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Effects of Dynamic Perturbations on Optical Spectra of Impurities in Insulators

D. E. McCumber
Bell Telephone Laboratories, Murray Hill, New Jersey

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Detailed expressions, derived from a phenomenological Hamiltonian, are given for optical spectra of experimental and theoretical interest for a two-level impurity complex in interaction with the quantized phonon field of lattice vibrations. These results can readily be extended to treat other quantized impurity-perturbing fields which, like the electromagnetic and lattice-vibration fields, have classical analogs (Bose-Einstein statistics). The formulas indicate how different properties of the spectral line are interrelated through the system Hamiltonian and how parameters of that Hamiltonian relate to measurable effects induced by external static stresses. The relationship of the semiclassical Franck-Condon approach (valid for strong phonon-impurity interactions) to the purely quantum treatment (necessary for an accurate analysis of weak perturbations and "motional narrowing") is discussed in detail. It is shown how the results relate to various models proposed to describe Urbach's rule and in particular how the Toyozawa-Mahr model follows from the semiclassical spectral formulas. With only minor modifications, the mathematical expressions can also be used to interpret spin-resonance spectra.

1. INTRODUCTION

USING results of the type derived in detail in two preceding mathematical papers,[1,2] we here discuss in more practical terms the effect of dynamic perturbations on the optical spectra of impurities in insulators. We have restricted ourselves to insulators in the sense that the mechanisms of energy transport within the crystals we consider do not involve conduction electrons or other Fermi-Dirac fields. In our discussion we assume for definiteness that lattice vibrations constitute the sole mechanism for transporting energy to and from the impurity sites; however, the theory we present is applicable to any transport mechanism which can be described in terms of a complete set of normal modes of a (Bose-Einstein) field which has a classical analog. Typical fields other than the phonon field of lattice vibrations and the photon field of electromagnetic waves might be the fields which describe magnetic waves or defect diffusion.

In this paper we treat only the simplest case of impurity transitions between a single pair of impurity "electronic" energy states (a,b). We postpone the discussion of effects particular to multilevel systems to a later paper. We assume that within a spontaneous-emission lifetime the probability for radiationless transitions from the excited state b to the ground state a is negligible, so that the dynamics of the phonon-impurity system can be described by an effective Hamiltonian in which lattice vibrations shift the energies of the two states (a,b) but do not mix those states. A number of authors have treated similar systems.[3–7] (The case with significant mixing and its concomitant radiationless transitions will be discussed elsewhere.) Specifically, we assume that with the impurity in its states (a,b) the lattice-impurity system is governed by the respective Hamiltonians

$$H_a=\hbar\omega_a+\sum_q \hbar\omega_q a_q^\dagger a_q\,, \tag{1.1a}$$

$$H_b=\hbar\omega_b+\sum_q \hbar\omega_q a_q^\dagger a_q+\hbar P(\mathbf{Q})\,. \tag{1.1b}$$

Here the a_q, $a_q^\dagger$ are a complete set of phonon annihilation-creation operators (fields) having the familiar Bose-Einstein commutation relations

$$[a_q,a_{q'}]=[a_q^\dagger,a_{q'}^\dagger]=0,\quad [a_q,a_{q'}^\dagger]=\delta(q,q')\,, \tag{1.2}$$

and $P(\mathbf{Q})$ is an arbitrary totally symmetrized real function of a set of dimensionless Hermitian phonon coordinate operators $\mathbf{Q}=\{Q_j\}$. The operators $\mathbf{Q}$ are linear in the a_q, $a_q^\dagger$:[8]

$$Q_j=\sum_q(C_{jq}a_q^\dagger+C_{jq}^*a_q)\,. \tag{1.3}$$

They measure the various lattice strains which perturb the impurity.

It has been shown elsewhere[2] that the important *intrinsic* modifications of the impurity spectra produced by diagonal phonon interactions of the type (1.1) are governed primarily by the difference (H_b-H_a) and depend only indirectly upon the distribution of that difference between H_a and H_b. For this reason and because our choice simplifies a number of results and facili-

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[7] E. O. Kane, Phys. Rev. **119**, 40 (1960); W. E. Lamb, Jr., *ibid.* **55**, 190 (1939); R. C. O'Rourke, *ibid.* **91**, 265 (1953); E. D. Trifonov, Dokl. Akad. Nauk (USSR) **147**, 826 (1962) [English transl.: Soviet Phys.—Doklady **7**, 1105 (1963)].

[8] Symmetrization [of the operator ordering within each term of $P(Q)$] implies no loss of generality because it follows from Eqs. (1.2) and (1.3) that any commutators $[Q_j,Q_k]$ which might arise in the symmetrization of an arbitrary $P(Q)$ can be absorbed in the numerical coefficients of a new $P(Q)$.

tates their application to experimental spectra, we have deliberately chosen the ground-state Hamiltonian H_a to have a simple-harmonic dependence upon the normal-mode coordinates a_q, $a_q^\dagger$. (The excited-state Hamiltonian H_b is arbitrary and not necessarily harmonic.) Except in so far as anharmonic phonon interactions produce *extrinsic* changes in the impurity spectra through temperature-dependent modifications (such as thermal expansion) of the average lattice structure,[9] we do not expect the weak anharmonic forces ordinarily present in lattices to significantly modify our results.[10] The effect on the spectra of thermal changes in lattice structure can be estimated from the changes produced by externally induced lattice strains.

In discussing the properties of impurities in insulating lattices, we assume that the impurity is a more or less distinct ionic complex imbedded in a crystal lattice and weakly perturbed by the lattice motion. The presence of the impurity will in general affect the lattice dynamics in the neighborhood of the impurity,[11] and such local-mode modifications are understood to be included in our choice of phonon normal modes in Eqs. (1.1).

There are two basic problems in the theoretical analysis of dynamic perturbations to the impurity spectra: (1) the calculation from first principles of the structure and numerical coefficients of the effective phonon-impurity Hamiltonian, and (2) the calculation from such a Hamiltonian of the observable spectra of the phonon-coupled impurity. In this paper we consider only the second problem. The results provide a framework for the orderly interpretation and correlation of experimental data, and they indicate which first-principles calculations will have relevance to particular experimental results. In many cases it is possible to estimate plausible forms for the coefficients $\{C_{jq}\}$ in those operators (1.3) which describe deformation-potential, piezoelectric, or optical-mode polar coupling to the impurity. Using such estimates with measurements of the dependence of the impurity spectra upon external stresses (Sec. 3), it is possible to obtain a rather clear understanding of the processes underlying particular spectral properties—even without difficult detailed first-principles calculations.

In Sec. 2 we indicate optical spectra of experimental significance and note their relation to the spectra we subsequently compute. Making the so-called Condon approximation in Sec. 3, we neglect the phonon-coordinate dependence of the optical matrix element M_{ab} and compute the spectrum for absorption from the ground impurity state a to the excited state b. In Sec. 4 we consider the effects of phonon-coordinate dependence in M_{ab}. In both Secs. 3 and 4 we treat three distinct cases: (A) that for which all phonon-impurity interactions are weak, (B) that for which all such interactions are strong, and (C) a mixed case for which some are weak and the others strong. The spectra for the weakly and strongly interacting situations are actually quite different. For weak interactions quantum effects are important, and the spectra display detailed dynamic properties of the phonon-impurity system (Fig. 1).[6,7,12] As the strength of the phonon-impurity interaction increases and multiphonon processes become more important (Fig. 2),[13] the detailed features become smeared and less prominent until in the limit of very strong interactions the result is a broad smooth spectrum adequately described by a few low-order moments.[4]

In Sec. 5 we indicate how our results relate to Urbach's rule,[14] an empirical expression describing the low-energy tails of certain absorption cross sections. In Sec. 6 we remark about the application of some of our results and indicate how our strong-interaction spectra have relevance to Franck-Condon configuration-coordinate analyses.[4,15,16]

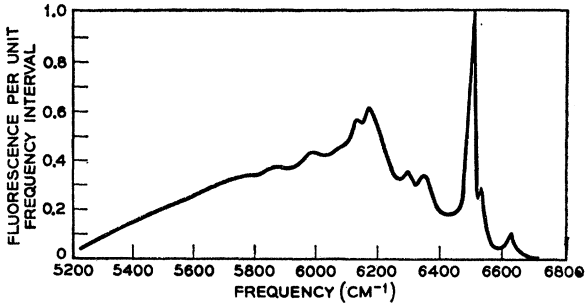

FIG. 1. Fluorescence spectrum (photons/sec per unit frequency interval) for $MgF_2:Ni^{2+}(1\%)$ at 77°K (Ref. 12). The no-phonon line at 6500 cm^{-1} is accompanied on its low-frequency side by vibrational structure involving the emission of a few phonons. (The two small peaks above 6500 cm^{-1} are weak no-phonon lines from higher lying excited states.) The complete spectrum clearly cannot be accurately described in terms of its first few moments nor can it be well approximated by a simple Gaussian spectrum.

2. ABSORPTION AND EMISSION SPECTRA

The optical spectra we consider in this paper derive from impurity complexes dilutely distributed throughout an insulating crystal. The impurity wave functions are localized in a neighborhood of the impurity site which is small compared to optical wavelengths and to the distance between impurities. We neglect spatial

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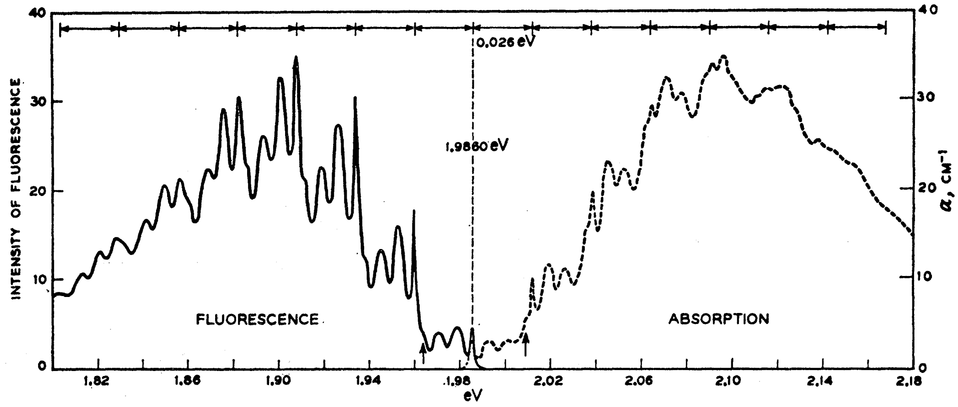

FIG. 2. Fluorescence spectrum (photons/sec per unit wavelength interval) and absorption cross section (times impurity density) of "center" in ZnTe at 20°K (Ref. 13). The no-phonon line at 1.986 eV is accompanied, as was the line of Fig. 1, by vibrational structure associated predominantly with phonon emission. Here the phonon-impurity interaction is stronger than in the system of Fig. 1: The no-phonon line contains a much smaller fraction of the total intensity, and many-phonon processes are clearly visible in the vibrational structure. The broad general features of the present spectra can be described by a few low-order moments, although such an approximation would not accurately represent the detailed phonon peaks evident in the figure. Moment methods and semiclassical approximations become increasingly more appropriate as the strength of the phonon-impurity interaction increases.

dispersion, treat local-field corrections[17] by means of an effective field, and assume that the radiation-impurity interaction is sufficiently weak that the spatial properties of the radiation field everywhere within the crystal can be described by a real wave vector $\mathbf{k}$ whose magnitude $k=\omega n_\lambda(\mathbf{k},\omega)/c$, where $n_\lambda(\mathbf{k},\omega)$ is the real part of the index of refraction of the impurity-doped crystal. It depends upon the direction of $\mathbf{k}$, upon the radiation frequency $\omega=2\pi\nu$, and upon a polarization index λ. This index λ specifies one of two possible plane-wave solutions of Maxwell's equations for the doped crystal; for degenerate cases it alternatively specifies plane or circular polarization.

