

crystal is normally considered to be in the $\Gamma^{(4+)}$ electronic state (single Slater determinant with all orbitals doubly occupied), in which the linear term in (1) can be taken to vanish. If a "configurational instability" mechanism applies to these phenomena we must then ask which degenerate state or states are involved and which

normal modes excited. We thereby focus attention on interactions heretofore largely ignored.

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Ground-State Energy of Bound Polarons

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A variational expression for the binding energy of a single electron coupled simultaneously to a Coulomb potential and to a longitudinal optical mode phonon field, is obtained using the Feynman path integral technique. No assumption is made about the strength of the couplings. The binding is explicitly evaluated by numerically minimizing the variational expression for a set of physical parameters which correspond to cadmium sulfide. The effective mass of the electron in the periodic potential is retained as a parameter and is determined by matching the observed binding to the variational result. An effective mass of $0.2m_0$ is found to give good agreement. The results of the variational calculation are found to be consistent with a perturbation treatment of the phonon interaction.

INTRODUCTION

AN electron in the interior of a crystal interacts with its surroundings. In many cases of practical interest the coupling between the electron and the longitudinal optical modes of vibration of the crystal lattice is sufficiently strong so that the usual perturbation techniques do not apply.

In this paper we make use of a variational path integral formulation, similar to the one employed by Feynman,¹ to compute the ground-state energy of a single electron coupled simultaneously to an attractive Coulomb potential and a longitudinal optical mode phonon field. No assumption is made concerning the strength of the coupling. The crystal is treated as a polarizable continuum and the effect of the periodic potential is replaced by an effective mass.

In Sec. I, a variational expression for the energy is obtained and its various limiting forms are discussed. In Sec. II the binding is explicitly evaluated by numerically minimizing the variational expression for a set of physical parameters (high-frequency dielectric constant, low-frequency dielectric constant, and optical-mode phonon frequency), which corresponds to cadmium sulfide. In Sec. III the phonon interaction is treated by the usual weak coupling methods and the equivalent of the nonrelativistic S -state Lamb shift for the electron-phonon field is computed.

I. VARIATIONAL EXPRESSION

The Hamiltonian characterizing the interaction of an infinitely heavy singly charged ion and an electron

¹R. P. Feynman, *Phys. Rev.* **97**, 660 (1955), hereafter to be called *I*.

coupled to a phonon field is taken as

$$H = H_0 + N + H_c + H_I, \quad (1a)$$

with

$$H_0 = \mathbf{P}^2/2, \quad (1b)$$

$$N = \sum_K a_K^\dagger a_K, \quad (1c)$$

$$H_c = -e^2/r\epsilon_\infty, \quad (1d)$$

$$H_I = (V^{-1})ig \sum_K \frac{1}{K} [a_K^\dagger (e^{-i\mathbf{K} \cdot \mathbf{X}} - 1) - a_K (e^{+i\mathbf{K} \cdot \mathbf{X}} - 1)]. \quad (1e)$$

In this expression a_K^\dagger and a_K are the annihilation and creation operators for the phonons. The phonon frequency is assumed to be independent of the wave number. The momentum of the electron is \mathbf{P} and its coordinate is \mathbf{X} ; V is the crystal volume. The ion is assumed localized at the origin; hence the -1 in H_I . Our units are such that \hbar , the frequency of the phonon's ω , and the mass of the electrons m (in the periodic potential), are unity. Conventionally g is defined in terms of a quantity α :

$$g \equiv (2\sqrt{2}\pi\alpha)^{\frac{1}{2}},$$

where α in ordinary units is given by

$$\alpha = \frac{1}{2} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \frac{e^2}{\hbar\omega} \left(\frac{2m\omega}{\hbar} \right)^{\frac{1}{2}},$$

and ϵ_0 , ϵ_∞ are respectively the static and high-frequency dielectric constants of the medium.

