGURE 1. Theoretical and experimental absorption curves for F-centres in KBr. — experimental, – – – – theoretical. $S=22{\cdot}4$; $\omega_l=3{\cdot}0\times10^{13}$/sec.; $E_{\mu'\mu'}=1{\cdot}67$ eV; $B=-0{\cdot}1$ eV.

and $\overline{n}$, or the difference between the probabilities of an oscillator going up and down. Owing to his conclusion, however, he also finds it necessary to explain the shift of the absorption maximum with temperature; we believe that the explanation given by him correctly accounts for most of the discrepancy in the absolute positions in the absorption curves. We can put the idea as follows: when an F-centre changes its state, the lattice frequency is on the average altered by an amount of the order $1/N$,

although this does not appear in the harmonic forces approximation, which we have effectively used as regards the lattice. The total energy change associated with a transition is thus given by

$$\begin{aligned} h\nu &= E_{\mu''\mu'} + \Delta \sum_j (n_j + \tfrac{1}{2}) \hbar\omega_l \\ &= E_{\mu''\mu'} + \hbar\omega_l \sum_j \Delta n_j + \sum_j (n_j + \tfrac{1}{2}) B/N \\ &= E_{\mu''\mu'} + p\hbar\omega_l + B(\bar{n} + \tfrac{1}{2}). \end{aligned} \tag{5·2}$$

If this idea is correct, (5·2) should take the place of (4·5) as the relation between p and the absorption frequency ν.

With suitable choice of the constants $E_{\mu''\mu'}$ and B, we have plotted the theoretical curves for k on the absolute frequency scale in figure 1, in the same figure are also given the experimental curves of Pohl. The values used for the constants are given under the figure; ω_l has been calculated from the experimental values of $\epsilon_0, \epsilon_\infty, \omega_0$ (cf. Szigeti 1949). The agreement between the two sets of curves is seen to be satisfactory.

S is by far the most important constant in the theory. Once the wave functions of the F-centre electron in the ground and excited states are known, the electric fields $\mathscr{E}_{\mu'}, \mathscr{E}_{\mu''}$ can be calculated and hence also the value of S (cf. (3·7), (4·21)). We have made calculations of S, using wave functions given by Simpson (1949) for the NaCl lattice. Simpson considered two models for a positive impurity centre, namely, a vacant negative-ion site and a positive interstitial ion; the wave functions of the trapped electron are relatively more extended in the latter than the former. From the wave functions for the vacant negative-ion site, the value calculated for S is 3·6, which is small compared with the value 22·4 (for KBr !). Simpson, however, explained that the $2p$ wave function in this case is expected to be much too compact, therefore we repeated the calculation, using the $2p$ function for the interstitial ion model, with the result $S = 16$.

It is interesting to remark that theoretically an upper limit exists for the value of S. This corresponds to the case when the ground-state wave function is so localized that the field of the positive centre is completely screened off and the excited state wave function is so diffuse that the lattice is completely exposed to the field of the centre. The value of this upper limit is found to be $S = 55$.

6. Probability for non-radiative transitions

For the discussion of the non-radiative transitions, a closer description of the wave function for the complete system: F-centre + lattice is necessary. The natural characterization of the states does not correspond to true stationary states, but follows from the Born-Oppenheimer approximation, according to which the wave functions can be written in the following form:

$$\Psi_{\alpha,n}(\mathbf{x}, X, t) = \exp[-i\omega_{\alpha n} t]\, \psi_\alpha(\mathbf{x}, X)\, \mathrm{X}_{\alpha n}(X), \tag{6·1}$$

where $\mathbf{x}$, X stand respectively for the co-ordinates of the F-centre electron and the lattice particles, and α, n are the respective quantum numbers for the electronic motion in the F-centre and the lattice vibrations.

The Hamiltonian for the whole system can be written as

$$H(\mathbf{x}X) = K(\mathbf{x}) + V(\mathbf{x}) + K(X) + V(X) + V(\mathbf{x}X), \tag{6·2}$$

where $K(\mathbf{x})$ = kinetic energy of the F-centre electron,

$V(\mathbf{x})$ = interaction between the electron and the impurity centre,

$K(X)$ = kinetic energy of the lattice particles,

$V(X)$ = potential energy of the lattice,

$V(\mathbf{x}, X)$ = interaction between the F-centre and the lattice.