For the two-state impurity system of Eq. (1.1) we introduce a dimensionless function $f_\lambda(\mathbf{k},\omega)_{ba}$ such that $f_\lambda(\mathbf{k},\omega)_{ba}d\Omega_{\mathbf{k}\lambda}$ is the average intensity in photons/sec *per unit frequency interval* of λ-polarized frequency-ω radiation emitted into the solid angle $d\Omega_{\mathbf{k}\lambda}$ as a result of the spontaneous radiative decay of an impurity from the excited state b to the lower lying state a. If τ_{ba} is the spontaneous-emission radiative lifetime for the transition, then

$$\tau_{ba}{}^{-1}=\sum\nolimits_\lambda\int_{4\pi}d\Omega_{\mathbf{k}\lambda}\int_0^\infty\frac{d\omega}{2\pi}f_\lambda(\mathbf{k},\omega)_{ba}. \tag{2.1}$$

Let $\sigma_{a\lambda}(\mathbf{k},\omega)_{ab}$ be the cross section for a single impurity in the state a to be excited to the state b by the absorption of a plane-wave $(\lambda,\mathbf{k},\omega)$ photon. Let $\sigma_{e\lambda}(\mathbf{k},\omega)_{ba}$ be the cross section for a single impurity in the state b to decay to the state a by the stimulated emission of a $(\lambda,\mathbf{k},\omega)$ photon. Applying the thermal-equilibrium arguments of Einstein[18] to the $(\lambda,\mathbf{k},\omega)$ photons, we find that, when the initial lattice-impurity configurations are described by the impurity populations and by a lattice temperature T,[19]

$$\sigma_{a\lambda}(\mathbf{k},\omega)_{ab}=\sigma_{e\lambda}(\mathbf{k},\omega)_{ba}\exp[\hbar(\omega-\mu)/kT] \tag{2.2}$$

and

$$\sigma_{e\lambda}(\mathbf{k},\omega)_{ba}=f_\lambda(\mathbf{k},\omega)_{ba}[2\pi c/\omega n_\lambda(\mathbf{k},\omega)]^2, \tag{2.3}$$

where $\hbar\mu$ in Eq. (2.2) is a temperature-dependent excitation potential equal to the net free energy required to excite one impurity while maintaining the surrounding lattice temperature T. The potential $\hbar\mu$, which is independent of the parameters $(\lambda,\mathbf{k},\omega)$, is equal to $kT\ln(N_a/N_b)_{eq}$, where $(N_a/N_b)_{eq}$ is the ratio of impurity ground-state and excited-state populations in *thermal equilibrium* at temperature T. To derive Eqs. (2.2) and (2.3), we used the fact that with our assumptions the frequency density of radiation states per unit volume $\rho(\lambda,\mathbf{k},\omega)$ multiplied by the group velocity of light in the crystal is $[\omega n_\lambda(\mathbf{k},\omega)/2\pi c]^2$. The rate of absorption (or stimulated emission) per impurity equals this quantity times the cross section, the Bose-Einstein occupation factor $[\exp(\hbar\omega/kT)-1]^{-1}$ for frequency-ω radiation modes, and the number of impurities in state a (or state b). The rate of spontaneous emission is simply $f_\lambda(\mathbf{k},\omega)_{ba}$ times the state-b occupation.

To relate these observables to microscopic properties, we let $\mathbf{j}(\mathbf{r},t)_{ab}$ be that part of the electric-current operator which couples the state a to the state b and let $\rho(\mathbf{r},t)_{ab}$ be the corresponding component of the charge-density operator. If $\mathbf{e}_\lambda(\mathbf{k},\omega)$ is the unit polarization vec-

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[17] S. L. Adler, Phys. Rev. **126**, 413 (1962).

[18] A. Einstein, Physik Z. **18**, 121 (1917).

[19] D. E. McCumber, Phys. Rev. **134**, A299 (1964).

tor for the $(\lambda,\mathbf{k},\omega)$ electric field, then[20]

$$\sigma_{a\lambda}(\mathbf{k},\omega)_{ab}=\left[\left(\frac{E_{\text{eff}}}{E}\right)^2\frac{n_\lambda(\mathbf{k},\omega)}{\epsilon_\lambda(\mathbf{k},\omega)}\right]\frac{2\pi}{\omega\hbar c}$$

$$\times\int_{-\infty}^{\infty}d(t-t_1)e^{i\omega(t-t')}\int_V d^3(\mathbf{r}-\mathbf{r}')e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}$$

$$\times\langle\mathbf{e}_\lambda(\mathbf{k},\omega)\cdot\mathbf{j}(\mathbf{r},t)_{ab}\mathbf{e}_\lambda(\mathbf{k},\omega)^*\cdot\mathbf{j}(\mathbf{r}',t')_{ab}{}^\dagger\rangle_{a,T}. \quad (2.4)$$

Here $\langle\cdots\rangle_{a,T}$ is the normalized expectation value for an ensemble of temperature T in which the impurity is in its initial state a.[21] The factors in the square brackets take account of the ways the crystal modifies the electromagnetic field seen by the impurity: The factor $n_\lambda(\mathbf{k},\omega)/\epsilon_\lambda(\mathbf{k},\omega)$ corrects for the average refractive-index and dielectric properties; the factor $(E_{\text{eff}}/E)^2$ introduces the additional local-field corrections which result because the solid is not strictly a homogeneous medium.[4]

Because each impurity is small relative to optical wavelengths, we can usefully express the operator $\int(dr)\mathbf{j}(\mathbf{r},t)_{ab}\exp(-i\mathbf{k}\cdot\mathbf{r})$ in terms of electric and magnetic multipoles. Assuming that the lowest nonvanishing multipoles dominate, we have in the three simplest cases of electric dipole, magnetic dipole, and electric quadrupole, respectively,

$$\sigma_{a\lambda}(\mathbf{k},\omega)_{ab}=\left(\frac{E_{\text{eff}}}{E}\right)^2\frac{2\pi\omega n_\lambda(\mathbf{k},\omega)}{\hbar c\epsilon_\lambda(\mathbf{k},\omega)}$$

$$\times\langle|\mathbf{e}(\mathbf{k},\omega)\cdot\mathbf{d}(0)_{ab}|^2\rangle_{a,T}\mathfrak{D}_\lambda(\mathbf{k},\omega)_{ab};$$

$$\sigma_{a\lambda}(\mathbf{k},\omega)_{ab}=\left(\frac{E_{\text{eff}}}{E}\right)^2\frac{2\pi\omega[n_\lambda(\mathbf{k},\omega)]^3}{\hbar c\epsilon_\lambda(\mathbf{k},\omega)}$$

$$\times\langle|\boldsymbol{\kappa}\times\mathbf{e}_\lambda(\mathbf{k},\omega)\cdot\mathbf{m}(0)_{ab}|^2\rangle_{a,T}\mathfrak{M}_\lambda(\mathbf{k},\omega)_{ab}; \quad (2.5)$$

$$\sigma_{a\lambda}(\mathbf{k},\omega)_{ab}=\left(\frac{E_{\text{eff}}}{E}\right)^2\frac{2\pi\omega^3[n_\lambda(\mathbf{k},\omega)]^3}{4\hbar c^3\epsilon_\lambda(\mathbf{k},\omega)}$$

$$\times\langle|\boldsymbol{\kappa}\cdot\mathbf{Q}(0)_{ab}\cdot\mathbf{e}_\lambda(\mathbf{k},\omega)|^2{}_{a,T}\mathfrak{Q}_\lambda(\mathbf{k},\omega)_{ab}.$$

If several multipoles are significant simultaneously, the total cross section must include interference terms. In Eqs. (2.5), $\mathbf{k}$ is the unit vector $\mathbf{k}/k$. The dipole and quadrupole operators are

$$\mathbf{d}(t)_{ab}=\int(dr)\mathbf{r}\rho(\mathbf{r},t)_{ab};$$

$$\mathbf{m}(t)_{ab}=\int(dr)\mathbf{r}\times\mathbf{j}(\mathbf{r},t)_{ab}/2c; \quad (2.6)$$

$$\mathbf{Q}(t)_{ab}=\int(dr)\mathbf{r}\mathbf{r}\rho(\mathbf{r},t)_{ab}.$$

The spectral function $\mathfrak{D}_\lambda(\mathbf{k},\omega)_{ab}$ is defined such that

$$\mathfrak{D}_\lambda(\mathbf{k},\omega)_{ab}=\int_{-\infty}^{\infty}dt$$

$$\times e^{i\omega t}\frac{\langle\mathbf{e}_\lambda(\mathbf{k},\omega)\cdot\mathbf{d}(t)_{ab}\mathbf{e}_\lambda(\mathbf{k},\omega)^*\cdot\mathbf{d}(0)_{ab}{}^\dagger\rangle_{a,T}}{\langle\mathbf{e}_\lambda(\mathbf{k},\omega)\cdot\mathbf{d}(0)_{ab}\mathbf{e}_\lambda(\mathbf{k},\omega)^*\cdot\mathbf{d}(0)_{ab}{}^\dagger\rangle_{a,T}}; \quad (2.7)$$

$\mathfrak{M}_\lambda(\mathbf{k},\omega)_{ab}$ and $\mathfrak{Q}_\lambda(\mathbf{k},\omega)_{ab}$ have similar definitions. These functions are normalized such that, typically,

$$\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\mathfrak{D}_\lambda(\mathbf{k},\omega)_{ab}=1. \quad (2.8)$$

In what follows we restrict ourselves to calculating a basic spectral function which, except for normalization, is of the type (2.7):

$$\mathfrak{F}(\omega)_{ab}=\int_{-\infty}^{\infty}dte^{i\omega t}F(t)_{ab}, \quad (2.9\text{a})$$

where

$$F(t)_{ab}=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-i\omega t}\mathfrak{F}(\omega)_{ab} \quad (2.9\text{b})$$

$$\equiv\langle e^{iH_at/\hbar}M_{ab}e^{-iH_bt/\hbar}M_{ab}{}^\dagger\rangle_{a,T}. \quad (2.10)$$

For spectra of the type we shall consider, which display broad-band vibrational structure extending over a frequency range of the order of and sometimes much greater than the lattice Debye frequency, one should not neglect the frequency dependence of the various factors preceding the spectral functions in Eqs. (2.2), (2.3), and (2.5).

