Intensity of Optical Absorption by Excitons

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The intensity of optical absorption close to the edge in semiconductors is examined using band theory together with the effective-mass approximation for the excitons. Direct transitions which occur when the band extrema on either side of the forbidden gap are at the same **K**, give a line spectrum and a continuous absorption of characteristically different form and intensity, according as transitions between band states at the extrema are allowed or forbidden. If the extrema are at different **K** values, indirect transitions involving phonons occur, giving absorption proportional to $(\Delta E)^{\frac{1}{2}}$ for each exciton band, and to $(\Delta E)^2$ for the continuum. The experimental results on Cu_2O and Ge are in good qualitative agreement with direct forbidden and indirect transitions, respectively.

1. INTRODUCTION

INSULATING and semiconducting crystals are transparent below a certain photon energy above which the absorption increases rapidly. It has been known for some time that this edge often shows a complicated structure which may take the form of a series of lines. This led Frenkel[1] to introduce the concept of excitons: individual atoms are excited to higher atomic states and this excitation moves through the crystal because of interatomic interactions. More recent work[2] has shown that a complicated structure may exist on the absorption edge in semiconductors. In these substances an alternative theory due to Wannier[3] provides a better description. Band theory is known to provide a good basic description of the electron states: the ground state of the crystal corresponding to all states in the valence bands full, and all those in the conduction bands empty. Light is absorbed in exciting an electron from a full to a vacant band across the energy gap—a process which may be considered as creation of a hole-electron pair. Because of the Coulomb attraction between the pair, a hydrogen-like (or positronium-like) state is formed with smaller energy than that given by band theory. In media of high dielectric constant, where the interaction is weak, this description of an exciton may be carried out in the effective-mass approximation. Impurity states in semiconductors have been treated extensively in this way by Kohn, Luttinger, and others,[4] and Dresselhaus[5] has recently demonstrated the way in which the method may be used for excitons. In the case of strong interaction the hole-electron pairs are confined to a single atom, corresponding to Frenkel's description.

Detailed measurements of the absorption edge in germanium by Macfarlane, McLean, Quarrington, and Roberts[6] show a structure of a different kind which we believe, is also due to excitons. In this substance the maximum in the valence band and the minima in the conduction band have different wave vectors $\mathbf{K}_e^0$ and $\mathbf{K}_h^0$, so that creation of hole-electron pairs of lowest energy are forbidden by momentum-conservation considerations. Hall, Bardeen, and Blatt[7] have shown that such indirect transitions can take place if a phonon of wave vector $\mathbf{K}_e^0-\mathbf{K}_h^0$ is simultaneously created or destroyed. Excitons will be formed with lower energy but those of minimum energy will have a wave vector $\mathbf{K}_e^0-\mathbf{K}_h^0$. Indirect transitions using a phonon can also take place to these states.[8]

The theory of the intensities of both direct and indirect transitions is considered in this paper, the effective-mass approximation being used. As well as the bound exciton states, the effect of the Coulomb interaction on the unbound hole-electron pairs is included. Unfortunately, detailed calculations using the known form of the energy bands in a substance like germanium are exceedingly complex. Quantitative calculations are therefore only carried out on a simple model with spherical bands, but qualitative results can be derived which allow some comparison with experiment and which should be of use in analyzing new data.

2. EXCITON WAVE FUNCTIONS

It is convenient to use the formalism employed by Dresselhaus with some change of notation. The exciton state is expanded in terms of the Bloch functions for the perfect periodic lattice. For this case of weak electron-hole interaction, only the functions belonging to the highest valence and lowest conduction bands need be considered. In fact, for the exciton states of lowest energy which are most prominent spectroscopically, only the band states near the extrema are important. If, however, one or both of the extrema are degenerate, summations over these bands are necessary. For this case the exciton of type n and wave vector **K**

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[1] J. Frenkel, Phys. Rev. **37**, 17, 1276 (1931).

[2] For original references and a review in English of the work of Gross and co-workers in Russia and Nikitine and co-workers in France, see E. F. Gross, Suppl. Nuovo cimento **3**, 672 (1956).

[3] G. Wannier, Phys. Rev. **52**, 191 (1937).

[4] W. Kohn and J. M. Luttinger, Phys. Rev. **97**, 883, **98**, 915 (1955); C. Kittel and A. H. Mitchell, Phys. Rev. **96**, 1488 (1954).

[5] G. Dresselhaus, Phys. Chem. Solids **1**, 14 (1956).

[6] Macfarlane, McLean, Quarrington, and Roberts, Phys. Rev. **108**, 1377 (1957), preceding paper.

[7] Hall, Bardeen, and Blatt, Phys. Rev. **95**, 559 (1954).