The Born-Oppenheimer wave functions satisfy the following equations:

$$\{K(\mathbf{x}) + V(\mathbf{x}) + V(\mathbf{x}X) - E_\alpha(X)\}\psi_\alpha(\mathbf{x}X) = 0, \tag{6·3}$$

$$\{K(X) + V(X) + E_\alpha(X) - E_{\alpha n}\}\,\mathrm{X}_{\alpha n}(X) = 0. \tag{6·4}$$

(6·3) is the wave equation of the electron with the nuclei held in the configuration X. The corresponding eigenvalue $E_\alpha(X)$ is a function of X and acts as an effective potential for the lattice motion in equation (6·4).

As the states are not strictly stationary, transitions can occur between states of equal energy. As pointed out long ago by Kronig (1928), in cases such as this, when there is no perturbation term, the transition probabilities can still be obtained by perturbation methods. In fact, so long as the approximate wave functions are strictly orthogonal, one can apply Dirac's perturbation method in the usual way and show that the total transition probability from an initial state i to final states of approximately the same energy is given by

$$\frac{2\pi}{\hbar^2}\frac{1}{\Delta\nu}\sum_f^{0<\nu_{fi}<\Delta\nu} |<f|\,H - E_i\,|\,i>|^2, \tag{6·5}$$

where the summation over f is restricted by the frequency condition $0 < \nu_{fi} < \Delta\nu$ and E_i is the eigenvalue of state i.

In the present case, the matrix element in (6·5) can be expressed in a form suitable for calculation as follows: Multiplying (6·3) and (6·4) respectively by $\mathrm{X}_{\alpha n}(X)$ and $\psi_\alpha(\mathbf{x}X)$ and adding the equations, one obtains

$$(H - E_{\alpha n})\,\psi_\alpha(\mathbf{x}X)\,\mathrm{X}_{\alpha n}(X) = K(X)\,\psi_\alpha(\mathbf{x}X)\,\mathrm{X}_{\alpha n}(X) - \psi_\alpha(\mathbf{x}X)\,K(X)\,\mathrm{X}_{\alpha n}(X). \tag{6·6}$$

Writing $K(X)$ in terms of the normal co-ordinates q_j,

$$K(X) = -\tfrac{1}{2}\hbar^2 \sum_j \frac{\partial^2}{\partial q_j^2},$$

and ignoring the second derivatives of $\psi_\alpha(\mathbf{x}X)$ with respect to q_j, one obtains from (6·6) the following expression for the required matrix element:

$$<\beta n'\,|\,H - E_{\alpha n}\,|\,\alpha n> = -\hbar^2 \sum_j \int \mathrm{X}^*_{\beta n'}(X)\frac{\partial}{\partial q_j}\mathrm{X}_{\alpha n}(X)\,dX\left[\int \psi^*_\beta(\mathbf{x}X)\frac{\partial}{\partial q_j}\psi_\alpha(\mathbf{x}X)\,d\mathbf{x}\right]. \tag{6·7}$$

Following the same approximation as that already used in applying the Franck-Condon principle (Condon & Morse 1929), we shall take the electronic integral outside the integration over the lattice co-ordinates. If, for simplicity, we write

$$\frac{1}{\sqrt{N}} P_j(\beta\alpha) = \left\{ \int \psi^*_\beta(\mathbf{x}X) \frac{\partial}{\partial q_j} \psi_\alpha(\mathbf{x}X)\, d\mathbf{x} \right\}, \tag{6·8}$$

the transition probability (6·5) from the state α to the state β of the F-centre becomes

$$\frac{h^2}{2\pi\Delta\nu} \sum_{n'}^{(0\to\Delta\nu)} \left| \sum_j \frac{1}{\sqrt{N}} P_j(\beta\alpha) \int \mathrm{X}^*_{\beta n'}(X)\, \mathrm{X}_{\alpha n}(X)\, dX \right|^2, \tag{6·9}$$

where the summation over the final vibrational states is restricted by the transition frequency which must lie within the range $0 \to \Delta\nu$.