In Eq. (2.10) M_{ab} is generally an operator in the lattice coordinates. In a Born-Oppenheimer theory[22] it would be the matrix element, evaluated for each particular lattice configuration, of the approximate multipole operator (2.6) between the states a and b. As an illustration, let us assume that the "impurity" states are the Born-Oppenheimer states of a single electron

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[20] The correlation-function theory which underlies Eq. (2.4) ff has been reviewed by R. Kubo, in *Lectures in Theoretical Physics*, edited by W. E. Brittin and L. G. Dunham (Interscience Publishers, Inc., New York, 1959), Vol. 1, p. 120.

[21] If $\mathcal{O}$ is an arbitrary operator, $\langle\mathcal{O}\rangle_{a,T}=\text{tr}_a[\mathcal{O}\exp(-H_a/kT)]/\text{tr}_a[\exp(-H_a/kT)]$, where "tr$_a$" indicates the trace over all impurity-phonon states in which the impurity is in its initial state a.

[22] D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 353; M. Born and K Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954), Appendix 8.

(coordinates $\mathbf{r}$) described for a fixed lattice (coordinates $\mathbf{X}$) by the state-n wave function $\varphi_n(\mathbf{r},\mathbf{X})$. If the electronic dipole operator (2.6) is the relevant coupling operator, we would have typically

$$M_{ab}(\mathbf{X})=e\int(dr)\,\varphi_a{}^*(\mathbf{r},\mathbf{X})\mathbf{r}\cdot\mathbf{e}_\lambda(\mathbf{k},\omega)\varphi_b(\mathbf{r},\mathbf{X})\,,\quad(2.11)$$

where $\mathbf{X}$ is now to be replaced by the *operator* which measures the displacement $\mathbf{X}$.

In the present paper we use the diagonal Hamiltonians (1.1) and assume that M_{ab} is a symmetrized[8] function of the lattice coordinates $\{Q_j\}$ defined in Eq. (1.3): $M_{ab}=M_{ab}(\mathbf{Q})$. We write $F(t)_{ab}$ of Eq. (2.9) as the product

$$F(t)_{ab}=M(t)G(t)\exp[-i(\omega_b-\omega_a)t]\,,\quad(2.12)$$

where

$$G(t)\equiv\langle e^{iH_at/\hbar}e^{-iH_bt/\hbar}\rangle_{a,T}\exp[i(\omega_b-\omega_a)t]\,,\quad(2.13)$$

and where Eq. (2.12) defines $M(t)$. In the next section we discuss $G(t)$, which alone determines the spectral properties of $F(t)_{ab}$ in the (Condon) approximation that M_{ab} is independent of lattice coordinates.[4] Because the phonon components of H_a and H_b do not commute, we cannot replace $\exp(iH_at/\hbar)\exp(-iH_bt/\hbar)$ in Eq. (2.13) by $\exp[-i(H_b-H_a)t/\hbar]$ except as a semiclassical approximation. $M(t)$, a function linear in M_{ab} and in $M_{ab}{}^\dagger$, is considered in Sec. 4.

3. THE CONDON APPROXIMATION

When the matrix elements M_{ab} are independent of lattice coordinates (the Condon approximation), the spectral properties of $F(t)_{ab}$ are contained in the function $G(t)$ of Eq. (2.13). If we introduce the Fourier transform $\mathcal{G}(\omega)$ such that

$$G(t)=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-i\omega t}\mathcal{G}(\omega)\,,\quad(3.1)$$

it follows immediately that

$$\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\omega^m\mathcal{G}(\omega)=\left(i\frac{\partial}{\partial t}\right)^mG(t)\,|_{t=0}\,.\quad(3.2)$$

Because $G(0)=1$, $\mathcal{G}(\omega)$ is normalized as in Eq. (2.8). If $P(\mathcal{Q};t)^a$ indicates the Heisenberg time development with respect to the Hamiltonian H_a of the phonon function $P(\mathbf{Q})$,

$$P(\mathbf{Q};t)^a=\exp(iH_at/\hbar)P(\mathbf{Q})\exp(-iH_at/\hbar)\,,\quad(3.3)$$

then we have proved elsewhere[1] that

$$G(t)=1+(-i)\int_0^t dt_1\langle P(\mathbf{Q};t_1)^a\rangle_{a,T}+(-i)^2\int_0^t dt_1$$
$$\times\int_0^{t_1}dt_2\langle P(\mathbf{Q};t_1)^aP(\mathbf{Q};t_2)^a\rangle_{a,T}+\cdots\quad(3.4\text{a})$$
$$=\exp\bigg\{(-i)\int_0^t dt_1\langle P(\mathbf{Q};t_1)^a\rangle_{a,T}+(-i)^2\int_0^t dt_1$$
$$\times\int_0^{t_1}dt_2[\langle P(\mathbf{Q};t_1)^aP(\mathbf{Q};t_2)^a\rangle_{a,T}$$
$$-\langle P(\mathbf{Q};t_1)^a\rangle_{a,T}\langle P(\mathbf{Q};t_2)^a\rangle_{a,T}]+\cdots\bigg\}\,.\quad(3.4\text{b})$$

When the lattice is harmonic, as it is for H_a of Eq. (1.1a), it is useful to express the time-dependent $P(\mathbf{Q})$ correlation functions in Eqs. (3.4) in terms of the pair correlation functions

$$\langle Q_j(t)^aQ_k(t')^a\rangle_{a,T}$$
$$=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-i\omega(t-t')}\rho_{jk}(\omega)[1+n(\omega)]\,,\quad(3.5)$$

where

$$\rho_{jk}(\omega)=\int_{-\infty}^{\infty}dte^{i\omega(t-t')}[Q_j(t)^a,Q_k(t')^a]\quad(3.6)$$

describes the density of phonon states relevant to the relative motion of the coordinates (Q_j,Q_k) and where

$$n(\omega)=[\exp(\hbar\omega/kT)-1]^{-1}\quad(3.7)$$

describes the occupation of phonon states in a thermal ensemble. To do this simply, a compact notation is essential. For this reason we introduce a *numerical* function

$$p(\boldsymbol{\xi})\equiv\langle P(\mathbf{Q}+\boldsymbol{\xi})\rangle_{a,T}\quad(3.8)$$

of a numerical vector variable $\boldsymbol{\xi}$ whose components $\{\xi_j\}$ are in one-to-one correspondence with the phonon operator coordinates $\{Q_j\}$. We also introduce an abbreviated differentiation notation.

$$Q_m\partial_mp(\boldsymbol{\xi}_m)\equiv\sum_jQ_j(t_m)^a(\partial/\partial\xi_{mj})p(\boldsymbol{\xi}_m)\,,\quad(3.9)$$

etc. It will be shown that $p(\boldsymbol{\xi})$ describes the displacement of the mean frequency of the spectrum $\mathcal{G}(\omega)$ as a function of lattice strains.

To interpret the function $p(\boldsymbol{\xi})$ and the variable $\boldsymbol{\xi}$, it is useful to perturb the system by applying external stresses $\{F_j\}$ which act through the lattice coordinates $\{Q_j\}$:

$$H_a\rightarrow H_a-\sum_jF_jQ_j\,.\quad(3.10)$$

If $\langle\cdots\rangle_{a,T,\mathbf{F}}$ indicates averages with respect to the thermal ensemble for the force-perturbed Hamiltonian (3.10), it is easy to verify that

$$S_{jk}\equiv\frac{\partial}{\partial F_k}\langle Q_j\rangle_{a,T,\mathbf{F}}=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}[\rho_{jk}(\omega)+\rho_{kj}(\omega)]/\hbar\omega\,, \tag{3.11}$$

where, for the harmonic Hamiltonian (1.1a), the *elastic constants* S_{jk} are independent of the forces $\mathbf{F}$ and of the temperature T. The effect of the forces $\mathbf{F}$ on the function $p(\xi)$ or on any other similar expectation-value function of the coordinate operators $\mathbf{Q}$ is described by the equation

$$p(\xi)_{\mathbf{F}}=p(\xi+\langle\mathbf{Q}\rangle_{\mathbf{F}})_{\mathbf{F}=0}. \tag{3.12}$$

It follows from these results that the coordinates ξ can be identified with static lattice displacements $\langle\mathbf{Q}\rangle$ and the ξ dependence of functions $p(\xi)$ can be inferred phenomenologically from the dependence of system properties upon crystal strain.[23]

For harmonic phonon systems[24] of the type H_a we can establish the following important result which describes the temperature dependence of the functions $p(\xi)$ formed from expectation values of symmetrized combinations of the operators $\{Q_j\}$:

$$p(\xi)=\sum_{m=0}^{\infty}\frac{1}{m!}\left(\sum\nolimits_{jk}\int_0^{\infty}\frac{d\omega}{2\pi}\rho_{jk}(\omega)n(\omega)\frac{\partial}{\partial\xi_j}\frac{\partial}{\partial\xi_k}\right)^m p(\xi)_{0^\circ\mathrm{K}}. \tag{3.13}$$

Here $p(\xi)_{0^\circ\mathrm{K}}$ is the value of $p(\xi)$ at zero temperature. For temperatures below the Debye temperature the first few terms of the series (3.13) generally give an adequate approximation to $p(\xi)$.

Using harmonic-phonon-ensemble factorization properties[24] of the same type as were used to derive Eq. (3.13), we obtain from Eqs. (3.4) in the notation of Eqs. (3.8) and (3.9)

$$G(t)=1+(-i)\int_0^t dt_1 p(\xi_1)+(-i)^2\int_0^t dt_1\int_0^{t_2} dt_2\exp(\langle Q_1Q_2\rangle\partial_1\partial_2)p(\xi_1)p(\xi_2)+\cdots \tag{3.14a}$$

$$\begin{aligned}=\exp\Big\{-ip(\xi)t&+(-i)^2\int_0^t dt_1\int_0^{t_1} dt_2[\exp(\langle Q_1Q_2\rangle\partial_1\partial_2)-1]p(\xi_1)p(\xi_2)\\&+(-i)^3\int_0^t dt_1\cdots\int_0^{t_2} dt_3[\exp(\langle Q_1Q_2\rangle\partial_1\partial_2+\langle Q_1Q_3\rangle\partial_1\partial_3+\langle Q_2Q_3\rangle\partial_2\partial_3)\\&-\exp(\langle Q_1Q_2\rangle\partial_1\partial_2)-\cdots-\exp(\langle Q_2Q_3\rangle\partial_2\partial_3)+2]p(\xi_1)\cdots p(\xi_3)+\cdots\Big\}.\end{aligned} \tag{3.14b}$$

For the unstrained crystal we set all $\xi_m=0$; otherwise we set $\xi_m=\xi$ and interpret ξ as in (3.12). Using the first time derivative of (3.14a) with Eq. (3.2), we see that the function $p(\xi)$ describes the dependence of the mean frequency

$$\bar{\omega}_G=\int\frac{d\omega}{2\pi}\omega\mathcal{G}(\omega)=p(\xi) \tag{3.15}$$

upon lattice strain.

