

Thermal Ionization of Impurities in Polar Crystals. I. Formal Theory

H. D. VASILEFF

Physics Laboratories, Sylvania Electric Products, Bayside, New York

(Received June 28, 1954)

The method of O'Rourke is used to obtain an expression for the thermal ionization rate of an impurity in a polar crystal. The interaction energy of the trapped electron with the optical vibrational modes is assumed to be linear in the normal vibrational coordinates of the lattice. The eigenvalue equations and perturbation of the Born-Oppenheimer adiabatic potential method are employed, leading to a result identical to that of Huang and Rhys. Multiphonon transitions occur only when the configurational constant $S \neq 0$. An approximation of simple form, for the transition rate, can be made only for low temperatures, where the frequency factor s is independent of temperature.

I. INTRODUCTION

IN luminescent materials, the rate of thermal ionization of an impurity center containing a trapped electron is one of the fundamental reaction processes. Afterglow phenomena can in some cases be ascribed to the ejection of an electron from a trap into the empty conduction band, whence the electron returns to an empty luminescent center with the emission of a light quantum. The decay of the afterglow is determined by the rate of ionization P of the traps and a monomolecular decay of emitted light intensity is described by an equation of the form $I = I_0 \exp(-Pt)$. Generally the rate P is assumed to have the form $P = s \exp(-E/kT)$, where s is the frequency factor, of the same order as the vibrational frequency of the lattice, and E is the activation energy corresponding to the depth of the trap below the bottom of the conduction band. It is recognized that calculations of E are quite insensitive to choice of values of s , so that from crystal to crystal one finds values of s ranging from 10^7 to 10^{16} sec^{-1} . Since there appears to be no way of predicting s from known characteristics of the crystal and impurity center, a better understanding of the nature of s is required.

In the analysis of thermostimulated emission, the same expression for P , with s constant, is used. Randall and Wilkins¹ have shown how to calculate trap depths from the temperatures at which glow peaks occur. It is difficult to conclude whether a single glow peak is due to one trap species with discrete values of s and E or whether it is caused by a distribution of traps in depth or s value. Hoogenstraaten² is of the opinion that the latter is more likely.

Recently Ellickson³ has discussed the effect of the variation of energy gap with temperature, on the rate of thermal ionization of traps in phosphors. His assumption that the trap depth varies to the same extent with temperature ($E = E_0 - \beta T$) is not justified, but he has called attention to the fact that the frequency factor is temperature dependent. The analysis of a first-order glow curve depends upon the functional dependence of

s on the temperature T . Williams and Eyring,⁴ in their discussion of metastable levels, obtain from absolute rate theory, $s = AT$. It can be shown by modifying the analysis of Grossweiner,⁵ that the Williams' form of s alters very little the estimated trap depths, provided they are not too shallow.

Several theoretical investigations⁶⁻¹⁰ have shown that the rate of thermal ionization of impurities in crystals involves a frequency factor which depends on temperature as well as upon trap depth, so that P has the form

$$P = s(E, T) \exp(-E/kT). \quad (1)$$

Except for the work of Huang and Rhys, these calculations do not apply to traps in polar crystals. However, it will be shown that in this case Eq. (1) gives the general form of P and that $s(E, T)$ decreases with decrease in temperature.

In addition to determining the correct form of $s(E, T)$ it is of interest to examine the problem of multiphonon transitions, which according to Kubo⁹ have a high probability of occurring. He ascribes this to the difference of the lattice vibrational frequencies in different electronic states. In the present calculation it will be seen that a multiphonon transition is due fundamentally to a different mechanism, namely, the displacement of the lattice normal coordinates after excitation.

Within the approximation employed the final expression for P reduces identically to that of Huang and Rhys¹⁰ who have omitted all details of its derivation. However, in their theory of light absorption by F centers, they have utilized two constants, S and c , which we shall henceforth term the configurational constant and displacement constant respectively. Lax¹¹ has utilized these constants in his complete treatment of light absorption by the use of ordered operators and O'Rourke¹² has dealt with the same problem by the use

⁴ F. Williams and H. Eyring, *J. Chem. Phys.* **15**, 289, (1947).

⁵ L. I. Grossweiner, *J. Appl. Phys.* **24**, 1306 (1953).

⁶ F. Mglic and R. W. Rompe, *Z. Physik* **115**, 707 (1940).

⁷ Goodman, Lawson, and Schiff, *Phys. Rev.* **71**, 191 (1947).

⁸ D. Curie, *J. phys. et radium* **12**, 920 (1951).

⁹ R. Kubo, *Phys. Rev.* **86**, 929 (1952).

¹⁰ K. Huang and A. Rhys, *Proc. Roy. Soc. (London)* **A204**, 406 (1950).

¹¹ M. Lax, *J. Chem. Phys.* **20**, 1752 (1952).

¹² R. C. O'Rourke, *Phys. Rev.* **91**, 265 (1953).

¹ J. T. Randall and M. H. Wilkins, *Proc. Roy. Soc. (London)* **A184**, 366 (1945).

² W. Hoogenstraaten, *J. Electrochem. Soc.* **100**, 356 (1953).

³ R. T. Ellickson, *J. Opt. Soc. Am.* **43**, 196 (1953).

of the density matrix for a harmonic oscillator. It is the latter method, whose effectiveness and simplicity is to be emphasized, that is to be applied to the Huang-Rhys model. In addition, use is made of the "Condon" approximation which becomes exact when the second derivative of the electronic wave function with respect to any normal coordinate vanishes.