By means of the canonical transformation,

$$a_K \rightarrow a_K + ig/K, \quad (2a)$$

$$a_K^\dagger \rightarrow a_K^\dagger - ig/K, \quad (2b)$$

we can eliminate in H_I the term

$$H_2 = -i \frac{g}{\sqrt{V}} \sum_K \frac{1}{K} [a_K^\dagger - a_K].$$

The net effect of the transformation is to add an infinite constant to the Hamiltonian (the infinite self-energy of a static point charge) to eliminate H_e , and to replace $1/\epsilon_\infty$ by $1/\epsilon_0$ in H_c . We will assume throughout this paper that we have made this transformation and have subtracted off the infinite constant. The final Hamiltonian for the problem is then

$$H = H_0 + N + H_c' + H_I', \quad (3a)$$

where

$$H_c' = -e^2/r\epsilon_0 \equiv -\beta/r, \quad (3b)$$

and

$$H_I' = ig(V^{-1/2}) \sum_K \frac{1}{K} [a_K^\dagger e^{-i\mathbf{K} \cdot \mathbf{X}} - a_K e^{i\mathbf{K} \cdot \mathbf{X}}]. \quad (3c)$$

The ground-state energy of the system may be obtained from an expression for the complete propagator, $\exp(iHt)$. In setting up this propagator we integrate out the field oscillators,² assuming that they all are in their ground state, that is to say, at zero temperature and cast the resulting expression into Lagrangian form.¹ With the transition to imaginary time,

$$t \rightarrow it,$$

we find that we must evaluate the sum over all trajectories of the functional, $\exp(S)$, where

$$S = -\frac{1}{2} \int \left(\frac{d\mathbf{X}(t)}{dt} \right)^2 dt + \frac{g^2}{4\pi} \iint \frac{1}{|\mathbf{X}(t) - \mathbf{X}(s)|} \times e^{-|t-s|} dt ds + \int \frac{\beta}{|\mathbf{X}(t)|} dt \quad (4)$$

is the "action" describing the properties of the interacting system.

Feynman¹ shows that in general the true ground-state energy³

$$E_T \leq E \equiv E_1 - s. \quad (5)$$

Here, E_1 is the ground-state energy of a system characterized by the trial functional S_1 . This ground state energy may be found from the asymptotic expression:

$$\lim_{T \rightarrow \infty} \int \exp S_1 \mathcal{D}\mathbf{X}(t) \sim \exp(-E_1 T). \quad (6)$$

² R. P. Feynman, Phys. Rev. 84, 108 (1951).

³ This inequality is only valid for systems characterized by a real action of the form Eq. (4).

Small s is a suitably defined average value of the difference $(S - S_1)$. [See I, Eq. (11).]

$$s = \frac{1}{T} \int (S - S_1) \exp(S_1) \mathcal{D}\mathbf{X}(t) \int \exp(S_1) \mathcal{D}\mathbf{X}(t). \quad (7)$$

We choose as a trial action the following quadratic functional,

$$S_1 = -\frac{1}{2} \int \left(\frac{d\mathbf{X}(t)}{dt} \right)^2 dt - \frac{C}{2} \iint |\mathbf{X}(t) - \mathbf{X}(s)|^2 e^{-W|t-s|} dt ds + \frac{\mathcal{K}}{2} \int [\mathbf{X}(t)]^2 dt. \quad (8)$$

In effect the phonon field has been replaced by another particle of unknown mass bound harmonically to the electron, (the term proportional to C) and the central Coulomb potential has been replaced by the term $(\mathcal{K}\mathbf{X}^2)/2$, a harmonic binding to a fixed point in space.

Since S_1 contains \mathbf{X} only quadratically, all the necessary path integrals are easily performed as in I. The resulting variational expression for the energy is,

$$E = \frac{3}{2}(v_1 + v_2 - W) - \alpha\pi^{-1/2} \int_0^\infty \exp(-y) [G(y)]^{1/2} dy - \frac{3}{4}(v^2 - W^2)/(v_2 + v_1) - 2\beta\pi^{-1/2}(v_1 v_2)(v_1 + v_2)/(v_1 v_2 + W^2) - \frac{3}{4}\mathcal{K}(v_1 v_2 + W^2)/[(v_1 v_2)(v_1 + v_2)], \quad (9)$$

where

$$G(y) = \frac{1}{v_1} \frac{[(W^2 - v_1^2)]}{[(v_2^2 - v_1^2)]} [1 - e^{-v_1 y}] + \frac{1}{v_2} \frac{[(W^2 - v_2^2)]}{[(v_1^2 - v_2^2)]} [1 - e^{-v_2 y}], \quad (10)$$

and

$$v_{1,2}^2 = \frac{1}{2} \{ (v^2 + \mathcal{K}) \pm [(v^2 + \mathcal{K})^2 - 4\mathcal{K}W^2]^{1/2} \}. \quad (11)$$