A. Weak Interactions, Low Temperatures

When the phonon interactions are weak and the lattice temperature low, we may usefully approximate the exponent of the expansion (3.14b) by its first few low-order terms. For this purpose we classify the "order" of a term by the number of ξ derivatives which it contains. Through terms of the fourth order—all odd-order terms vanish—we have

$$\begin{aligned}G(t)=\exp\Big\{-ipt&+(-i)^2\sum_{jk}\frac{\partial p}{\partial\xi_j}\frac{\partial p}{\partial\xi_k}\int_0^t dt_1\int_0^{t_1} dt_2\langle Q_j(t_1)Q_k(t_2)\rangle\\&+(-i)^2\sum_{jklm}\frac{1}{2}\frac{\partial^2 p}{\partial\xi_j\partial\xi_l}\frac{\partial^2 p}{\partial\xi_k\partial\xi_m}\int_0^t dt_1\int_0^{t_1} dt_2\langle Q_j(t_1)Q_k(t_2)\rangle\langle Q_l(t_1)Q_m(t_2)\rangle\\&+(-i)^3\sum_{jklm}\frac{\partial p}{\partial\xi_m}\frac{\partial^2 p}{\partial\xi_j\partial\xi_k}\frac{\partial p}{\partial\xi_l}\int_0^t dt_1\cdots\int_0^{t_2} dt_3[\langle Q_k(t_1)Q_l(t_2)\rangle\langle Q_j(t_1)Q_m(t_3)\rangle\\&+\langle Q_m(t_1)Q_j(t_2)\rangle\langle Q_k(t_2)Q_l(t_3)\rangle+\langle Q_m(t_1)Q_j(t_3)\rangle\langle Q_l(t_2)Q_k(t_3)\rangle]+\cdots\Big\},\end{aligned} \tag{3.16}$$

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[23] The usefulness of this method is severely limited by the fact that "thermal strains" are exceedingly large and can often produce nonlinear effects which could not be predicted from measurements with laboratory stresses (except perhaps hydrostatic pressure) applicable without sample fracture.

[24] Cf. Eq. (4.3), Ref. 1.

where here and in all that follows the ensemble averages and the operator time dependence are implicitly those appropriate to H_a of (1.1a). The result (3.16) can be written in the general form

$$G(t)=\exp\left\{-ipt+\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{\rho_G(\omega)}{\omega^2}(e^{i\omega t}-1-i\omega t)\right\} \tag{3.17a}$$

$$=\exp\left\{-\gamma_G-i\omega_G t-\tfrac{1}{2}\Gamma_G|t|+\frac{i}{2}\gamma_G'\operatorname{sgn}t\right\}\exp\left\{\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{\rho_G(\omega)e^{i\omega t}}{(\omega+i\epsilon t)^2}\right\}, \tag{3.17b}$$

where $\epsilon=0^+$, where $\operatorname{sgn} t=t/|t|$, where

$$\rho_G(\omega)=\sum_{jk}\frac{\partial p}{\partial\xi_j}\frac{\partial p}{\partial\xi_k}\rho_{kj}(\omega)n(\omega)+\tfrac{1}{2}\sum_{jklm}\frac{\partial^2 p}{\partial\xi_j\partial\xi_l}\frac{\partial^2 p}{\partial\xi_k\partial\xi_m}\int_{-\infty}^{\infty}\frac{d\bar\omega}{2\pi}\rho_{kj}(\omega-\bar\omega)n(\omega-\bar\omega)$$
$$\times\rho_{ml}(\bar\omega)n(\bar\omega)+\sum_{jklm}\frac{\partial^2 p}{\partial\xi_j\partial\xi_k}\frac{\partial p}{\partial\xi_l}\frac{\partial p}{\partial\xi_m}P\int_{-\infty}^{\infty}\frac{d\bar\omega}{2\pi}\left\{\frac{n(\omega)n(\bar\omega)}{\bar\omega}\right.$$
$$\times[\rho_{jm}(\omega)\rho_{kl}(\bar\omega)+\rho_{mj}(\omega)\rho_{lk}(\bar\omega)]+\frac{n(\omega)n(\bar\omega)}{\bar\omega-\omega}[\rho_{jm}(\omega)\rho_{lk}(\bar\omega)+\rho_{mj}(\omega)\rho_{kl}(\bar\omega)]$$
$$\left.-\frac{n(\omega-\bar\omega)n(\bar\omega)}{\bar\omega}[\rho_{jm}(\omega-\bar\omega)\rho_{kl}(\bar\omega)+\rho_{mj}(\omega-\bar\omega)\rho_{lk}(\bar\omega)]\right\}+\cdots, \tag{3.18}$$

and where

$$\omega_G=p(\xi)+P\int_{-\infty}^{\infty}\frac{d\bar\omega}{2\pi}\frac{\rho_G(\bar\omega)}{\bar\omega}, \tag{3.19a}$$

$$\gamma_G=\frac{\partial}{\partial\omega}P\int_{-\infty}^{\infty}\frac{d\bar\omega}{2\pi}\frac{\rho_G(\bar\omega)}{\bar\omega-\omega}\bigg|_{\omega=0}, \tag{3.19b}$$

$$\Gamma_G=\rho_G(0), \tag{3.19c}$$

$$\gamma_G'=(\partial/\partial\omega)\rho_G(\omega)\,|_{\omega=0}. \tag{3.19d}$$

If, as is usually the case because of phase-space limitations, $\rho_{jk}(\omega)n(\omega)=0$ when $\omega=0$, then to the lowest nonvanishing order

$$\Gamma_G=\sum_{jklm}\frac{\partial^2 p}{\partial\xi_j\partial\xi_l}\frac{\partial^2 p}{\partial\xi_k\partial\xi_m}\times\int_0^{\infty}\frac{d\omega}{2\pi}\rho_{jk}(\omega)\rho_{ml}(\omega)n(\omega)[1+n(\omega)]. \tag{3.20}$$

If the second and all higher derivatives of $p(\xi)$ vanish, then the series in Eq. (3.18) terminates after its first term.[1]

When the phonon-impurity interaction is weak ($\gamma_G\lesssim 10$ is a reasonable criterion), it is practical to expand the last exponential of Eq. (3.17b) in powers of its argument. The lowest order term of that expansion $[\exp(\cdots)\approx 1]$ is the only term which does not explicitly contain phonon frequencies. We shall call the spectral component associated with this term the no-phonon line.[1,7] The remaining terms generate what we call "vibrational structure." The width (3.20) of the Lorentz-shaped "motionally narrowed" no-phonon line vanishes in the limit of zero temperature. Physically, this width can be associated with low-frequency secular excursions of the impurity energy levels resulting from random phonon perturbations. These excursions appear as a finite linewidth to an experimenter making line-shape measurements over macroscopic time intervals.[6] Expression (3.20) can alternatively be interpreted in terms of Raman scattering of lattice phonons by the impurity.[25] The parameter γ_G governs the fraction $\exp(-\gamma_G)$ of the total intensity of $\mathcal{G}(\omega)$ which is present in the no-phonon line.

In the limit of zero temperature the excitation potential $\hbar\mu$, which appears in the relation (2.2) connecting emission and absorption cross sections, equals the frequency of the no-phonon line. Comparing Eqs. (3.15) and (3.19a), we see that this frequency differs from the mean spectral frequency by the amount

$$\omega_G-\bar\omega_G=-\sum_{jk}\frac{\partial p}{\partial\xi_j}\frac{\partial p}{\partial\xi_k}\int_0^{\infty}\frac{d\omega}{2\pi}\rho_{jk}(\omega)/\omega+\cdots. \tag{3.21}$$

B. Strong Interactions, High Temperatures

It is useful and instructive to consider briefly the case for which all phonon frequencies in Eq. (3.5) are vanishingly small. In that case we can neglect the time dependence of all expectation values in Eqs. (3.4) and (3.14) to obtain

$$G(t)_{\mathrm{SC}}=\langle\exp[-itP(\mathbf{Q})]\rangle_{a,T}. \tag{3.22}$$

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[25] D. E. McCumber and M. D. Sturge, J. Appl. Phys. 34, 1682 (1963).

This result would follow directly from the definition (2.13) of $G(t)$ if we could write

$$\exp(iH_a t/\hbar)\exp(-iH_b t/\hbar) =\exp[-i(H_b-H_a)t/\hbar]. \quad (3.23)$$

The approximation (3.23) is what Lax calls the semiclassical approximation.[4] It follows, as we have noted, from the neglect of all time dependence in the phonon operator function $P(\mathbf{Q})$—that is, from the neglect of all commutators of that function with H_a.

Lax has considered criteria for the validity of the semiclassical approximation. It is useful to review those criteria briefly in the context of Eqs. (3.14). We have already seen how, by expanding the last exponential of Eq. (3.17b), we can interpret the spectrum $\mathcal{G}(\omega)$ as a relatively sharp no-phonon line accompanied by vibrational structure. That expansion technique emphasizes the detailed quantum features of the spectrum $\mathcal{G}(\omega)$; however, the resulting expression for $G(t)$ is not particularly simple mathematically, is difficult to use for strong phonon-impurity interactions ($\gamma_G\gg1$), and is generally not well suited to studies of the tails of the vibrational structure well away from the no-phonon line.[26] An alternative approach, which conveniently describes the general features of the spectrum, but which does not usefully describe detailed spectral structure, can be based jointly upon the semiclassical approximation (3.22) and a representation of $G(t)$ in terms of the semi-invariants χ_m:[27]

$$G(t)=\exp\{\sum_{m=0}^{\infty}(-it)^m\chi_m/m!\}. \quad (3.24)$$

When the differences $\Delta\chi_m$ between the exact semi-invariants χ_m and the semi-invariants $\chi_m{}^0$ of the semiclassical approximation are small, we can legitimately approximate $G(t)$ by the semiclassical function (3.22) and, in some cases, replace the χ_m in Eq. (3.24) by a *finite* number of the semiclassical semi-invariants $\chi_m{}^0$.

The semi-invariant χ_1 equals the *mean* frequency (3.15) of the distribution $\mathcal{G}(\omega)$. The semi-invariant χ_2 equals the *variance* (square of the *standard deviation*) of $\mathcal{G}(\omega)$. The dimensionless ratios

$$r_m=\chi_m/(\chi_2)^{m/2}, \quad m\geq3, \quad (3.25)$$

measure the deviation of $\mathcal{G}(\omega)$ from a normal or Gaussian distribution, for which they all vanish. The ratios r_3 and r_4 are, respectively, the coefficients of *skewness* and of *excess*.[27]

From Eqs. (3.4b) and (3.14b) we infer that for the semiclassical approximation

$$\chi_0{}^0=0, \quad \chi_1{}^0=\langle P(\mathbf{Q})\rangle_{a,T}=p(\xi), \quad (3.26a)$$

$$\begin{aligned}\chi_2{}^0&=\langle P(\mathbf{Q})P(\mathbf{Q})\rangle_{a,T}-[\langle P(Q)\rangle_{a,T}]^2\\ &=[\exp(\langle Q_1Q_2\rangle\partial_1\partial_2)-1]p(\xi_1)p(\xi_2), \quad (3.26b)\end{aligned}$$

etc. In these equations the operators Q_j and Q_k in $\langle Q_jQ_k\rangle$ both occur at the same time: $t_j=t_k$.