II. BASIC EQUATIONS

Following Kubo, we treat the crystal plus impurity center, as a polyatomic molecule, whose Hamiltonian H is given by

$$H = H_R + H_r + V(\mathbf{r}, \mathbf{R}), \quad (2)$$

where H_R is the vibratory energy of the crystal nuclei, H_r the energy of the trapped electron, and $V(\mathbf{r}, \mathbf{R})$ the interaction of the electron with the nuclei. On the basis of the Born-Oppenheimer¹³ adiabatic potential method, we seek solutions of the eigenvalue equations

$$[H_r + V(\mathbf{r}, \mathbf{R})]\phi_l(\mathbf{r}, \mathbf{R}) = E_l(\mathbf{R})\phi_l(\mathbf{r}, \mathbf{R}), \quad (3)$$

$$[H_R + E_l(\mathbf{R})]\zeta_{l,n}(\mathbf{R}) = E_{l,n}\zeta_{l,n}(\mathbf{R}), \quad (4)$$

where $E_l(\mathbf{R})$ is the adiabatic potential of the l th electronic state and n signifies a vibration state of the nuclei. The wave function of the system in the l th electronic state is thus

$$\Psi_{l,n}(\mathbf{r}, \mathbf{R}) = \phi_l(\mathbf{r}, \mathbf{R})\zeta_{l,n}(\mathbf{R}). \quad (5)$$

The perturbation on the system for a process such as thermal ionization, is determined from the approximate nature of the wave function (5) and is given by

$$H'\Psi_{l,n} = H_R\phi_l\zeta_{l,n} - \phi_l H_r \zeta_{l,n}. \quad (6)$$

Treating the lattice as a continuum and considering the vibratory motion of the nuclei as lattice waves, the Hamiltonian H_R becomes

$$H_R = \frac{1}{2} \sum_i^N (\dot{q}_i^2 + \omega^2 q_i^2), \quad (7)$$

where q_i is the normal lattice coordinate, ω the angular frequency of vibration, and N the total number of unit cells in the crystal. Since it is generally assumed that the electron interaction with the optical modes is predominant, ω is approximately constant for all modes of vibration in the optical branch. By substituting the corresponding operator in (6), there results

$$H'\Psi_{l,n} = -\hbar^2 \sum_i^N \left(\frac{\partial \phi_l(\mathbf{r}, \mathbf{R})}{\partial q_i} \cdot \frac{\partial \zeta_{l,n}}{\partial q_i} \right) - \frac{\hbar^2}{2} \sum_i^N \frac{\partial^2 \phi_l(\mathbf{r}, \mathbf{R})}{\partial q_i^2} \cdot \zeta_{l,n}(\mathbf{R}). \quad (8)$$

¹³ M. Born and F. Oppenheimer, Ann. Physik 84, 457 (1927).

From time-dependent perturbation theory, the transition probability from the state (l, n') to a final state (k, n'') in the conduction band is

$$\omega(l, n' \rightarrow k, n'') = (2\pi/\hbar) \int_{-\infty}^{+\infty} \rho(E_k) |\langle k, n'' | H' | l, n' \rangle|^2 \times \delta(E_{k,n''} - E_{l,n'}) dE_k, \quad (9)$$

where $\rho(E_k)$ is the state density of the electronic state in the conduction band, and the matrix element is defined as

$$\langle k, n'' | H' | l, n' \rangle = \int \Psi_{k,n''}^* H' \Psi_{l,n'} d\mathbf{r} d\mathbf{R}. \quad (10)$$

Thus the total transition probability P is found by averaging (9) over all the initial lattice states n' and summing over all the final n'' :

$$P = (2\pi/\hbar) \int_{-\infty}^{+\infty} \rho(E_k) \sum_{n'', n'} p_{n'} |\langle k, n'' | H' | l, n' \rangle|^2 \times \delta(E_{k,n''} - E_{l,n'}) dE_k, \quad (11)$$

where the weighting factor $p_{n'}$ is given by

$$p_{n'} = [\sum_{n'} \exp(-E_{l,n'}/kT)]^{-1} \exp(-E_{l,n'}/kT), \quad (12)$$

and the quantities $E_{l,n'}$ and $E_{k,n''}$ are the energies of the system in the initial and final states, respectively.

The thermal ionization rate is found by evaluating expression (11). To this end we shall follow the notation and procedure of O'Rourke. The initial and final state wave functions of the system are

$$\begin{aligned} \Psi_{l,n'} &= \phi_l(\mathbf{r}, \mathbf{R}) \cdot \zeta_{l,n'}(\mathbf{R}), \\ \Psi_{k,n''} &= \Omega^{-\frac{1}{2}} \exp(i\mathbf{k} \cdot \mathbf{r}) \cdot \zeta_{k,n''}(\mathbf{R}), \end{aligned} \quad (13)$$

with the vibrational wave function expressed as a product of N harmonic oscillator wave functions,

$$\zeta_{l,n'}(\mathbf{R}) = \prod_i^N X_{n_j'}(q_j') = \prod_i^N |l, n_j'\rangle, \quad (14)$$

$$\zeta_{k,n''}(\mathbf{R}) = \prod_i^N X_{n_j''}(q_j'') = \prod_i^N |k, n_j''\rangle.$$

The primes on the coordinates indicate that the normal coordinates for each electronic state are modified by the coupling constants A_j^l and A_j^k for the initial and final states as follows:

$$\begin{aligned} q_j' &= q_j - N^{-\frac{1}{2}} \omega'^2 A_j^l = q_j - c_j', \\ q_j'' &= q_j - N^{-\frac{1}{2}} \omega''^2 A_j^k = q_j - c_j''. \end{aligned} \quad (15)$$

It is assumed that the electronic wave function in the free state is a plane wave independent of the lattice coordinates, and is normalized by the introduction of

the crystal volume Ω . For the present the analytical form of the electronic function for the ground state remains unspecified.