When the vibrational wave functions (3·12) are substituted in (6·9), we can once more consider all the transitions in which the number of oscillators going up exceeds the number going down by p and replace $\Delta\nu$ in (6·9) by $\omega_l/2\pi$; here as the transition frequency is in the neighbourhood of zero, so we are only concerned with the value of p given by

$$p\hbar\omega_l + E_{\beta\alpha} = 0. \tag{6·10}$$

The essential considerations required to work out (6·9) are the same as in §4; they are more involved, because the matrix element in (6·9) is a sum of overlap integrals rather than a single term as in §4. To save space, we shall not reproduce the arguments but write down the result directly:

$$\frac{h^2}{\omega_l} \{ \tfrac{1}{2} Z^2 (\overline{n} R_{p+1} + (\overline{n}+1) R_{p-1}) + |Y|^2 [(\overline{n}+\tfrac{1}{2})^2 + \tfrac{1}{2}\overline{n}(\overline{n}+1)] R_p$$
$$- |Y|^2 (\overline{n}+\tfrac{1}{2}) [\overline{n} R_{p+1} + (\overline{n}+1) R_{p-1}] + \tfrac{1}{4} |Y|^2 [\overline{n}^2 R_{p+2} + (\overline{n}+1)^2 R_{p-2}] \}, \tag{6·11}$$

where

$$R_p = \exp[-(2\overline{n}+1) S] \left(\frac{\overline{n}+1}{\overline{n}} \right)^{\frac{1}{2}p} I_p(2S\sqrt{[\overline{n}(\overline{n}+1)]}), \tag{6·12}$$

$$Z^2 = \left(\frac{v_a \omega_l}{\hbar} \right) \sum_\lambda \int |P_{\mathbf{y}\lambda}(\beta\alpha)|^2 d\mathbf{y}, \tag{6·13}$$

$$Y = \frac{v_a}{\hbar\omega_l} \sum_\lambda \int P_{\mathbf{y}\lambda}(\beta\alpha) (A^\beta_{\mathbf{y}\lambda} - A^\alpha_{\mathbf{y}\lambda})\, d\mathbf{y} \tag{6·14}$$

7. Discussion of the non-radiative transition probabilities

We shall ignore the small differences in the indices of R in (6·11). Thus we have

$$\frac{h^2}{\omega_l} (\overline{n}+\tfrac{1}{2}) Z^2 R_p, \tag{7·1}$$

which we shall use as the basis for discussion in this section.

The value of Z^2 depends on the quantities $P_{\mathbf{y}\lambda}(\beta\alpha)$ defined in (6·8) which can be obtained readily with the help of the usual perturbation theory. To the normal modes are associated the electric field (Huang 1950):

$$\mathscr{E}(\mathbf{r}) = \omega_l \left[\frac{8\pi}{v_a} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \right]^{\frac{1}{2}} \frac{1}{\sqrt{N}} \left\{ -\sum_{\mathbf{y}} q_{\mathbf{y}1}(\mathbf{y}/|\mathbf{y}|) \cos 2\pi\mathbf{y}.\mathbf{r} + \sum_{\mathbf{y}} q_{\mathbf{y}2}(\mathbf{y}/|\mathbf{y}|) \sin 2\pi\mathbf{y}.\mathbf{r} \right\}. \tag{7·2}$$

Taking this as a perturbing field on the F-centre electron and assuming it to be roughly uniform over the F-centre, one can immediately write down the first-order perturbed wave function for the F-centre electron in state α. It follows readily from the definition of $P_{\mathbf{y}\lambda}(\beta\alpha)$ that the coefficient of the β-component of the perturbed wave function of the α-state should be identical with

$$\frac{1}{\sqrt{N}}\sum_{\mathbf{y}\lambda} P_{\mathbf{y}\lambda} q_{\mathbf{y}\lambda}.$$