For the exact spectrum we see from Eq. (3.17a) that

$$\chi_0=0, \quad \chi_1=p(\xi), \quad (3.27a)$$

and for $m\geq2$

$$\chi_m=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\omega^{m-2}\rho_G(\omega). \quad (3.27b)$$

As a useful alternative to Eq. (3.27b) we may expand the $\langle Q_j(t_j)Q_k(t_k)\rangle$ in Eq. (3.14b) as a power series in the time difference (t_j-t_k) times a magnitude-ordering parameter α subsequently to be set equal to unity. Using this expansion in Eq. (3.14b) and then identifying the semi-invariants χ_m, we would obtain for $m\geq2$

$$\chi_m=\sum_{n=0}^{m-2}\alpha^n\chi_m{}^n, \quad \alpha=1. \quad (3.28)$$

The first (α-independent) term of the series (3.28) is the semiclassical invariant $\chi_m{}^0$. The term of highest order in α in χ_m is of order α^{m-2}. It follows from this for $m=2$ and from Eqs. (3.26a) and (3,27a) for $m=0$, 1 that the lowest order moments of the semiclassical approximation are equal to the corresponding moments of the exact distribution:

$$\chi_0=\chi_0{}^0, \quad \chi_1=\chi_1{}^0, \quad \chi_2=\chi_2{}^0, \quad (3.29)$$

consistent with the observations of Lax.[4]

In estimating the validity of the semiclassical approximation, we can usefully compare the component $\chi_m{}^n$, $0<n\leq m-2$, of Eq. (3.28) with the semiclassical semi-invariant $\chi_{m-n}{}^0$ through the dimensionless ratios

$$\gamma_m{}^n=\chi_m{}^n/(\chi_{m-n}{}^0)^{m/(m-n)}. \quad (3.30)$$

These ratios compare coefficients in Eq. (3.28) which belong to different semi-invariants, but which derive from the same term in the exponent of Eq. (3.14b). If for any fixed $m>2$ we compare successive terms of the series (3.28), we would be comparing contributions from different terms of Eq. (3.14b). This comparison, which seems superficially to be the most logical, is actually not satisfactory because the different terms of Eq. (3.14b) can have appreciably different magnitudes without greatly influencing the validity of the semiclassical approximation.

To illustrate the application of our criterion, we consider the simplest case for which $m=n+2$ and the relevant invariants all derive from the second term of the exponent (3.14b). To avoid inessential mathematical complications, we assume that $p(\xi)$ is a linear function

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[26] An exceptional system is that of Huang and Rhys, Ref. 3, for which with $P(\mathbf{Q})$ linear in a single variable Q_j the expansion (3.14b) terminates after its second term and for which the spectral function $\rho_{jk}(\omega)$ in Eq. (3.5) is a Dirac δ function at a single Einstein-model optical-phonon frequency. In this case $\mathcal{G}(\omega)$ is a series of δ functions at integral multiples of the optical-phonon frequency with coefficients appropriate to a Poisson distribution.

[27] H. Cramér, *Mathematical Methods of Statistics* (Princeton University Press, Princeton, New Jersey, 1946), pp. 180–187.

of a single component ξ of $\boldsymbol{\xi}$.[28] Using Eq. (3.5) in Eq. (3.14b), we find with this assumption that for $n\geq 0$

$$\chi_{n+2}{}^{n}=\left(\frac{\partial p}{\partial \xi}\right)^{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\omega^{n}\rho(\omega)[1+n(\omega)]. \tag{3.31}$$

Using these expressions with Eq. (3.30), we find for $n\geq 1$ that

$$\gamma_{n+2}{}^{n}=\frac{\displaystyle\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\omega^{n}\rho(\omega)[1+n(\omega)]}{\displaystyle\left(\frac{\partial p}{\partial \xi}\right)^{n}\left[\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\rho(\omega)[1+n(\omega)]\right]^{(n+2)/2}}. \tag{3.32}$$

In the limit of strong interactions ($\partial p/\partial\xi\rightarrow\pm\infty$) the ratio (3.32) vanishes. Likewise, in the limit of high temperatures, for which

$$n(\omega)\rightarrow kT/\hbar\omega \quad \text{for} \quad T\gg T_D, \tag{3.33}$$

the ratio vanishes as $T^{-n/2}$. In the same way that the ratios (3.25) measure the deviation of $\mathcal{G}(\omega)$ from a Gaussian distribution, the ratios (3.30) measure the extent to which $\mathcal{G}(\omega)$ deviates from the semiclassical spectrum (3.22). We originally derived the semiclassical approximation (3.22) by neglecting phonon frequencies; the quantitative connection between the low-frequency, strong-interaction, and high-temperature limits is reflected in the ratios (3.30).

We wish to re-emphasize that the validity of the semiclassical approximation concerns the ratios (3.30), *not* the ratios (3.25). The latter measure the deviation of $\mathcal{G}(\omega)$ from a Gaussian distribution, not from the semiclassical distribution. While it is often true that in actual systems the semiclassical spectrum is Gaussian, there are important cases for which it is not.[29] Also, we wish to note that while the semiclassical approximation is always valid for sufficiently high lattice temperatures, the semiclassical spectrum is not *per se* a high-temperature classical spectrum. The semiclassical result is essentially a strong-interaction low-phonon-frequency result. High temperatures have relevance only to the extent that, when Eq. (3.33) obtains, the "effective strength" of the phonon-impurity interaction is not $\partial p/\partial\xi$ but rather $(T/T_D)^{1/2}\partial p/\partial\xi$, which increases with temperature.

Summarizing briefly but somewhat too simply, we conclude from Eq. (3.32) that *the semiclassical approximation is appropriate to all lattice coordinates* Q_j *for which*

$$[\langle(\Delta Q_j)^2\rangle_{\text{av}}]^{1/2}\partial p(\xi)/\partial\xi_j\gg\bar{\omega}_j, \tag{3.32$'$}$$

where $\bar{\omega}_j$ is the average frequency of the phonons contributing to the dynamics of Q_j and where $\langle(\Delta Q_j)^2\rangle_{\text{av}}=\langle(Q_j-\langle Q_j\rangle)^2\rangle$, the mean-square excursion of the coordinate Q_j. In the limit of high temperatures [compare Eq. (3.36) below] this mean-square excursion is $kT\,S_{jj}$, where S_{jj} is the elastic constant defined in Eq. (3.11).

The expression (3.22) obtains for arbitrary H_a. When H_a is harmonic as in Eq. (1.1a), we can rewrite the semiclassical approximation in the form[4,30]

$$\begin{aligned}\mathcal{G}(\omega)_{SC}=&[(2\pi)^N\det\boldsymbol{\Lambda}]^{-1/2}\\&\times\int_{-\infty}^{\infty}dq_1\cdots dq_N\delta[\omega-P(\mathbf{q})]\\&\times\exp\{-\tfrac{1}{2}\textstyle\sum_{jk}q_j(\boldsymbol{\Lambda}^{-1})_{jk}q_k\},\end{aligned} \tag{3.34}$$

where $\boldsymbol{\Lambda}^{-1}$ is the inverse of the $N\times N$ real symmetric matrix $\boldsymbol{\Lambda}$ having components

$$(\boldsymbol{\Lambda})_{jk}=\tfrac{1}{2}\langle Q_jQ_k+Q_kQ_j\rangle_{a,T} \tag{3.35a}$$

$$=\frac{1}{2}\int_0^{\infty}\frac{d\omega}{2\pi}[\rho_{jk}(\omega)+\rho_{kj}(\omega)][1+2n(\omega)]. \tag{3.35b}$$

In the high-temperature limit when (3.33) obtains, we obtain the classical equipartition result

$$(\boldsymbol{\Lambda})_{jk}|_{\text{classical}}=kT\int_0^{\infty}\frac{d\omega}{2\pi}[\rho_{jk}(\omega)+\rho_{kj}(\omega)]/\hbar\omega \tag{3.36a}$$

$$=kTS_{jk}, \tag{3.36b}$$

where S_{jk} is the elastic constant defined in Eq. (3.11). In the important case where $P(\mathbf{Q})$ is approximately a linear function of its arguments, $\mathcal{G}(\omega)_{\text{SC}}$ is Gaussian.

C. Mixed Cases

In the two preceding subsections we have considered cases in which the phonon coordinates $\mathbf{Q}=\{Q_j\}$ either all interact weakly with the impurity or all interact strongly. In this section we consider the situation which obtains when some of the coordinates $\mathbf{Q}$ belong to a subset $\mathbf{Q}_W$ which interacts weakly with the impurity while the remainder belong to a subset $\mathbf{Q}_S$ which interacts strongly.

With no significant loss of generality we assume that the subsets $\mathbf{Q}_W$ and $\mathbf{Q}_S$ are uncorrelated in the sense that

$$\langle[Q_{Wj}(t)^a,Q_{Sk}(t')^a]\rangle_{a,T}=0. \tag{3.37}$$

With this assumption, the nonvanishing correlation functions $\langle Q_j(t_j)^aQ_k(t_k)^a\rangle$ in Eqs. (3.14) contain either pairs of weakly coupled coordinates ($\mathbf{Q}_W$) or pairs of strongly coupled coordinates ($\mathbf{Q}_S$). If Q_j and Q_k are both strongly coupled, we proceed as in the semiclassical approximation of Sec. 3B above and set $t_j=t_k$ in the correlation function. With this semiclassical treatment

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[28] With this assumption the only nonvanishing components of (3.28) are the components $\chi_m{}^{m-2}$. This example illustrates the futility of judging the validity of the semiclassical approximation by comparing, for example, $\chi_m{}^{m-2}$ with $\chi_m{}^0$ for $m>2$.

[29] Cf. Sec. 5 below.

[30] Cramer, Ref. 27, pp. 310–312.

of the N_S strongly coupled coordinates, we obtain the following generalization of Eq. (3.34):

$$G(t)_{Q(W);\ \mathrm{SC}(S)}=[(2\pi)^{N_S}\det\mathbf{\Lambda}_S]^{-1/2}\int_{-\infty}^{\infty}dq_1\cdots dq_{N_S}\exp\{-\tfrac{1}{2}\sum_{jk}q_j(\mathbf{\Lambda}_S{}^{-1})_{jk}q_k\}$$
$$\times\exp\left\{-ip(\xi_W;\mathbf{q}_S)+(-i)^2\int_0^t dt_1\int_0^{t_1}dt_2[\exp(\langle Q_{W1}\partial_{W2}\rangle\partial_{W1}\partial_{W2})-1]p(\xi_{W1};\mathbf{q}_S)p(\xi_{W2};\mathbf{q}_S)+\cdots\right\}. \quad (3.38)$$

Here [compare Eq. (3.8)]

$$p(\xi_W;\mathbf{q}_S)=\langle P(\mathbf{Q}_W+\xi_W;\mathbf{q}_S)\rangle_{a,T} \quad (3.39)$$

and $\mathbf{\Lambda}_S$ is the $N_S\times N_S$ real symmetric matrix with elements [compare Eqs. (3.35) and (3.36)]

$$(\mathbf{\Lambda}_S)_{jk}=\tfrac{1}{2}\langle Q_{Sj}Q_{Sk}+Q_{Sk}Q_{Sj}\rangle \quad (3.40\mathrm{a})$$

$$\xrightarrow[\text{classical}]{} kTS_{(Sj)(Sk)}\,. \quad (3.40\mathrm{b})$$

4. PHONON-DEPENDENT MATRIX ELEMENTS

In the preceding section we considered the situation which obtains when the matrix elements M_{ab} are independent of the lattice coordinates. When M_{ab} is an operator function of those ocordinates so that the Heisenberg operator

$$M_{ab}(\mathbf{Q};t)^a=\exp(iH_at/\hbar)M_{ab}(\mathbf{Q})\exp(-iH_at/\hbar) \quad (4.1)$$

is not independent of t, the spectral function $G(t)$ must be supplemented as in Eq. (2.12) by a function $M(t)$.