The form of the wave function for a simple harmonic oscillator is given by

$$X_{n_j}(q_j) = \left(\frac{\omega}{\pi\hbar}\right)^{\frac{1}{2}} (2^{n_j} n_j!)^{-\frac{1}{2}} H_{n_j} \left[q_j \left(\frac{\omega}{\hbar}\right)^{\frac{1}{2}} \right] \times \exp \left\{ -\frac{1}{2} \left[q_j \left(\frac{\omega}{\hbar}\right)^{\frac{1}{2}} \right]^2 \right\}, \quad (16)$$

where the variable q_j and the angular frequency ω correspond to the appropriate electronic state. The connection between the initial state frequency ω' and the final state frequency ω'' is expressed by the phenomenological constant ρ such that $(\omega'' - \omega') = \rho\omega'$.

In addition, the system energy is required for each of the two electronic states under consideration; these become

$$E_{k, n''} = \frac{\hbar^2 k^2}{2m^*} - \frac{1}{2N} \sum_i \frac{(A_j^k)^2}{\omega'^2} + \sum_i (n_j'' + \frac{1}{2}) \hbar\omega'', \quad (17)$$

$$E_{l, n'} = -E_l - \frac{1}{2N} \sum_i \frac{(A_j^l)^2}{\omega'^2} + \sum_i (n_j' + \frac{1}{2}) \hbar\omega',$$

where $(\hbar^2 k^2 / 2m^*)$ and $-E_l$ are the electron energies in the conduction band (with m^* the effective electron mass) and in the trapped state, respectively, in the absence of electron interaction with the lattice vibrational modes.

Evaluation of Transition Probability

It is convenient to express Eq. (11) in a different manner, by the introduction of the integral representation for the Dirac delta function

$$\delta(\phi) = (1/2\pi\hbar) \int_{-\infty}^{+\infty} dt \exp(i\phi t/\hbar),$$

so that P becomes

$$P = (1/\hbar^2) \int_{-\infty}^{+\infty} \rho(E_k) P' dE_k, \quad (18)$$

with

$$P' = \int_{-\infty}^{+\infty} dt \exp(i t \omega_{k, l}) G_{k, l}(t), \quad (19)$$

$$G_{k, l}(t) = \sum_{n'', n'} p_{n''} |\langle k, n'' | H' | l, n' \rangle|^2 \times \exp[i t \sum_i (n_j'' + \frac{1}{2}) \omega'' - (n_j' + \frac{1}{2}) \omega'], \quad (20)$$

$$\hbar\omega_{k, l} = (\hbar^2 k^2 / 2m^*) + E_l^*,$$

$$E_l^* = E_l - \frac{1}{2N} \sum_i [(A_j^k)^2 / \omega'^2 - (A_j^l)^2 / \omega'^2].$$

Since the weight factor (12) may be written¹⁴ as the product of the Boltzmann factors for each oscillator we have

$$p_{n''} = \prod_i^N 2 \sinh(\beta'/2) \exp\{-(n_j' + \frac{1}{2})\beta'\},$$

with $\beta' = (\hbar\omega' / kT)$, then the function $G_{k, l}(t)$ becomes

$$G_{k, l}(t) = \sum_{n'', n'} 2 \sinh(\beta'/2) \exp[-(n_j' + \frac{1}{2})\lambda_j'] \times \exp[-(n_j'' + \frac{1}{2})\mu_j''] |\langle k, n'' | H' | l, n' \rangle|^2, \quad (21)$$

with $\lambda_j' = i\omega' t + \beta'$ and $\mu_j'' = -i\omega'' t$. From Eq. (8) we obtain for the matrix element of the perturbation due to the i th vibrational mode:

$$\begin{aligned} \langle k, n'' | H_i' | l, n' \rangle &= \int_{\mathbf{R}} \zeta_{k, n''}^*(\mathbf{R}'') \left[-\hbar^2 \int_{\mathbf{r}} \phi_k^*(\mathbf{r}, \mathbf{R}'') \cdot \frac{\partial \phi_l(\mathbf{r}, \mathbf{R}')}{\partial q_i} d\mathbf{r} \right] \frac{\partial \zeta_{l, n'}}{\partial q_i}(\mathbf{R}') d\mathbf{R}' \\ &+ \int_{\mathbf{R}} \zeta_{k, n''}^*(\mathbf{R}'') \left[-\frac{\hbar^2}{2} \int_{\mathbf{r}} \phi_k^*(\mathbf{r}, \mathbf{R}'') \cdot \frac{\partial^2 \phi_l(\mathbf{r}, \mathbf{R}')}{\partial q_i^2} d\mathbf{r} \right] \cdot \zeta_{l, n'}(\mathbf{R}') d\mathbf{R}'. \end{aligned} \quad (22)$$