The quantity v is defined in terms of the parameters W and C as

$$v^2 = W^2 + 4C/W. \quad (12)$$

If we allow β and \mathcal{K} to approach zero, Eq. (9) reduces to

$$E_{\text{free}} = \frac{3}{2}(v - W)^2/v - \alpha\pi^{-1/2} \int \exp(-y) [G(y)]^{1/2} dy. \quad (13)$$

Equation (13) is identical with Eq. (33) of I and thus gives the free polaron binding.

On the other hand if C and α are set equal to zero in (9) we find that

$$E = \frac{3}{4}\mathcal{K}^2 - 2\beta\pi^{-1/2}\mathcal{K}^{1/2}. \quad (14)$$

If (14) is minimized with respect to \mathcal{K} , then

$$E_{\text{min}} = -4\beta^2/(3\pi). \quad (15)$$

This result is precisely the value obtained by fitting the "hydrogen atom" problem by using a Gaussian trial wave function in the usual variational approximation. The Gaussian wave function is an eigenfunction of the model problem, and the "Feynman Variational Principle"⁴ is identical to the usual variational principle for an arbitrary fixed central potential in S_1 . It is approximately 13% higher than the true value $-\beta^2/2$ (in these units).

Unfortunately, as in the case of the free polaron problem, the second term in Eq. (9) cannot be evaluated analytically. However, it is possible to discuss some interesting limiting cases. Consider first the case of vanishingly small β ; in this limit $\mathcal{K} \rightarrow 0$ and we may expand the square root in (11) to obtain an approximate expression for v_1 and v_2 .

$$v_1 \approx v, \quad v_2 \approx (W/v)\mathcal{K}^{1/2}. \quad (16)$$

If subsequently the terms in Eq. (5) are expanded to first order in v_2 (i.e., $\mathcal{K}^{1/2}$), we find

$$E = E_{\text{free}} + \frac{3}{4}v_2\Delta - 2\beta\pi^{-1/2}(v/W)v_2^{1/2}, \quad (17)$$

where

$$\Delta = \left[1 - \frac{\alpha}{3\sqrt{\pi}} \left(\frac{W}{v} \right)^2 \int_0^\infty \frac{y^2 e^{-y} dy}{[G(y)]^{1/2}} + \frac{(v^2 - W^2)}{v^2} \right]. \quad (18)$$

The second two terms in Eq. (17) correspond to the binding energy of our weakly bound polaron. To order β^2 Eq. (17) may be minimized with respect to v_2 using free polaron values for v and W and the result is

$$E - E_{\text{free}} = -(4/3\pi)(v/W)^2(1/\Delta). \quad (19)$$

In the weak coupling polaron limit small α ,

$$E - E_{\text{free}} = -(4/3\pi)\beta^2[1 + \alpha/6 + \mathcal{O}(\alpha^2)], \quad (20)$$

while in the strong coupling polaron limit, large α ,

$$E - E_{\text{free}} = -(4/3\pi)\beta^2[16\alpha^4/(8\pi^4)]. \quad (21)$$

In both cases the weak central potential limit gives us an effective mass correction to the zero order variational fit to the binding.⁵

Secondly we give the expression in the strong central potential limit ($\beta \rightarrow \infty$). In this case $\mathcal{K} \gg v$ and W and we find,

$$E = -(4/3\pi)\beta^2 - (4/3\pi)\beta\alpha - 3(\ln 2)/2\beta - \alpha^2/3\pi + \mathcal{O}(1/\beta^2). \quad (22)$$

II. NUMERICAL EVALUATION OF GROUND-STATE ENERGY

For intermediate values of β and α Eq. (9) must be minimized numerically. A set of parameters correspond-

TABLE I. Results of minimizing the variational expression for the energy.