Proceeding as in the derivation of Eqs. (3.4) and (3.14), we can verify that

$$M(t)=\langle M_{ab}(t)^aM_{ab}{}^{\dagger}\rangle_{a,T}+(-i)\int_0^t dt_1[\langle M_{ab}(t)^aP(t_1)^aM_{ab}{}^{\dagger}\rangle_{a,T}$$
$$-\langle P(t_1)^a\rangle_{a,T}\langle M_{ab}(t)^aM_{ab}{}^{\dagger}\rangle_{a,T}]+\cdots \quad (4.2)$$
$$=\exp\Big\{(-i)\int_0^t dt_1[\exp(\langle Q_tQ_1\rangle\partial_t\partial_1+\langle Q_1Q_0\rangle\partial_1\partial_0)-1]p(\xi_1)+(-i)^2\int_0^t dt_1\int_0^{t_1}dt_2[\exp(\langle Q_tQ_1\rangle\partial_t\partial_1$$
$$+\langle Q_1Q_0\rangle\partial_1\partial_0+\langle Q_1Q_2\rangle\partial_1\partial_2+\langle Q_tQ_2\rangle\partial_t\partial_2+\langle Q_2Q_0\rangle\partial_2\partial_0)-\exp(\langle Q_tQ_1\rangle\partial_t\partial_1+\langle Q_1Q_0\rangle\partial_1\partial_0+\langle Q_tQ_2\rangle\partial_t\partial_2$$
$$+\langle Q_2Q_0\rangle\partial_2\partial_0)-\exp(\langle Q_1Q_2\rangle\partial_1\partial_2)+1]p(\xi_1)p(\xi_2)+\cdots\Big\}\exp(\langle Q_tQ_0\rangle\partial_t\partial_0)m(\xi_t)m^*(\xi_0). \quad (4.3)$$

Here we have used [compare Eq. (3.8)]

$$m(\xi)\equiv\langle M_{ab}(\mathbf{Q}+\xi)\rangle_{a,T} \quad (4.4)$$

and the symbolic notation of Eq. (3.9). It is sometimes useful to recall [compare Eqs. (3.4) and (3.14)] that

$$\exp(\langle Q_tQ_0\rangle\partial_t\partial_o)m(\xi_t)m^*(\xi_0)=\langle M_{ab}(\mathbf{Q}(t)^a+\xi_t)M_{ab}{}^{\dagger}(\mathbf{Q}(0)^a+\xi_0)\rangle_{a,T}\,. \quad (4.5)$$

The coordinate ξ and temperature dependence of the function (4.4) is as in Eqs. (3.12) and (3.13).

If the phonon operators in $M_{ab}(\mathbf{Q})$ and $P(\mathbf{Q})$ are independent in the sense that

$$\langle M_{ab}(t)^aP(t_1)^a\cdots P(t_n)^aM_{ab}{}^{\dagger}\rangle_{a,T}=\langle M_{ab}(t)^aM_{ab}{}^{\dagger}\rangle_{a,T}\langle P(t_1)^a\cdots P(t_n)^a\rangle\,, \quad (4.6)$$

then Eq. (4.2) simplifies [compare Eq. (4.5)] to

$$M(t)_{\text{uncorrelated}}=\langle M_{ab}(\mathbf{Q};t)^aM_{ab}{}^{\dagger}(\mathbf{Q};0)^a\rangle_{a,T}\,. \quad (4.7)$$

This situation obtains, for example, when $M_{ab}(\mathbf{Q})$ and $P(\mathbf{Q})$ depend upon operators Q_j which are uncorrelated in the sense of Eq. (3.37):

$$\langle[Q_{Mj}(t)^a,Q_{Pk}(t')^a]\rangle=0\,.$$

If $p(\xi)$ is a linear function of ξ, we may rigorously terminate the series in the first exponent of Eq. (4.3) after its first term to obtain [compare Eq. (4.5)]

$$M(t)_{p\text{-linear}}=\exp\left\{(-i)\int_0^t dt_1[\langle Q_tQ_1\rangle\partial_t\partial_1+\langle Q_1Q_0\rangle\partial_0\partial_1]p(\boldsymbol{\xi}_1)\right\}\langle M_{ab}(\mathbf{Q}(t)^a+\boldsymbol{\xi}_t)M_{ab}{}^\dagger(Q(0)^a+\boldsymbol{\xi}_0)\rangle_{a,T} \tag{4.8a}$$

$$=\left\langle M_{ab}\left(\mathbf{Q}(t)^a+\boldsymbol{\xi}-i\int_0^t dt_1\langle Q_tQ_1\rangle\partial_1p(\boldsymbol{\xi}_1)\right)M_{ab}{}^\dagger\left(\mathbf{Q}(0)^a+\boldsymbol{\xi}-i\int_0^t dt_1\langle Q_1Q_0\rangle\partial_1p(\boldsymbol{\xi}_1)\right)\right\rangle_{a,T}. \tag{4.8b}$$

For this special case the correlations between the phonon-dependent matrix elements $M_{ab}(\mathbf{Q})$ and the energy function $P(\mathbf{Q})$ appear as time-dependent modulations of the coordinates $\boldsymbol{\xi}_t$ and $\boldsymbol{\xi}_0$.

Using Eq. (2.12) on the left-hand side of Eq. (2.9b), we find upon setting $t=0$ that the total integrated intensity of $\mathfrak{F}(\omega)_{ab}$ is

$$\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\mathfrak{F}(\omega)_{ab}=M(0)=\langle|M_{ab}|^2\rangle\geq|\langle M_{ab}\rangle|^2. \tag{4.9}$$

Other moments can be computed as in Eq. (3.2) by evaluating time derivatives of Eq. (2.9b) at $t=0$.

A. Weak Interactions, Low Temperatures

In the case of weak phonon-impurity interactions it is convenient to expand the first exponent of Eq. (4.3) as a power series, ordering each term as in Sec. 3A by the number of $\boldsymbol{\xi}$ derivatives of $p(\boldsymbol{\xi})$ or of $m(\boldsymbol{\xi})$ which it contains. Through terms of second order, the results of such an expansion are contained in Eqs. (4.8) which, as we have noted, are exact when $p(\boldsymbol{\xi})$ is linear in $\boldsymbol{\xi}$. Alternatively,

$$M(t)=\exp\left\{-\sum_{jk}\frac{\partial p}{\partial\xi_j}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{e^{i\omega t}}{\omega}n(\omega)\left[\rho_{jk}(\omega)\frac{\partial}{\partial\xi_k{}'}+\rho_{kj}(\omega)\frac{\partial}{\partial\xi_k{}''}\right]+\cdots\right\}$$
$$\times\exp\left\{\sum_{lm}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{i\omega t}n(\omega)\rho_{ml}(\omega)\frac{\partial}{\partial\xi_l{}'}\frac{\partial}{\partial\xi_m{}''}\right\}m\left(\xi_l{}'+\sum_j\frac{\partial p}{\partial\xi_j}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{n(\omega)}{\omega}\rho_{jl}(\omega)+\cdots\right)$$
$$\times m^*\left(\xi_m{}''+\sum_j\frac{\partial p}{\partial\xi_j}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{n(\omega)}{\omega}\rho_{mj}(\omega)+\cdots\right). \tag{4.10}$$

Expanding the two exponentials as power series in their arguments, we separate the lowest order (time-independent) term

$$M_0\equiv\left|m\left(\xi_l+\sum_j\frac{\partial p}{\partial\xi_j}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{n(\omega)}{\omega}\rho_{jl}(\omega)+\cdots\right)\right|^2 \tag{4.11}$$

from the remaining (time-dependent) terms. When used with Eq. (2.12), the term (4.11) does not modify the spectral properties of the function $\mathcal{G}(\omega)$, whereas the time-dependent terms of $M(t)$ displace $\mathcal{G}(\omega)$ by phonon frequencies.

Any no-phonon component which remains in the spectrum $\mathfrak{F}(\omega)_{ab}$ of Eq. (2.9) must derive from the no-phonon part of $G(t)$ and the component (4.11) of $M(t)$:

$$\mathfrak{F}(\omega)_{ab}|_{\text{no-phonon}}=M_0\exp\{-\gamma_G-i(\omega_G+\omega_b-\omega_a)t$$
$$-\tfrac{1}{2}\Gamma_G|t|-\tfrac{1}{2}i\gamma_G{}'t/|t|\}. \tag{4.12}$$

The lattice dependence of the matrix element M_{ab} does not modify the frequency or the width of the no-phonon line. It does however influence its strength.

In Eq. (4.11) the coordinates $\boldsymbol{\xi}$ in $m(\boldsymbol{\xi})$ are displaced by approximately one-half of the difference of the lattice distortion in the ground-state and excited-state ensembles. This is not unexpected because detailed-balance arguments indicate that in the limit of zero temperature the strength of the no-phonon line in emission equals that in absorption, whatever the lattice dependence of M_{ab}.

Expressions describing the vibrational structure accompanying the no-phonon component (4.12) can easily be derived from Eqs. (3.17)ff. and Eq. (4.10).

B. Strong Interactions, High Temperatures

If as in Sec. 3B we replace all $\langle Q_j(t_j)Q_k(t_k)\rangle$ in Eqs. (3.4) and (4.3) by $\langle Q_j(t_j)Q_k(t_j)\rangle$, we obtain the following generalization of (3.22):

$$M(t)_{\text{SC}}G(t)_{\text{SC}}=\langle(|M_{ab}(Q)|^2$$
$$\times\exp[-itP(Q)])_{\text{symm}}\rangle_{a,T}. \tag{4.13}$$

Here $(\cdots)_{\mathrm{symm}}$ indicates that the operator function within the parenthesis is to be totally symmetrized with respect to the ordering of the phonon operators $\mathbf{Q}$. When H_a is harmonic as in (1.1a), we can rewrite this semiclassical approximation in the form [compare Eq. (3.34)]

$$\mathfrak{F}(\omega)_{ab}=[(2\pi)^N \det\mathbf{\Lambda}]^{-1/2}\int_{-\infty}^{\infty} dq_1\cdots dq_N \times\exp\{-\tfrac{1}{2}\textstyle\sum_{jk} q_j(\mathbf{\Lambda}^{-1})_{jk}q_k\}\,|M_{ab}(q_1\cdots q_N)|^2 \times\delta[\omega-(\omega_b-\omega_a)-P(q_1\cdots q_N)]\,, \quad (4.14)$$

where the $N\times N$ symmetric matrix $\mathbf{\Lambda}$ is defined in Eqs. (3.35)–(3.36).