In this way one obtains

$$|P_{\mathbf{y}1}|^2+|P_{\mathbf{y}2}|^2=\omega_l^2\left[\frac{8\pi}{v_a}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\right]\frac{|<\beta|e\mathbf{x}.\mathbf{y}|\alpha>|^2}{|\mathbf{y}|^2 E_{\beta\alpha}^2}. \tag{7·3}$$

Z^2 defined in (6·13) is thus given approximately by

$$Z^2=\frac{8\pi\omega_l^3}{3\hbar v_a}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\frac{|<\beta|e\mathbf{x}|\alpha>|^2}{E_{\beta\alpha}^2}. \tag{7·4}$$

Substituting (7·4) in (7·1), we obtain the following expression for the probability for an F-centre making a non-radiative transition from the state α to β:

$$\frac{16\pi^2\hbar\omega_l^2}{3v_a}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\frac{|<\beta|e\mathbf{x}|\alpha>|^2}{E_{\beta\alpha}^2}(\bar{n}+\tfrac{1}{2})R_p. \tag{7·5}$$

It is our purpose to compare the non-radiative with the radiative transitions. The total radiative transition probability from an initial state i to final states f is given generally by

$$\frac{4}{3\hbar c^3}\sum_f |<i|e\mathbf{x}|f>|^2\omega_{fi}^3. \tag{7·6}$$

Following the same approximation as before, we can thus write the probability for an F-centre electron to return from the excited state μ'' to the ground state μ' as

$$\frac{4}{3\hbar c^3}|<\mu'|e\mathbf{x}|\mu''>|^2\sum_{n''}\left|\int \mathrm{X}^*_{\mu'n'}(X)\,\mathrm{X}_{\mu''n''}(X)\,dX\right|^2\omega^3_{\mu''n'',\mu'n'}. \tag{7·7}$$

When the vibrational wave functions (3·12) are substituted, the terms in the latter factor reduce to the overlap integrals already considered in § 4. Since for all transitions in which the net number of vibrational quanta created is p, the radiation frequency $\omega_{\mu''n'',\mu'n'}$ has the same value:

$$\omega(p)=\omega_{\mu''n'',\mu'n'}=\frac{E_{\mu''\mu'}}{\hbar}-p\omega_l. \tag{7·8}$$

It follows immediately from the results obtained in § 4 that the probability (7·7) can be written as

$$\frac{4}{3\hbar c^3}|<\mu'|e\mathbf{x}|\mu''>|^2\sum_p R_p\,\omega^3(p). \tag{7·9}$$

R_p, we remember, has a maximum at $p\simeq 22$, (7·9) can thus be written approximately as

$$\frac{4}{3\hbar^4 c^3}|<\mu'|e\mathbf{x}|\mu''>|^2[E_{\mu''\mu'}-22\hbar\omega_l]^3\sum_p R_p.$$

Using the series for I_p, it is easy to show that

$$\sum_{p=-\infty}^{\infty} R_p \equiv 1.$$

Hence the probability of radiative transitions is given approximately by

$$\frac{4}{3\hbar^4 c^3} |<\mu'|e\mathbf{x}|\mu''>|^2 [E_{\mu''\mu'} - 22\hbar\omega_l]^3. \tag{7·10}$$

An F-centre electron, raised to the excited state by light absorption, can either return to the ground state by (i) radiative transitions or (ii) non-radiative transitions, or (iii) be thrown into the conduction band by lattice vibrations. Mott (1938) has considered it possible that (ii) might jointly with (i) compete with the process (iii), which alone leads to photo-current. Thus let us consider first the relative probabilities of (i) and (ii). Putting in (7·5)

$$\beta = \mu', \quad \alpha = \mu'' \quad \text{and} \quad p = E_{\mu''\mu'}/(\hbar\omega_l) \quad \text{(cf. (6·10))}$$

and dividing the result by (7·10), we obtain the ratio of the probabilities for (ii) and (i):

$$\frac{(2\pi)^3 \hbar^5 \omega_l^2 c^3}{v_a} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right) \frac{(\bar{n} + \tfrac{1}{2}) R_p}{E_{\mu''\mu'}^2 (E_{\mu''\mu'} - 22\hbar\omega_l)^3}. \tag{7·11}$$

On putting in the numerical values (for KBr, $E_{\mu''\mu'}$ as given in figure 1), one finds

$$4 \times 10^5 (\bar{n} + \tfrac{1}{2}) R_{87}. \tag{7·12}$$

From the following values of this ratio:

T	$-245°$ C	$20°$ C	$200°$ C	$600°$ C
ratio (ii)/(i)	4×10^{-19}	2×10^{-9}	2×10^{-6}	0·8

it is seen that in the temperature range of interest, an excited F-centre returns to the ground state mainly by radiative transitions.