Within our approximation $\phi_k^*(\mathbf{r}, \mathbf{R}'')$ is independent of the lattice coordinates, and we can apply the "Condon" approximation if the first derivative of the ground-state electronic wave function varies slowly with lattice coordinates \mathbf{R} . Under this condition the second term on the right-hand side may be ignored since $\partial^2 \phi_l(\mathbf{r}, \mathbf{R}') / \partial q_i^2$ is approximately zero, and Eq. (22) becomes

$$\langle k, n'' | H_i' | l, n' \rangle = M_i(k, l) \int \zeta_{k, n''}^*(\mathbf{R}'') \cdot \frac{\partial \zeta_{l, n'}}{\partial q_i}(\mathbf{R}') d\mathbf{R},$$

where

$$M_i(k, l) = -\hbar^2 \int_{\mathbf{r}} \phi_k^*(\mathbf{r}, \mathbf{R}'') \frac{\partial \phi_l(\mathbf{r}, \mathbf{R}')}{\partial q_i} d\mathbf{r}.$$

Substituting the vibrational wave functions (14), squaring the modulus and the summing over all vibrational modes, we obtain

$$\begin{aligned} |\langle k, n'' | H' | l, n' \rangle|^2 &= \sum_i^N |M_i(k, l)|^2 \left| \int_{-\infty}^{+\infty} X_{n_i''}(q_i'') \frac{\partial}{\partial q_i} X_{n_i'}(q_i') dq_i \right|^2 \\ &\times \prod_{i \neq i}^N \left| \int_{-\infty}^{+\infty} X_{n_j''}(q_j'') X_{n_j'}(q_j') dq_j \right|^2 \\ &= \sum_i^N |M_i(k, l)|^2 \left| \left\langle n_i'' \left| \frac{\partial}{\partial q_i} \right| n_i' \right\rangle \right|^2 \prod_{j \neq i}^N |\langle n_j'' | n_j' \rangle|^2, \end{aligned} \quad (23)$$

¹⁴ J. Mayer and M. Goeppert-Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940).

the quantity required in expression (21), which may be simplified to

$$G_{k,l}(t) = \sum_i^N |M_i(k,l)|^2 H_i \prod_{j \neq i}^N G_j, \quad (24)$$

where

$$H_i = \sum_{n_i'', n_i'} \left| \left\langle n_i'' \left| \frac{\partial}{\partial q_i} \right| n_i' \right\rangle \right|^2 2 \sinh(\beta'/2) \\ \times \exp\{-(n_i'' + \frac{1}{2})\lambda_i'\} \exp\{-(n_i'' + \frac{1}{2})\mu_i''\}, \\ G_j = \sum_{n_j'', n_j'} | \langle n_j'' | n_j' \rangle |^2 2 \sinh(\beta'/2) \\ \times \exp\{-(n_j' + \frac{1}{2})\lambda_j'\} \exp\{-(n_j'' + \frac{1}{2})\mu_j''\}.$$

The procedure followed by both Kubo and O'Rourke in evaluating the matrix elements in H_i and G_j , was to make use of the Slater sum,

$$\rho(x, x' | \xi) = \sum_{n=0}^{\infty} \frac{e^{-(n+\frac{1}{2})\xi}}{\pi^{\frac{1}{2}} \cdot 2^n \cdot n!} H_n(x) H_n(x') \exp\{-\frac{1}{2}(x^2 + x'^2)\} \\ = (2\pi \sinh \xi)^{-\frac{1}{2}} \exp\{-\frac{1}{4}[(x+x')^2 \\ \times \tanh(\frac{1}{2}\xi) + (x-x')^2 \coth(\frac{1}{2}\xi)]\},$$

where $H_n(x)$ are the Hermite polynomials. By the use of the vibrational wave function (16), it is easily seen that

$$G_j = 2 \sinh(\beta'/2) \sum_{n_j'', n_j'} \frac{\alpha'' \exp[-(n_j'' + \frac{1}{2})\mu_j'']}{(\pi^{\frac{1}{2}} 2^{n_j''} n_j''!)^{\frac{1}{2}}} \cdot \frac{\alpha' \exp[-(n_j' + \frac{1}{2})\lambda_j']}{(\pi^{\frac{1}{2}} 2^{n_j'} n_j'!)^{\frac{1}{2}}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dq_j d\bar{q}_j \\ \times H_{n_j''}(\alpha'' q_j'') H_{n_j'}(\alpha' q_j') \exp\{-\frac{1}{2}\alpha''^2(q_j''^2 + \bar{q}_j''^2)\} H_{n_j'}(\alpha' q_j') H_{n_j'}(\alpha' \bar{q}_j') \exp\{-\frac{1}{2}\alpha'^2(q_j'^2 + \bar{q}_j'^2)\} \\ = 2\alpha'\alpha'' \sinh(\beta'/2) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dq_j d\bar{q}_j \rho(\alpha'' q_j'', \alpha'' \bar{q}_j'' | \mu_j'') \rho(\alpha' q_j', \alpha' \bar{q}_j' | \lambda_j') \\ = \frac{2\alpha'\alpha''}{2\pi} \sinh(\beta'/2) [\sinh \lambda_j' \sinh \mu_j'']^{-\frac{1}{2}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dq_j d\bar{q}_j \exp\{-\frac{1}{4}[(q_j'' + \bar{q}_j'')^2 \alpha''^2 \tanh(\frac{1}{2}\mu_j'') \\ + (q_j'' - \bar{q}_j'')^2 \alpha''^2 \coth(\frac{1}{2}\mu_j'')] \} \exp\{-\frac{1}{4}[(q_j' + \bar{q}_j')^2 \alpha'^2 \tanh(\frac{1}{2}\lambda_j') + (q_j' - \bar{q}_j')^2 \alpha'^2 \coth(\frac{1}{2}\lambda_j')] \},$$