The semiclassical approximations (4.13) and (4.14) are valid for conditions which are essentially the same as those discussed in Sec. 3. Whereas the three semi-invariants χ_0, χ_1, χ_2 of $G(t)$ are retained in the semiclassical approximation $G(t)_{\mathrm{SC}}$ of Sec. 3, only the single semi-invariant χ_0 is precisely correct in the semiclassical approximations (4.13) and (4.14) when M_{ab} is a function of the phonon coordinates. This feature cannot be rectified without destroying the essential simplicity of the semiclassical expressions. Fortunately, the errors in the mean frequency χ_1 and in the variance χ_2 are generally insignificant when the criteria of Sec. 3 are met, because those criteria insure that the standard deviation $(\chi_2)^{1/2}$ is much greater than the effective Debye frequency whereas the errors in χ_1 and $(\chi_2)^{1/2}$ in Eq. (4.14) are of the order of that frequency.

C. Mixed Cases

As in Sec. 3C we assume that the coordinates $\mathbf{Q}$ may be separated into a weak set ($\mathbf{Q}_W$) and a strong set ($\mathbf{Q}_S$) which are uncorrelated in the sense (3.37). Proceeding as in Sec. 3C, we obtain for the present case

$$M(t)G(t)\,|_{\mathrm{Q}(W);\ \mathrm{SC}(S)}=[(2\pi)^{N_S} \det\mathbf{\Lambda}_S]^{-1/2} \times\int_{-\infty}^{\infty} dq_1\cdots dq_{N_S}\exp\{-\tfrac{1}{2}\textstyle\sum_{jk} q_j(\mathbf{\Lambda}_S{}^{-1})_{jk}q_k\} \times M_W(t;q_1\cdots q_{N_S})G_W(t;q_1\cdots q_{N_S})\,, \quad (4.15)$$

where $M_W(t;\mathbf{q}_S)$ and $G_W(t;\mathbf{q}_S)$ are, respectively, the functions $M(t)$ and $G(t)$ appropriate to a system in which the weak coordinates $\mathbf{Q}_W$ are treated as quantum-mechanical operators, and the strong coordinates $\mathbf{Q}_S$ are replaced by N_S numerical parameters $\mathbf{q}_S$. The $N_S\times N_S$ symmetric matrix $\mathbf{\Lambda}_S$ which governs the $\mathbf{q}_S$ average in Eq. (4.15) is defined in Eq. (3.40).

5. THE URBACH EFFECT

In studying the spectral region near the fundamental absorption edge of direct-gap silver halides, Urbach[14] observed that over a range of several decades the absorption cross section accurately follows the empirical rule

$$\sigma_a(\omega)=K_0\exp[\sigma\hbar(\omega-\omega_0)/kT]\,, \quad (5.1)$$

where K_0, σ, and ω_0 are parameters. Subsequent experimenters have verified this rule in other direct-gap materials, most notably the alkali halides.[31,32] Mahr has verified that the same rule applies to absorption by small concentrations of KBr or KI in KCl.[33] In most situations for which Urbach's rule has been verified $\sigma\sim 1$.

Redfield[34] has suggested that Urbach's rule derives from electric-field perturbations generated by randomly located impurities; however, the Boltzmann-like temperature dependence in Eq. (5.1) strongly suggests that Urbach's rule derives from the interaction of thermally excited lattice vibrations (phonons) with the electronic systems primarily responsible for the absorption. Hopfield[35] has suggested an explanation of this type which he based upon an admittedly incomplete first-order calculation of phonon-exciton interactions. We can qualitatively understand his model if we assume that the absorption on the low-frequency side of the edge results from electronic excitation by the simultaneous absorption of the incident photon and a lattice phonon. This absorption will reflect the density of phonon modes at the frequency $\Delta\omega$ below the edge and their average occupation $n(\Delta\omega)$ [compare Eq. (3.7)]. When $\hbar\Delta\omega\gg kT$, the average occupation

$$n(\Delta\omega)\to\exp(-\hbar\Delta\omega/kT)\,, \quad (5.2)$$

an expression very suggestive of Eq. (5.1).

Equation (2.2) is a nonperturbative expression whose physical interpretation is closely related to the mechanism proposed by Hopfield. If the emission cross section $\sigma_e(\omega)$ is roughly constant over the frequency range of interest, the factor $\exp[\hbar(\omega-\mu)/kT]$ in Eq. (2.2) will produce an absorption tail of the Urbach type. In this description the parameter σ in Eq. (5.1) compensates for the fact that $\sigma_e(e)$ is not strictly constant. There are cases for which Eq. (2.2) does indeed predict an Urbach-like low-frequency absorption edge, especially when the temperature is low and the exponential cutoff in $\exp[\hbar(\omega-\mu)/kT]$ restricts the measurable frequency interval to be close to the zero-temperature edge.[32,35] However, we have not been successful in attempts to fit broad high-temperature Urbach edges[31,33] by this model. The difficulty, quite simply, is that over the required large frequency interval the frequency dependence of $\sigma_e(\omega)$ is neither small nor capable of description in Eq. (5.1) by measured values of the parameter σ.

Dexter[36] has analyzed the band-edge absorption in a

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[31] W. Martienssen, Phys. Chem. Solids **2**, 256 (1957); **8**, 294 (1959); U. Haupt, Z. Physik **157**, 232 (1959); H. Zinngrebe, *ibid.* **154**, 495 (1959); S. Tutihasi, Phys. Chem. Solids **12**, 344 (1960).

[32] D. Dutton, Phys. Rev. **112**, 785 (1958).

[33] H. Mahr, Phys. Rev. **125**, 1510 (1962).

[34] D. Redfield, Phys. Rev. **130**, 916 (1963).

[35] J. J. Hopfield, Phys. Chem. Solids **22**, 63 (1961).

[36] D. L. Dexter, Suppl. Nuovo Cimento **7**, 245 (1958).

semiclassical model of the type (3.34) with $P(\mathbf{Q})$ a linear function of a single phonon coordinate Q_j. By suitably adjusting the parameters, he was able to reproduce the observed exponential dependence over a limited frequency range. Outside that range the Gaussian spectral shape implicit in his model destroys the agreement with the experiment. Toyozawa[37] extended Dexter's treatment by assuming $P(\mathbf{Q})$ to be a quadratic function of a coordinate Q_j. For example, if

$$P(\mathbf{Q})=C_2Q_2^2\,, \tag{5.3a}$$

then it follows from Eq. (3.34) that ($C_2 \gtrless 0$)

$$\mathcal{G}(\omega)=\frac{\exp[-\omega/2C_2kTS_{22}]}{[2\pi C_2kTS_{22}\omega]^{1/2}}\theta(\pm\omega)\,, \tag{5.3b}$$

where $\theta(x)=\frac{1}{2}(1+x/|x|)$ and where we have used the high-temperature result (3.36b). For $C_2<0$, Eq. (5.3b) reproduces the Urbach low-frequency tail.[38]

In his analysis Toyozawa recognized that the modes of vibration which dominate the quadratic interaction (5.3a) cannot at the same time have large linear interactions with the impurity. While an Urbach tail would eventually be predicted from Eq. (3.34) even if this did occur, the characteristic exponential behavior would only begin much too far down the edge of a Gaussian curve characteristic of the linear coupling. Mahr[39] extended Toyozawa's work by simultaneously considering two independent phonon coordinates, one which couples linearly to the impurity and a second which couples quadratically:

$$P(Q_1,Q_2)=C_1Q_1+C_2Q_2^2,\quad \langle Q_1Q_2\rangle=0\,. \tag{5.4}$$

By adjusting the coupling constants C_j and the properties of the phonons, Mahr was able to achieve an excellent fit (over a range of four decades) to his absorption data[33] for KI in KCl.

If we use the phonon coupling (5.4) in Eq. (4.14), we find with the assumption that M_{ab} is independent of $\mathbf{Q}$ that

$$\mathfrak{F}(\omega)_{ab}=K_0(T)e^{\sigma(T)\hbar(\omega-\omega_{ba})/kT}\times\int_{\alpha(\omega,T)}^{\infty}dye^{-y^2}[y-\alpha(\omega,T)]^{-1/2}\,, \tag{5.5}$$

where[40]

$$\sigma(T)=-kT/2\hbar C_2\langle Q_2^2\rangle\,, \tag{5.6a}$$

$$\alpha(\omega,T)=[\sigma(T)/2\tau(T)+\hbar(\omega-\omega_{ba})\tau(T)]/(kT)^{1/2}\,, \tag{5.6b}$$

$$\tau(T)=-C_2/\{|C_2|\hbar C_1[2\langle Q_1^2\rangle/kT]^{1/2}\}\,, \tag{5.6c}$$

and $\omega_{ba}=\omega_b-\omega_a$. Expressions (5.6a) and (5.6c) can usefully be written in terms of the phonon spectral functions of Eq. (3.5) or at high temperatures in terms of elastic constants [compare Eqs. (3.35) and (3.36)]. In the neighborhood of that frequency $\omega_{\max}$ for which $\mathfrak{F}(\omega)_{ab}$ is a maximum, $\alpha(\omega,T)$ is large and positive. For that case

$$\mathfrak{F}(\omega)_{ab}=K_0(T)e^{\sigma(T)\hbar(\omega-\omega_{ba})/kT}e^{-[\alpha(\omega,T)]^2}\times\left[\frac{\pi}{2\alpha(\omega,T)}\right]^{1/2}\left\{1-\frac{3}{16\alpha^2}+\cdots\right\}. \tag{5.7}$$

Keeping only the first term of the series, we find that

$$\omega_{\max}=\omega_{ba}-\frac{\sigma(T)}{4\hbar[\tau(T)]^2}\left\{1-\left[1-kT\left(\frac{\tau(T)}{\sigma(T)}\right)^2\right]^{1/2}\right\}\xrightarrow[(\sigma/\tau)^2\gg kT\gg kT_D]{}\omega_{ba}-kT/8\hbar\sigma(\infty)\,. \tag{5.8}$$

These results are essentially identical to those of Mahr, who neglected the factor $[y-\alpha(\omega,T)]^{-1/2}$ in the integral of Eq. (5.5).[41]

In relating the experimental and the theoretical spectra, Mahr neglected the frequency dependence of factors in Eqs. (2.5) which connect the absorption cross section to the spectral function $\mathfrak{F}(\omega)_{ab}$. When the exponentials in Eq. (5.5) dominate the frequency dependence of $\mathfrak{F}(\omega)_{ab}$ and when the absorption strength is not so strong as to significantly influence the refractive properties of the impurity-doped crystal, this is a reasonable approximation. However, as Mahr has noted, it is not reasonable for the treatment of the intrinsic absorption edge of the host crystal[42] and is probably responsible for the deviation he found when he attempted to fit such spectra to an expression of the type (5.5).

It is important to realize that the Toyozawa-Mahr model of Urbach's rule is not necessarily intrinsic to band-gap spectra. It obtains whenever the phonon-impurity coupling can be approximated in the strong-coupling semiclassical domain by Eq. (5.4). Klick *et al.*[43] have recently scrutinized the low-energy absorption edge of F centers in KCl. They were unable to detect any evidence of an Urbach tail which would accompany a strong quadratic coupling ($C_2<0$) in (5.4).

Contrast the Toyozawa-Mahr model with the model based on Eq. (2.2) which we briefly discussed earlier. For an impurity line Eq. (2.2) would predict that any Urbach-like tails would lie to the low-frequency side of the line in absorption and to the high-frequency side in emission. The Toyozawa-Mahr model predicts that the Urbach tail remains on the *same* side of the line in both absorption and emission. If $C_2<0$ in Eq. (5.4), the tail

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[37] Y. Toyozawa, Suppl. Progr. Theoret. Phys. (Kyoto) **12**, 111 (1959).