α	(m/m_e)	$-E/\hbar\omega$	$-E_{\text{free}}/\hbar\omega$	$-E_{\text{ionization}}/\hbar\omega$
0.46	0.1	0.81	0.45	0.36
0.65	0.2	1.37	0.63	0.74
0.79	0.3	1.95	0.78	1.17
2.0	1.9	10.7	2.0	8.7
3.0	4.3	23.4	3.1	20.3
5.0	11.8	64.4	5.4	59.0
7.0	23.4	125.7	8.1	117.6
9.0	38.4	215.7	11.5	204.1

ing to cadmium sulfide were chosen and Eq. (9) was minimized on an IBM 7090 computer using a 15-point Laguerre integration formula for the single numerical integral appearing in the calculation. The binding energy is then a function of ϵ_0 , ϵ_∞ , $\hbar\omega$, and m the effective mass of the electron. The ratio m/m_e , where m_e is the "bare electron mass," was retained as a parameter and the values $\epsilon_0 = 9.1$, $\epsilon_\infty = 5.3$,⁴ and $\hbar\omega = 0.038$ ev were chosen.⁶ The experimentally observed binding is⁷ 0.032 ± 0.002 ev. In conventional units,

$$\beta = (1/\epsilon_0)(27.2/\hbar\omega)^{1/2}(m/m_e)^{1/2}, \quad (23)$$

and

$$\alpha = [(\epsilon_0 - \epsilon_\infty)/(\epsilon_0\epsilon_\infty)](13.6/\hbar\omega)^{1/2}(m/m_e)^{1/2}. \quad (24)$$

The results of the minimization appear in Table I. In all cases W was fixed and the function minimized with respect to the two parameters K and v . The results were insensitive to the values of K and v chosen.

The energy evaluated at $m = 0.2m_e$ seems to be in reasonable (10%) agreement with the experimental value of $0.82 \pm 0.03(\hbar\omega)$. Hypothetically high values of the mass ratio were chosen to determine where the energy started to deviate from linearity. For values of α up to about 2, the binding energy is nearly linear scaling with the bare mass. For values of α larger than two, the magnitude of the binding energy decreases more rapidly; however, it does not decrease nearly as fast as an effective mass correction would indicate. The effective mass gets extremely heavy very rapidly for α above 2 (see Table II). We conclude then that for values of the ratio of β/α of the order of unity and for couplings α of unity or less, there are to within 10% no explicit polaron effects (weak coupling results are valid). The real parameter in the electron phonon coupling is not α but rather $\alpha/6$ or $\alpha/10$ as in the free-

TABLE II. Tabulation of effective mass values.

α	2	3	5	7	9
m_{eff}/m	1.31	1.8	3.8	14.2	62.5

⁴ S. J. Czyzak, W. M. Baker, R. C. Crane, and J. B. Howe, J. Opt. Soc. Am. 47, 240 (1957).

⁵ This is not a self-evident statement. In fact it is probably not true for intermediate values of α . It is true of course that there is an effective mass correction to the exact hydrogenic binding energy for all values of α .

⁶ R. J. Collins, J. Appl. Phys. 30, 1135 (1959).

⁷ W. W. Piper and R. E. Halsted, *Proceedings of the International Conference on Semiconductors Physics, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961), Vol. 2.

polaron case. If the hydrogenic binding energy is small compared with the phonon energy ($\hbar\omega$), then to lowest order in this ratio the bound-polaron system is hydrogenic with the bare mass replaced by the polaron mass. For binding energies of the order of $\hbar\omega$ the results of the variational calculation indicate that use of the effective mass is a good approximation at low α ; however, as we could have expected, it over corrects for a fixed β/α and large α . Crudely speaking, binding to the center is proportional to (m/m_e) whereas the coupling to the phonons is proportional to $(m/m_e)^{1/2}$. The electron in a "tightly bound orbit" has too high a velocity to be characterized by an effective mass. In fact, in the limit of strong central binding it fails to polarize the lattice at all. In this limit one should have a hydrogenic like system characterized by ϵ_∞ and the bare mass of the electron.