where $\alpha''^2 = \omega''/\hbar$ and $\alpha'^2 = \omega'/\hbar$. The integral¹⁵ occurring in the above expression has already been evaluated by O'Rourke so that it reduces to

$$G_j = \frac{2\alpha'\alpha''}{2\pi} \sinh(\beta'/2) [\sinh \lambda_j' \sinh \mu_j'']^{-\frac{1}{2}} 2\pi (\Lambda_j^2 \Omega_j^2)^{-\frac{1}{2}} \exp[-\alpha'^2 \alpha''^2 (c_j' - c_j'')^2 / \Omega_j^2] \dots, \quad (25)$$

where

$$\Omega_j^2 = \alpha''^2 \coth(\frac{1}{2}\mu_j'') + \alpha'^2 \coth(\frac{1}{2}\lambda_j'), \quad \bar{\Omega}_j^2 = \alpha'^2 \coth(\frac{1}{2}\mu_j'') + \alpha''^2 \coth(\frac{1}{2}\lambda_j'), \\ \Lambda_j^2 = \alpha''^2 \tanh(\frac{1}{2}\mu_j'') + \alpha'^2 \tanh(\frac{1}{2}\lambda_j'), \quad \bar{\Lambda}_j^2 = \alpha'^2 \tanh(\frac{1}{2}\mu_j'') + \alpha''^2 \tanh(\frac{1}{2}\lambda_j').$$

The last-defined quantity $\bar{\Lambda}_j^2$ occurs in the evaluation of H_i which may be carried out in the same manner.

$$H_i = 2 \sinh(\beta'/2) \sum_{n_i'', n_i'} \frac{\alpha'' \exp[-(n_i'' + \frac{1}{2})\mu_i'']}{(\pi^{\frac{1}{2}} 2^{n_i''} n_i''!)^{\frac{1}{2}}} \cdot \frac{\alpha' \exp[-(n_i' + \frac{1}{2})\lambda_i']}{(\pi^{\frac{1}{2}} 2^{n_i'} n_i'!)^{\frac{1}{2}}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dq_i d\bar{q}_i \\ \times H_{n_i''}(\alpha'' q_i'') H_{n_i'}(\alpha' q_i') \exp\{-\frac{1}{2}\alpha''^2(q_i''^2 + \bar{q}_i''^2)\} \frac{\partial}{\partial q_i} \frac{\partial}{\partial \bar{q}_i} H_{n_i'}(\alpha' q_i') H_{n_i'}(\alpha' \bar{q}_i') \exp\{-\frac{1}{2}\alpha'^2(q_i'^2 + \bar{q}_i'^2)\} \\ = 2\alpha'\alpha'' \sinh(\beta'/2) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dq_i d\bar{q}_i \rho(\alpha'' q_i'', \alpha'' \bar{q}_i'' | \mu_i'') \frac{\partial}{\partial q_i} \frac{\partial}{\partial \bar{q}_i} \rho(\alpha' q_i', \alpha' \bar{q}_i' | \lambda_i') \\ = \frac{2\alpha'\alpha''}{2\pi} \sinh(\beta'/2) [\sinh \lambda_i' \sinh \mu_i'']^{-\frac{1}{2}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dq_i d\bar{q}_i \exp\{-\frac{1}{4}[(q_i'' + \bar{q}_i'')^2 \alpha''^2 \tanh(\frac{1}{2}\mu_i'') \\ + \alpha''^2 (q_i'' - \bar{q}_i'')^2 \coth(\frac{1}{2}\mu_i'')] \} \frac{\partial}{\partial q_i} \frac{\partial}{\partial \bar{q}_i} \exp\{-\frac{1}{4}[(q_i' + \bar{q}_i')^2 \alpha'^2 \tanh(\frac{1}{2}\lambda_i') + \alpha'^2 (q_i' - \bar{q}_i')^2 \coth(\frac{1}{2}\lambda_i')] \}.$$

¹⁵ O'Rourke's evaluation of G_j is slightly in error. In his expression the exponent of the exponential contains Ω_j^2 rather than $\bar{\Omega}_j^2$. This does not affect his final result, however.