Consider next the relative magnitudes of (iii) and (ii). Let us represent a wave function of the electron in the conduction band approximately by

$$\exp(2\pi i \mathbf{k}.\mathbf{r}). \tag{7·13}$$

The corresponding state has the energy $(h^2\mathbf{k}^2/2m)$ and will be specified by the index $\mathbf{k}$. Since an electron in state μ'' can be thrown into any state in the conduction band by absorbing the appropriate number of vibrational quanta, in order to obtain the probability for (iii), we have to put $\alpha = \mu''$, $\beta = \mathbf{k}$ in (7·5) and sum the expression over all states $\mathbf{k}$. Supposing that the excited state μ'' is W below the bottom of the conduction band, we have

$$E_{\mathbf{k}\mu''} = W + \frac{\hbar^2\mathbf{k}^2}{2m}. \tag{7·14}$$

It follows thus that the probability for (iii) is

$$\frac{16\pi^2\hbar\omega_l^2}{3v_a} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right) (\bar{n} + \tfrac{1}{2}) \sum_{\mathbf{k}} \frac{|<\mathbf{k}|e\mathbf{x}|\mu''>|^2}{(W + \hbar^2\mathbf{k}^2/2m)^2} R_p, \tag{7·15}$$

where p is related to k by (cf. (6·10))

$$p = -E_{\mathbf{k}\mu''}/(\hbar\omega_l). \tag{7·16}$$

If the **k**-state wave function used in evaluating the matrix element is normalized as in (7·13), the summation over **k** becomes simply an integration over **k**-space (i.e. with unit weight function), so that (7·15) becomes

$$\frac{16\pi^2\hbar\omega_l^2}{3v_a}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)(\bar{n}+\tfrac{1}{2})\int\frac{|<\mathbf{k}\,|\,e\mathbf{x}\,|\,\mu''>|^2}{(W+\hbar^2\mathbf{k}^2/2m)^2}R_p\,d\mathbf{k}. \tag{7·17}$$

The matrix element of the electric moment does not depend appreciably on **k**, so long as the corresponding wave-length $1/|\,\mathbf{k}\,|$ is large compared with the μ''-orbit; in fact, the other factor in the **k**-integral falls off with k so rapidly, only such values of **k** are relevant. Hence we write the probability as

$$\frac{16\pi^2\hbar\omega_l^2}{3v_a}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)|<0\,|\,e\mathbf{x}\,|\,\mu''>|^2(\bar{n}+\tfrac{1}{2})\int\frac{R_p}{(W+\hbar^2\mathbf{k}^2/2m)^2}\,d\mathbf{k}, \tag{7·18}$$

or

$$\frac{8\pi}{3\hbar^4 v_a}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)|<0\,|\,e\mathbf{x}\,|\,\mu''>|^2(2m\hbar\omega_l)^{\frac{3}{2}}(\bar{n}+\tfrac{1}{2})\int_{-\infty}^{-p_0}\frac{(-p-p_0)^{\frac{3}{2}}}{p^2}\,dp, \tag{7·19}$$

where we have changed the integration variable from **k** to p with the help of (7·16) and p_0 is given by

$$p_0 = W/(\hbar\omega_l).$$

Dividing (7·19) by (7·10), we obtain the ratio of (iii) to (ii):

$$\frac{2\pi c^3}{v_a}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\frac{\left|\int\psi_{\mu''}\mathbf{x}\,d\mathbf{x}\right|^2}{\left|\int\psi^*_{\mu''}\mathbf{x}\psi_{\mu'}\,d\mathbf{x}\right|^2}\frac{(2m\hbar\omega_l)^{\frac{3}{2}}(\bar{n}+\tfrac{1}{2})}{[E_{\mu''\mu'}-22\hbar\omega_l]^3}\int_{-\infty}^{-p_0}R_p\frac{(-p-p_0)^{\frac{3}{2}}}{p^2}\,dp. \tag{7·20}$$