III. PERTURBATION TREATMENT OF THE PHONON INTERACTION

In the weak phonon coupling limit the second order energy shift of an S -like hydrogenic state is

$$\Delta E_2 = -\frac{g^2}{(2\pi)^3} \sum_n \int \frac{d^3K}{K^2} \frac{\langle i | e^{-i\mathbf{K}\cdot\mathbf{X}} | n \rangle \langle n | e^{+i\mathbf{K}\cdot\mathbf{X}} | i \rangle}{(E_n - E_i + 1)}. \quad (25)$$

Here E_n are the energies of the hydrogenic intermediate states. The denominator may be expanded as

$$\begin{aligned} \frac{1}{(E_n - E_i + 1)} &= \frac{1}{(1 + K^2/2)} = \frac{(E_n - E_i - K^2/2)}{(E_n - E_i + 1)(1 + K^2/2)}. \end{aligned} \quad (26)$$

The first term in Eq. (26) yields the first-order self-energy of a free polaron and must be subtracted from ΔE_2 to give the shift in the binding. Subtracting this term and expanding the denominator once more we find that

$$\Delta E_2 - E_{\text{free}} = E' + E'',$$

where

$$E' = \frac{g^2}{(2\pi)^3} \sum_n \int \frac{d^3K (E_n - E_i - K^2/2) \langle i | e^{-i\mathbf{K}\cdot\mathbf{X}} | n \rangle \langle n | e^{+i\mathbf{K}\cdot\mathbf{X}} | i \rangle}{K^2(1 + K^2/2)^2}, \quad (27)$$

and

$$E'' = -\frac{g^2}{(2\pi)^3} \sum_n \int \frac{d^3K (E_n - E_i - K^2/2)^2 \langle i | e^{-i\mathbf{K}\cdot\mathbf{X}} | n \rangle \langle n | e^{+i\mathbf{K}\cdot\mathbf{X}} | i \rangle}{K^2(1 + K^2/2)^2 (E_n - E_i + 1)}. \quad (28)$$

E' may be shown to be zero, since

$$\begin{aligned} \sum_n (E_n - E_i) \langle i | e^{-i\mathbf{K}\cdot\mathbf{X}} | n \rangle \langle n | e^{+i\mathbf{K}\cdot\mathbf{X}} | i \rangle \\ = \langle i | [e^{-i\mathbf{K}\cdot\mathbf{X}}, H] e^{+i\mathbf{K}\cdot\mathbf{X}} | i \rangle \\ = \langle i | H(\mathbf{P} + \mathbf{K}) - H(\mathbf{P}) | i \rangle. \end{aligned} \quad (29)$$

Since $\langle i |$ is an S state,

$$\langle i | H(\mathbf{P} + \mathbf{K}) - H(\mathbf{P}) | i \rangle = \langle i | K^2/2 - \mathbf{K} \cdot \mathbf{P} | i \rangle = K^2/2. \quad (30)$$

E'' is negative definite and may be bounded by replacing $E_n - E_i$ in the denominator of Eq. (28) by zero.

$$0 < -E'' < \frac{g^2}{(2\pi)^3} \sum_n \int \frac{d^3K (E_n - E_i - K^2/2)^2 \langle i | e^{-i\mathbf{K}\cdot\mathbf{X}} | n \rangle \langle n | e^{+i\mathbf{K}\cdot\mathbf{X}} | i \rangle}{K^2(1 + K^2/2)^2}. \quad (31)$$

The sum over intermediate states may be done as in the previous case by expressing it as an integral over a double commutator,

$$\begin{aligned} (E_n - E_i - K^2/2)^2 \langle i | e^{-i\mathbf{K}\cdot\mathbf{X}} | n \rangle \langle n | e^{+i\mathbf{K}\cdot\mathbf{X}} | i \rangle \\ = \langle i | (\mathbf{K} \cdot \mathbf{P})^2 | i \rangle. \end{aligned} \quad (32)$$

The result is that

$$0 < -E'' < \beta^2/3. \quad (33)$$

If we expand the denominator once again and neglect terms of order $(E_n - E_i - K^2/2)^4$ we arrive at an expansion in β for the perturbation correction to the ground-

state energy:

$$\begin{aligned} -E'' &\approx \frac{g^2}{(2\pi)^3} \int \frac{d^3K}{K^2(1 + K^2/2)^3} \langle i | (K^2 P^2/3) | i \rangle \\ &+ \frac{g^2}{(2\pi)^3} \int \frac{d^3K}{K^2(1 + K^2/2)}, \\ &\times \left\langle i \left| \frac{K^2}{3} \nabla^2 V(r) - K^2 \frac{\partial V(r)}{\partial r} \frac{\partial}{\partial r} \right| \right\rangle. \end{aligned} \quad (34)$$

For the ground state the integrals are easily evaluated to yield

$$-E'' \approx (\alpha/12)[\beta^2 + \beta^4 + \mathcal{O}(\beta^6)]. \quad (35)$$

The first term is precisely the effective mass correction since $-\beta^2/2 = E_{\text{hydrogen}}$. The second is a Lamb-shift-type correction for the phonon perturbed system. For $\beta < 1$, the "Lamb-shift"-like corrections are small; they are of the order of 10–15% of the hydrogen binding even for α 's of the order of unity. We might have expected, from order-of-magnitude arguments, corrections due to

phonon coupling of the order of the hydrogen binding energy itself.