After evaluating the integral, we obtain

$$H_i = (\alpha'\alpha'')^3 [\sinh\lambda_i' \sinh\mu_i'' \Lambda_i^2 \Omega_i^2]^{-1} \\ \times [(1-\rho)^{-\frac{1}{2}} \sinh\lambda_i' + (1-\rho)^{\frac{1}{2}} \sinh\mu_i''] G_i \\ + [(\alpha'\alpha'')^4 / \Lambda_i^2 \Omega_i^2] (\bar{\Lambda}_i / \bar{\Omega}_i)^2 (c_i' - c_i'')^2 G_i, \quad (26)$$

where the G_i are the functions defined in Eq. (25). Thus for Eq. (24) we obtain for the product:

$$H_i \prod_{j \neq i}^N G_j = \left[(\alpha'\alpha'')^3 \{ \sinh\lambda_i' \sinh\mu_i'' \Lambda_i^2 \Omega_i^2 \}^{-1} \right. \\ \times \{ (1-\rho)^{-\frac{1}{2}} \sinh\lambda_i' + (1-\rho)^{\frac{1}{2}} \sinh\mu_i'' \} \\ \left. + \frac{(\alpha'\alpha'')^4}{\Lambda_i^2 \Omega_i^2} \left(\frac{\Lambda_i}{\Omega_i} \right)^2 (c_i' - c_i'')^2 \right] \prod_i^N G_j = K_i \prod_i^N G_j. \quad (27)$$

When the displacement constants c_i' and c_i'' are put equal to zero, H_i reduces to the form obtained by Kubo. In the evaluation of K_i , we shall neglect ρ which enters as $O(N^{-1})$. The second term in K_i may be neglected in comparison with the first since the c 's are $O(N^{-\frac{1}{2}})$ and the first term is proportional to the angular frequency. Thus using the relation

$$[\sinh\lambda_i' \sinh\mu_i'' \Lambda_i^2 \Omega_i^2] = 4\alpha'^2 \alpha''^2 \sinh^2[\frac{1}{2}(\lambda_i' + \mu_i'')],$$

we obtain

$$K_i = \frac{1}{4} \alpha' \alpha'' \left\{ \frac{(1-\rho)^{-\frac{1}{2}} \sinh\lambda_i' + (1-\rho)^{\frac{1}{2}} \sinh\mu_i''}{\sinh^2[\frac{1}{2}(\lambda_i' + \mu_i'')]} \right\} \\ \simeq \frac{\omega'}{4\hbar} [\coth(\beta'/2) + 1] e^{i\omega' t} \\ + \frac{\omega'}{4\hbar} [\coth(\beta'/2) - 1] e^{-i\omega' t}. \quad (28)$$

O'Rourke has approximated the second factor in (27) by neglecting terms $O(N^{-2})$ under summation, so that

$$\prod_i^N G_j = \exp\{-S \coth(\beta'/2)\} \\ \times \exp\{-i\omega' t B \coth(\beta'/2) \\ + S \operatorname{csch}(\beta'/2) \cos(\omega' t - \phi)\}, \quad (29)$$

where

$$S = \sum_{i=1}^N \frac{1}{2} \alpha'^2 (c_i'' - c_i')^2, \quad B = \frac{1}{2} N \rho, \\ \sin\phi = i \sinh(\beta'/2), \quad \cos\phi = \cosh(\beta'/2).$$

Thus from Eqs. (19), (24), (27), and (28) we obtain, after dropping primes on the frequency factors,

$$P' = \frac{\omega}{4\hbar} \sum |M_i(k, l)|^2 \exp\left\{-S \coth \frac{\beta}{2}\right\} \\ \times [\{\coth(\beta/2) + 1\} I_- + \{\coth(\beta/2) - 1\} I_+], \quad (30)$$

with the integrals I_- and I_+ given by

$$I_{\pm} = \int_{-\infty}^{+\infty} dt \exp\left\{-i\omega t \left(B \coth(\beta/2) \pm 1 - \frac{\omega_{kl}}{\omega}\right) \right. \\ \left. + S \operatorname{csch}(\beta/2) \cos(\omega t - \phi)\right\} \\ = \frac{2\pi}{\omega} \exp\{i(y \mp 1)\phi\} \sum_{p=-\infty}^{+\infty} \delta(y - p) \frac{1}{2\pi} \int_0^{2\pi} dx \\ \times \exp\{i(y \mp 1)x + S \operatorname{csch}(\beta/2) \cos x\},$$

where the dimensionless quantity

$$y = (\omega_{kl}/\omega) - B \coth(\frac{1}{2}\beta),$$

may have any integral value p , with the result that the integrals may be expressed in terms of the modified Bessel functions.

$$I_y(z) = (2\pi)^{-1} \int_0^{2\pi} dx \exp\{iyx + z \cos x\}.$$

Using the defining relationships for ϕ given in (29) we find

$$\exp[i(y \pm 1)\phi] = \exp[-\frac{1}{2}(y \pm 1)\beta],$$

so that

$$[\coth(\beta/2) \pm 1] \exp[i(y \pm 1)\phi] \\ = 2(e^{\beta} - 1)^{-1} \exp[-\frac{1}{2}(y - 1)\beta].$$

Consequently expression P' may be simplified to

$$P' = \frac{\pi}{\hbar} \sum_i |M_i(k, l)|^2 \exp\{-S \coth(\beta/2)\} \frac{e^{-\frac{1}{2}(y-1)\beta}}{(e^{\beta} - 1)} \\ \times \sum_{-\infty}^{\infty} \delta(y - p) \left[I_{y+1}\left(S \operatorname{csch} \frac{\beta}{2}\right) + I_{y-1}\left(S \operatorname{csch} \frac{\beta}{2}\right) \right].$$