Assuming with Simpson (1949) the following radial functions respectively for the states μ' and μ'':

$$\left(\frac{4\alpha_{\mu''}^5}{3}\right)^{\frac{1}{2}}r\mathrm{e}^{-\alpha_{\mu''}r},\quad(4\alpha_{\mu'}^3)^{\frac{1}{2}}\mathrm{e}^{-\alpha_{\mu'}r}, \tag{7·21}$$

one finds

$$\frac{2\pi c^3}{v_a}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\frac{(\alpha_{\mu'}+\alpha_{\mu''})^{10}}{4\alpha_{\mu'}^3\alpha_{\mu''}^{10}}\frac{(2m\hbar\omega_l)^{\frac{3}{2}}(\bar{n}+\tfrac{1}{2})}{[E_{\mu''\mu'}-22\hbar\omega_l]^3}\int_{-\infty}^{-p_0}R_p\frac{(-p-p_0)^{\frac{3}{2}}}{p^2}\,dp. \tag{7·22}$$

When the values (Simpson 1949)

$$\alpha_{\mu''}\simeq\tfrac{1}{2}\alpha_{\mu'}=0{\cdot}66\text{ atomic units},$$

for $\alpha_{\mu''}, \alpha_{\mu'}$ as well as the numerical values for the other constants are put in, (7·22) becomes

$$1{\cdot}7\times10^9(\bar{n}+\tfrac{1}{2})\int_{-\infty}^{-p_0}R_p\frac{(-p-p_0)^{\frac{1}{2}}}{p^2}\,dp. \tag{7·23}$$

In order to estimate this ratio, the coupling constant S for the transition from μ'' to the ionized state has to be known. We have tentatively used the value for the $\mu'\rightarrow\mu''$ transition, namely, 22·4. The logarithm of the ratio calculated is plotted against $1/T$ for $W = 0{\cdot}1$, 0·2 and 0·4 eV in figure 2. Apart from the highest temperatures, the curves are practically straight. The curve for $W = 0{\cdot}1$ eV cuts the axis at $\sim 130°$ K (or $\sim -140°$ C). At this temperature, the probabilities of (i) and (ii) are

comparable; but at $\sim 100°$ K the non-radiative transitions have fallen by a factor ~ 1000. Thus the situation represented by this curve resembles quite closely the observed course of photo-current in NaCl and KCl (Pohl 1937). It is however to be borne in mind that the value for S used in calculating (iii) is only very tentative.

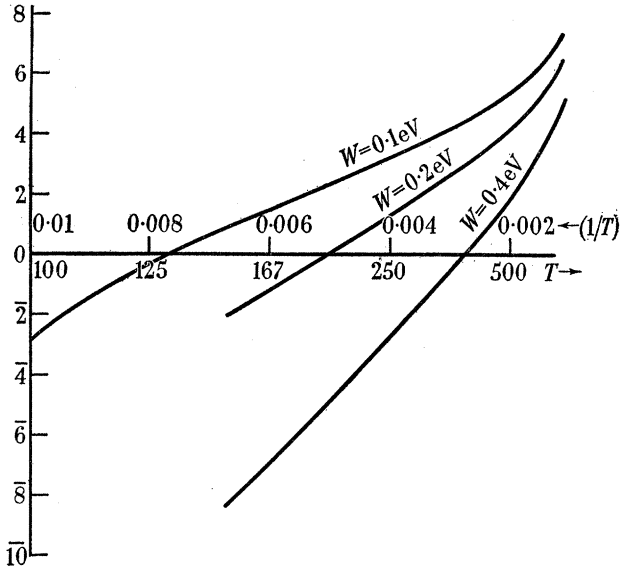

FIGURE 2. Logarithm of the ratio of the non-radiative to radiative transitions as function of $1/T$ (excited level of F-centre W below bottom of conduction band).

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