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Infrared Absorption in Heavily Doped *n*-Type Germanium

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Measurements of the infrared absorption spectrum of compensated and uncompensated heavily doped *n*-type germanium at 80, 200, and 295°K are reported. The edge absorption in the doped samples differs strongly from the edge absorption in pure germanium. Both the indirect and the direct energy gap change with doping. The change depends on the total impurity concentration $N_A + N_D$ approximately as $(N_A + N_D)^{1/2}$. For $N_A + N_D = 4.7 \times 10^{19} \text{ cm}^{-3}$ the change of the indirect gap is about 0.07 ev, the change of the direct gap about 0.06 ev. The absorption due

to indirect transitions rises more rapidly with the photon energy in *n*-type germanium than in pure germanium. This extra absorption is proportional to the free electron concentration and must be due to virtual electron-electron scattering between the $\langle 000 \rangle$ and $\langle 111 \rangle$ valleys.

It is shown that the effective electron density in heavily doped *n*-type germanium is larger than in most metals. The properties of the conduction electrons in germanium with $n > 10^{19} \text{ cm}^{-3}$ correspond to the properties of a dense electron gas ($r_s < 1$).

INTRODUCTION

THE optical properties of very pure germanium have been studied extensively, and a great deal of information on the band structure of this semiconductor has been obtained.^{1,2} Extensive studies have also been made of the energy states associated with impurities in not too large concentrations.³ Recently, the application of tunnel diodes has stimulated interest in the properties of heavily doped semiconductors. A number of optical studies on these "dirty semiconductors" have already been published by Pankove^{4,5,6} and by Cardona.^{7,8}

In a heavily doped *n*-type semiconductor the localized impurity states have disappeared, and the conduction electrons may be regarded as a dense degenerate electron gas perturbed by the presence of charged impurities. Electron-electron interaction in such a situation be-

comes important, giving rise to electron correlation and exchange energies just as in metals. As a result, the one-electron approximation will no longer give an adequate description of the properties of the system.

In this paper we report measurements of the absorption spectrum of heavily doped *n*-type germanium. The results are discussed and some conclusions pertaining to the band structure of heavily doped germanium are drawn.

EXPERIMENTAL PART

Single crystals of *n*-type germanium doped with various impurities were pulled from a melt containing the required dope. Donor and acceptor concentrations N_D and N_A in these crystals were determined by chemical analysis. The free-carrier concentration n was found from the Hall coefficient R_H and the formula $R_H = (en)^{-1}$. The relation $n = N_D - N_A$ was fulfilled in all cases within the experimental error. We remark that heavily doped crystals may contain precipitates and regions with an inhomogeneous impurity distribution as a result of "constitutional supercooling" during crystal growth.⁹ These regions are easily identified by etching. For the optical measurements crystals free from such precipitates were used. The impurity concentration in the crystals used is given in Table I.

⁹ J. A. M. Dikhoff (private communication).

¹ T. P. McLean, *Progress in Semiconductors* (John Wiley & Sons, Inc., New York, 1960), Vol. 5, p. 52.

² B. Lax and S. Zwerdling, *Progress in Semiconductors* (John Wiley & Sons, Inc., New York, 1960), Vol. 5, p. 221.

³ W. Kohn, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 258.

⁴ J. I. Pankove, *Phys. Rev. Letters* 4, 20 (1960).

⁵ J. I. Pankove, *Phys. Rev. Letters* 4, 454 (1960).

⁶ J. I. Pankove, *Ann. phys.* 6, 331 (1961).

⁷ M. Cardona and W. Paul, *Helv. Phys. Acta* 33, 329 (1960).

⁸ M. Cardona and H. S. Sommers, Jr., *Phys. Rev.* 122, 1382 (1961).