Inserting the quantity P' in Eq. (18), we finally obtain the total rate of thermal ionization P :

$$P = \frac{\pi}{\hbar^3} (e^{\beta} - 1)^{-1} \exp\{-S \coth(\beta/2)\} \\ \times \sum_i \int_{-\infty}^{+\infty} |M_i(k, l)|^2 \rho(E_k) dE_k e^{-\frac{1}{2}(y-1)\beta} \\ \times \sum_{-\infty}^{+\infty} \delta(y - p) \left[I_{y+1}\left(S \operatorname{csch} \frac{\beta}{2}\right) + I_{y-1}\left(S \operatorname{csch} \frac{\beta}{2}\right) \right]. \quad (31)$$

Integration over the electronic states E_k , in the conduction band, may be replaced by integration over the variable y , by employing the defining relationship for y ,

$$y = (\omega_{kl}/\omega) - B \coth(\frac{1}{2}\beta).$$

Thus,

$$\hbar\omega_{kl} = (\hbar^2 k^2 / 2m^*) + E_i^* = y\hbar\omega + B\hbar\omega \coth(\beta/2), \quad (32)$$

and hence

$$dE_k = \hbar\omega dy,$$

$$\rho(E_k) = (4\Omega m^*/\hbar^2)k = (4\Omega m^*/\hbar^2)(2m^*\omega/\hbar)^{1/2}(y-y_0)^{1/2},$$

where

$$y_0 = (E_i^*/\hbar\omega) - B \coth(\beta/2).$$

Since we are interested only in those values of y which correspond to transitions to the conduction band, then y must have a minimum positive integral value larger than or equal to y_0 , which may or may not be integral. Since thermal ionization implies a transition to any one of the states in the conduction band, the rate of thermal ionization must be the sum of all such transition probabilities as is given by expression (31). If we now make the Huang-Rhys assumption (contrary to Kubo) that the electronic matrix element $M_i(k, l)$ is an insensitive function of k (or y , which increases by unit steps), then it may be removed from under the sign of integration. Thus we put $k=0$ in $M_i(k, l)$. This procedure is valid if the wavelength $(1/k)$ is large compared with the electron orbit of the ground state. With this approximation, the rate of thermal ionization may be written,

$$P = A(e^\beta - 1)^{-1} e^{1/2\beta} \cdot \exp[-S \coth(\beta/2)]$$

$$\times \sum_{p=y_0}^{\infty} (p-y_0)^{1/2} e^{-1/2 p\beta} [I_{p+1} + I_{p-1}], \quad (33)$$

where

$$A = \frac{\pi\omega}{\hbar^2} \frac{4\Omega m^*}{\hbar^2} \left(\frac{2m^*\omega}{\hbar} \right)^{1/2} \sum_i |M_i(0, l)|^2.$$

The expression for P is identical with the result, expressed in different notation, of Huang and Rhys who employed a different method of derivation. A further approximation may be made by replacing the summation by an integration over the order p of the Bessel functions, the lower limit of integration being y_0 . As yet, however, the integral has not been evaluated. A different approach may be followed by putting in the summation $p = p_0 + m$ where p_0 and m are integral. The minimum value of p is then p_0 , so that $(p_0 - y_0) = \delta$ where $0 < \delta \leq 1$. Equation (33) becomes

$$P = A(e^\beta - 1)^{-1} e^{1/2\beta} \cdot \exp[-S \coth(\beta/2)] e^{-1/2 p_0 \beta} \sum_{m=0}^{\infty} (m+\delta)^{1/2} e^{-1/2 m\beta} [I_{p_0+m+2} + I_{p_0+m}]. \quad (34)$$

In evaluating the terms in the summation it is convenient to use the series expansion for the modified Bessel function.

$$I_p(x) = \frac{(x/2)^p}{\Gamma(p+1)} \left[1 + \frac{(x/2)^2}{1!(p+1)} + \frac{(x/2)^4}{2!(p+1)(p+2)} + \frac{(x/2)^6}{3!(p+1)(p+2)(p+3)} + \dots \right],$$

where Γ is the gamma function.

III. DISCUSSION

Since the argument of the Bessel functions occurring in the final expression (33) for P is proportional to the configurational constant S , the functions will have nonzero values for all finite integral values of p , greater than y_0 , provided S is not zero. Thus, multiphonon transitions occur when the displacement constants c_i'' and c_i' , for the final and initial states differ for each vibrational mode. A nonzero value of S corresponds physically to a displacement of the adiabatic potential minimum in configuration space, or to a change in the electron-lattice interaction with excitation. On the other hand, if S is zero, only a single-phonon transition is possible in spite of the fact that the lattice vibrational frequency changes on excitation. This is easily seen as follows. When $S=0$, the Bessel functions, and consequently the ionization rate P , reduce to zero except when p is unity, in which case only a single-phonon transition is possible, since from Eq. (32) we have for $y=1$,

$$E_i^* = \hbar\omega + B\hbar\omega \coth(\beta/2) - (\hbar^2 k'^2/2m^*), \quad (35)$$

where k' corresponds to the electronic state in the conduction band, to which the transition has occurred. For such a transition there is a range of permissible values for E_i^* , its maximum value corresponding to a minimum possible value for k' . Thus its maximum value is approximately