[38] D. M. Eagles, Phys. Rev. **130**, 1381 (1963).

[39] H. Mahr, Phys. Rev. **132**, 1880 (1963).

[40] Our $\sigma(T)$ is the analog of σ in Eq. (5.1); it differs from that of Mahr, Ref. 39, by the factor kT. Our $\tau(T)$ likewise differs by a factor $(kT)^{1/2}$. With these definitions $\sigma(T)$ and $\tau(T)$ both approach constant values for $T\gg T_D$.

[41] Compare Eq. (5.7) with the similar equation at the top of page 1881, Ref. 39.

[42] J. J. Hopfield, Phys. Rev. **112**, 1555 (1958).

[43] C. C. Klick, D. A. Patterson, and R. S. Knox, Phys. Rev. **133**, A1717 (1964).

lies on the low-frequency side; if $C_2>0$, it lies on the high-frequency side. Because the electronic configuration of excited states is generally less compact than that of the impurity ground state, we expect that in most cases $C_2<0$.

6. CONCLUDING REMARKS

In the preceding sections we derived expressions relating to the spectra of optical transitions between a pair of impurity levels in an insulator. We specifically discussed interactions of the impurity with lattice vibrations, although we briefly noted in Sec. 1 that the analysis pertains to all fields which have classical analog and which can be expressed in terms of a complete set of Bose-Einstein operators having the properties (1.1)ff.

Imbusch *et al.*[44] have studied the variation with temperature of the width of the sharp optical R lines of V^{2+} and of Cr^{3+} in MgO. Both of these ions are weakly coupled to the lattice phonons in the sense of Sec. 3. It has been speculated that both are also strongly coupled (in the sense of Sec. 3) to very low-frequency perturbations such as might be associated with the motion of lattice dislocations. This additional "strong" coupling is apparent at temperatures below about 100°K where the linewidth produced by the "weak" phonon-coupling mechanism (3.20) decreases rapidly ($\sim T^7$). The strong coupling produces a small Gaussian width in the no-phonon line which in the temperature region studied ($T\geq 4.2°\text{K}$) is proportional to $T^{1/2}$. This example of a "mixed system" in the sense of Sec. 3C is instructive because it illustrates how phonon interactions can be supplemented within the above theoretical framework by other dynamic interactions, such as those produced by dislocation motion. It also illustrates that, as the term is used in Secs. 3 and 4, the "strength" of impurity perturbations depends critically upon the frequency of those perturbations [compare Eqs. (3.30)–(3.33)] and is only indirectly related to the absolute strength of the coupling as measured through the second moment of the spectrum.

The semiclassical approximations which obtain for the strong-coupling case provide the theoretical basis for Franck-Condon analyses of impurity spectra. Two generalizations of the usual Franck-Condon configuration-coordinate description are apparent in Eq. (4.15), where we have included the coordinate dependence of the matrix element[16] M_{ab} and where we have provided for several lattice coordinates $\mathbf{q}=\{q_j\}$. Generally, the number of experimentally measured parameters in strong-interaction cases (for which the configuration-coordinate or semiclassical approach obtains) is insufficient to warrant complicating the single-coordinate approach. However, there are situations for which these additional degrees of freedom are necessary. In Sec. 5 we indicated that the Toyozawa-Mahr model of Urbach tails requires at least two independent configuration coordinates. Kleinman[45] has suggested a Raman measurement to determine if discrepancies between the absorption and emission spectra of F centers is a consequence of coordinate dependence in the matrix element M_{ab}.

Lax[4] has emphasized that configuration coordinates are not necessarily coordinates of normal modes of lattice vibration. This is also apparent in our Eqs. (3.34) and (4.15). The coordinates $\mathbf{q}$ in those equations derive from phonon coordinates $\mathbf{Q}_S$ which measure those lattice distortions which interact strongly with the impurity. The dynamics of the operators $\mathbf{Q}_S$ are conspicuous by their absence, since it was precisely the neglect of such dynamics which led us in Sec. 3B to the semiclassical approximation (3.22). Phonon dynamics has relevance to the semiclassical approximation only in so far as it is implicit in the elements of the matrix $\mathbf{\Lambda}$. As Lax has indicated, that limited dependence can readily be reproduced by the introduction of a fictitious temperature-dependent normal mode. To illustrate this fact in our own notation, we can assume with no loss of generality that $\mathbf{\Lambda}$ is diagonal:

$$(\mathbf{\Lambda})_{jk}=\langle Q_j^2\rangle\delta_{jk}=\delta_{jk}\int_0^\infty \frac{d\omega}{2\pi}\rho_{jj}(\omega)[1+2n(\omega)]. \qquad (6.1)$$

[A nondiagonal $\mathbf{\Lambda}$ can be diagonalized by a real orthogonal transformation, which is tantamount to a transformation of the coordinates $\{Q_j\}$ and $\{q_j\}$.] We *define* a parameter C_j and a temperature-dependent configuration frequency $\omega_j(T)$ such that

$$|C_j|^2=\int_0^\infty \frac{d\omega}{2\pi}\rho_{jj}(\omega),$$
$$(\mathbf{\Lambda})_{jj}=|C_j|^2[1+2n(\omega_j(T))]. \qquad (6.2)$$

It follows that in a configuration-coordinate treatment based upon Eq. (3.33) or (4.15) we can view the coordinates $\{Q_j\}$ as fictitious normal-mode coordinates appropriate to vibrations having the impurity coupling constants $\{C_j\}$ and the frequencies $\{\omega_j(T)\}$.[4] If $\rho_{jj}(\omega)$ in Eq. (6.1) is strongly peaked about a single frequency, $\omega_j(T)$ will be only weakly temperature-dependent and approximately equal to that frequency. In all cases $\omega_j(T)$ approaches a well-defined high-temperature limit:

$$\omega_j(T) \xrightarrow[T\gg T_D]{} |C_j|^2\left\{\int_0^\infty \frac{d\omega}{2\pi}\rho_{jj}(\omega)/\omega\right\}^{-1}. \qquad (6.3)$$

Because the semiclassical approximation neglects phonon dynamics except as it indirectly affects the elements of $\mathbf{\Lambda}$, Franck-Condon configuration analyses treat the phonon-impurity interaction as if it were an adiabatic, quasistatic, perturbation of the impurity. The coordinate averages in Eqs. (3.34) and (4.15) are equivalent to time averages over the various dynamic

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[44] G. F. Imbusch, W. M. Yen, A. L. Schawlow, D. E. McCumber, and M. D. Sturge, Phys. Rev. 133, A1029 (1964).

[45] D. A. Kleinman, Phys. Rev. 134, A423 (1964).

excursions of the coordinates. The distinction between such time averages and averages over strictly static random distortions only appears in the temperature dependence of the elements (6.1) of $\mathbf{\Lambda}$. In fact, we can describe the effect on the semiclassical spectra of static, continuously variable, random lattice strains due to imperfections by adding a constant component $\mathbf{\Lambda}^0$ to the matrix $\mathbf{\Lambda}$.[46]

Except in so far as "zero-point motion" introduces a certain minimum (zero-temperature) width into $\mathbf{\Lambda}$, quantum effects are not present in either the Franck-Condon or semiclassical analyses. They do, however, contribute in the weak-interaction analyses of Secs. 3A and 4A. For weak interactions the processes of phonon annihilation and creation which accompany electromagnetic transitions are in a sense so infrequent that the spectra show details which can be associated with the emission or absorption of small discrete numbers of lattice-vibration quanta (phonons). As the strength of the phonon-impurity interaction increases, the greatly increased profusion of these elementary quantum processes smears the detailed features and leads to a semiclassical description in which the gross spectral features are correctly described.

Two features of the detailed weak-interaction (quantum) spectrum are particularly noteworthy for the information they give about the nature of the impurity and the phonon spectra with which it interacts. The first of these is the so-called no-phonon line. Formulas in Secs. 3A and 4A relate properties of that line to the strength of the phonon-impurity coupling [as measured by derivatives of $p(\xi)$] and to certain temperature-dependent integrals of the effective (coupled) phonon spectra $\rho_{jk}(\omega)$. By making certain plausible assumptions about the nature of the phonon-impurity coupling, one can anticipate the temperature dependence of the strength, the width, and the position of the no-phonon line, and thereby gain increased understanding of experimental observations.[25,44] The no-phonon line is also important in the study of symmetry properties of the impurity center, because it does not reflect the often unknown symmetry properties of lattice phonons. (When the matrix element M_{ab} is coordinate-dependent, unique symmetry assignments for the vibrational structure are particularly elusive.) Krupa and Silsbee[47] have recently demonstrated, in experiments which clearly verify the van Doorn model of R-type color centers, that, even when the phonon-impurity interaction is relatively strong a wealth of symmetry information can be extracted from a small residual no-phonon line. Because the no-phonon line reflects the symmetry properties of the dynamically-unperturbed impurity, one might be tempted to identify the position of that line with the location of the unbroadened impurity level in a static lattice. This is not correct.[48] Equations (3.15) and (3.19a) clearly show that levels in static-crystal-field calculations should be identified with the mean frequency of the spectrum and not with the no-phonon line usually near one edge of that spectrum. This distinction is particularly important for broad bands, where the phonon-impurity interaction is strong and the displacement (3.21) of the no-phonon line from the mean frequency is large.

The second important feature of the weak-interaction spectrum is the vibrational structure in a Debye neighborhood of the no-phonon line. As is clear from an expansion of the last exponential in Eq. (3.17b), that vibrational structure reflects the frequency dependence of the combination $\rho_G(\omega)$ of the phonon spectral functions $\rho_{jk}(\omega)$ of (3.5). From the experimental spectrum one can use an electronic computer to extract the spectral function $\rho_G(\omega)$ of Eqs. (3.17)–(3.19).[49] If insufficient additional information is available to separate the individual components $\rho_{jk}(\omega)$ from $\rho_G(\omega)$, it is a reasonable first approximation to assume that only a single-spectral function, $\rho_{11}(\omega)$ say, is different from zero in Eq. (3.5) and that $\rho_{11}(\omega)n(\omega)=\rho_G(\omega)(\partial p/\partial \xi_1)^{-2}$ in Eqs. (3.13) and (3.20).[44] While this procedure is admittedly approximate, it is clearly less arbitrary than an *ad hoc* approximation of the $\rho_{jk}(\omega)$ by Debye spectra having adjustable Debye-frequency cutoffs.[25] The Schwarz inequality will sometimes indicate a bound on the errors involved in the approximation. Another measure of its validity is the degree to which it is able to reproduce the temperature dependence of the width and position of the no-phonon line.[24,44]

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[46] The central limit theorm (Ref. 27, p. 213) applies to continuously variable (*versus* discretely variable) random distributions, which therefore can be described by a Gaussian distribution.

[47] D. C. Krupa and R. H. Silsbee, Phys. Rev. Letters **12**, 193 (1964).

[48] M. H. L. Pryce and W. A. Runciman, Discussions Faraday Soc. **26**, 34 (1958).

[49] The results of such a procedure for the spectrum of Fig. 1 are shown in Fig. 5, Ref. 19.