$$(E_i^*)_{\max} \simeq \hbar\omega + B\hbar\omega \coth(\beta/2). \quad (36)$$

It may be remarked at this point that the approximation made in the formal theory of neglecting the second term in Eq. (26) has no effect on the preceding argument, since when $S=7$, the definition of S given by Eq. (29) implies that $c_i'' = c_i'$, so that the second term in Eq. (26) becomes identically zero. Returning now to Eq. (35) it would appear that when $B \coth(\beta/2) > 1$, single phonon transitions would take place from electronic levels (E_i^*) having depths greater than $2\hbar\omega$. However, this argument is not as yet conclusive since the magnitude of the phenomenological constant B is not known. We would expect intuitively that as E_i^* increases, so does B , with the result that for very shallow trap depths, B is also very small. Some idea, as to the magnitude of B may be obtained by comparing the theories of O'Rourke, and Huang and Rhys. The frequency of light absorbed corresponding to a transition from an initial state a to a final state b is given by

$$\hbar\nu = \hbar\omega_{b,a} + p\hbar\omega - B\hbar\omega \coth(\beta/2), \quad (\text{O'Rourke})$$

$$\hbar\nu = \hbar\omega_{b,a} + p\hbar\omega + B'(\bar{n} + \frac{1}{2}), \quad (\text{Huang and Rhys})$$

where $\bar{n} = (e^\beta - 1)^{-1}$.

Thus the relation between O'Rourke's constant B and the Huang-Rhys constant B' is expressed by

$$B = (-B'/2\hbar\omega).$$

On comparing their theoretical result, with Pohl's data on light absorption by F centers in KBr crystals, Huang and Rhys deduce that $B' = -0.1$ eV, so that we would conclude that O'Rourke's dimensionless quantity B would be about unity for this particular case. Thus for the case of ionization of shallow traps we would expect B to be much less than unity, with the result that only at very high temperatures will the condition $B \coth(\beta/2) > 1$, be obtained. We may conclude that the condition $S \neq 0$ is the more fundamental reason for multiphonon transitions, being contrary to the conclusion of Kubo that a change in lattice vibrational frequencies ($B \neq 0$) leads to an appreciable probability for a multiphonon transition.

In view of the series expansion for $I_n(S \cosh \beta/2)$, it is possible to simplify the expressions (33) or (34) subject to the condition

$$[\frac{1}{2}S \cosh(\beta/2)]^2 \ll p_0,$$

since in this case we need retain only the leading term of the series expansion, and Bessel functions of higher order in the summation may be neglected. Expression (34) for P , then yields

$$P = \frac{AS^{p_0-1}\delta^{\frac{1}{2}}}{2^{p_0-1}\Gamma(p_0)} (e^\beta - 1)^{-1} e^{\frac{1}{2}\beta} \cdot \exp[-S \coth(\beta/2)] \cdot e^{-\frac{1}{2}p_0\beta} [\sinh(\beta/2)]^{-p_0}. \quad (37)$$

The temperature range for which Eq. (37) is valid is determined by the values of S and p_0 , and hence by the nature of the impurity center. Calculations, which will be presented at a later time, indicate that, for interstitials in the cubic form of zinc sulfide, $S=1.2$, $A=2.66 \times 10^{15}$ and $p_0=12$ at 300°K (for $B \simeq 0$). These values were obtained on the basis of the Simpson¹⁶ model for interstitials. The value for S is reasonable since it is less than the value $S=16$ obtained by Huang and Rhys for excitation of F centers in NaCl. Here S must be smaller since the electronic wave function is more diffuse and the effective ionic charge is less. Since

¹⁶ J. H. Simpson, Proc. Roy. Soc. (London) A197, 269 (1949).

the condition for the validity of Eq. (37) may be expressed as

$$S^2 < 4p_0 \sinh^2(\beta/2) < 4[(E_i^*/\hbar\omega) - B \coth(\beta/2)] \sinh^2(\beta/2). \quad (38)$$

Equation (37) is valid up to 300°K where $(\beta/2) = 1.03$ corresponding to $\omega = 6.28 \times 10^{13} \text{ sec}^{-1}$ and where a maximum error of 10 percent occurs. Since Eq. (37) can be expressed in the form of a frequency factor $s(E^*, T)$ times a Boltzmann factor $\exp(-p_0\beta)$, typical values of $s(E^*, T)$ are $s(E^*, 300^\circ\text{K}) = 2.5 \times 10^8 \text{ sec}^{-1}$, $s(E^*, 75^\circ\text{K}) = 10^8 \text{ sec}^{-1}$ which are of the correct order of magnitude for values obtained from glow curve and phosphorescent decay measurements on zinc sulfide. However, it is seen that the frequency factor decreases with decrease in temperature, at high temperatures and remains constant at low temperature.

If β is large Eqs. (34) or (37) may be further simplified to

$$P = s(E^*) \exp(-p_0\beta), \quad (39)$$

where

$$s(E^*) = A e^{-S} S^{p_0-1} \delta^{\frac{1}{2}} / \Gamma(p_0).$$

For interstitials in zinc sulfide, Eq. (39) holds quite well up to 300°K where it is less than the correct value by approximately a factor of 10. Low-temperature measurements on phosphorescent decay times should lead to an estimate of the important factor S . We have been unable to simplify Eq. (33) or Eq. (34) for high temperatures.

IV. CONCLUSIONS

The method of O'Rourke leads in a straightforward manner to the expression obtained by Huang and Rhys, for the thermal rate of ionization of impurities in polar crystals. The use of the integral representation for the Dirac delta function is equivalent to the use of Kubo's generating function. The results indicate that the frequency factor depends both on temperature and trap depth.

The writer would like to express his thanks to Dr. J. Fajans for having initially suggested the investigation of the problem.