[8] This possibility was predicted independently by Dresselhaus.[5]

may be written

$$|\mathbf{K},r\rangle=\sum_{\mathbf{K}_e,\mathbf{K}_h,j,j'}\Psi_{\mathbf{K}_e,\mathbf{K}_h,j,j'}{}^{\mathbf{K},n}|\mathbf{K}_e,j;\mathbf{K}_h,j'\rangle, \tag{2.1}$$

where the state on the right has an electron with $\mathbf{K}_e$ in conduction band j and Bloch function $\psi_{\mathbf{K}_e,j}(\mathbf{r}_e)$ and a hole with $\mathbf{K}_h$ in valence band j', i.e., an electron missing with Bloch function $\psi_{-\mathbf{K}_h,j'}(\mathbf{r}_h)$. The states involved are restricted by the relation

$$\mathbf{K}_e+\mathbf{K}_h=\mathbf{K}. \tag{2.2}$$

The Fourier transform of $\Psi_{j,j'}{}^{\mathbf{K},n}$ may be written

$$\Phi_{j,j'}=(NB)^{-\frac{1}{2}}e^{i\mathbf{K}\cdot\mathbf{R}}\phi_{j,j'}{}^{\mathbf{K},n}(\mathbf{r}), \tag{2.3}$$

where $\mathbf{R}$ is the mean hole-electron position, $\mathbf{r}$ the relative position

$$\mathbf{R}=\tfrac{1}{2}(\mathbf{r}_e+\mathbf{r}_n)\quad \mathbf{r}=(\mathbf{r}_e-\mathbf{r}_h), \tag{2.4}$$

B is the volume of a unit cell, N the number of such cells in the crystal. Equation (2.3) represents the wave function of the exciton's over-all motion in the crystal. Superimposed upon this is a modulation produced by the atom cores. This effect is included by the Bloch functions in (2.1).

The effective-mass approximation gives (2.3) as a solution of a Schrödinger-like equation,

$$[\mathcal{H}_e(\mathbf{p}+\tfrac{1}{2}\mathbf{P}-\mathbf{p}_e{}^0)+\mathcal{H}_h(-\mathbf{p}+\tfrac{1}{2}\mathbf{P}-\mathbf{p}_h{}^0)+V(r)]\Phi =E\Phi. \tag{2.5}$$

Here $\mathbf{p}$, $\mathbf{P}$ are the momenta conjugate to $\mathbf{r}$, $\mathbf{R}$; and $\mathbf{p}_e{}^0$, $\mathbf{p}_h{}^0$ are $\hbar$ times $\mathbf{K}_e{}^0$ and $\mathbf{K}_h{}^0$, the wave vectors at the band extrema. $\mathcal{H}_e$ and $\mathcal{H}_h$ are obtained by writing the energy relations in these bands which are quadratic functions of the momenta $\hbar(\mathbf{K}-\mathbf{K}^0)$ in operator form. With degenerate bands, (2.5) becomes a set of simultaneous differential equations for the $\Phi_{jj'}$. $V(r)$ is the electron-hole interaction $-e^2/\epsilon r$, where ϵ is the dielectric constant.

It is sometimes convenient to transform (2.3) in this general case to

$$\Phi=\exp[i(\mathbf{K}_e{}^0+\mathbf{K}_h{}^0)\cdot\mathbf{R}]e^{i\mathbf{K}'\cdot\mathbf{R}} \times\exp[\tfrac{1}{2}i(\mathbf{K}_e{}^0-\mathbf{K}_h{}^0)\cdot\mathbf{r}]\phi'(\mathbf{r})/(NB)^{\frac{1}{2}}, \tag{2.6}$$

so that the equation for $e^{i\mathbf{K}'\cdot\mathbf{R}}\phi'(\mathbf{r})$ is the same as that which would hold if the two extrema were at $\mathbf{K}=0$.

A simple case which will be examined in some detail, since it has a well-known analytic solution, is that of two spherical single bands with effective masses m_e and m_h, which has the same equation (2.1) as in the hydrogen atom case. It is convenient to write the solution in a form slightly different from (2.3), namely

$$\Phi=\exp(i\mathbf{K}\cdot\boldsymbol{\varrho})H_n(r)/(NB)^{\frac{1}{2}}, \tag{2.7}$$

where $\boldsymbol{\varrho}$ is the coordinate of the center of mass,

$$\rho\equiv(m_e\mathbf{r}_e+m_h\mathbf{r}_h)/(m_e+m_h).$$

For the bound states, H_n is the normalized hydrogen-atom function with reduced mass $\mu=m_em_h/(m_e+m_h)$ and effective charge ϵ^{-1}. The energy

$$E=\frac{\hbar^2K^2}{2(m_e+m_h)}-\frac{\mu e^4}{2\hbar^2\epsilon^2n^2}=\frac{\hbar^2K^2}{2M}-\frac{G}{n^2}, \tag{2.8}$$

and the effective "Bohr" radius is

$$a=\hbar^2\epsilon/\mu e^2. \tag{2.9}$$

For the unbound states H_n is given by a Coulomb wave function which apart from the usual normalized spherical harmonic has radial dependence,[9] for angular momentum l,

$$R=e^{\frac{1}{2}\pi\alpha}|\Gamma(l+1-i\alpha)|(2kr)^l \times e^{ikr}F(-i\alpha+l+1;2l+2;-2ikr)/ (NB)^{\frac{1}{2}}(2l+1)!, \tag{2.10}$$

where the energy of relative motion $E=\hbar^2k^2/2\mu$, F is a hypergeometric function, and $\alpha=(G/E)^{\frac{1}{2}}$.

3. DIRECT TRANSITIONS

The transition probability per unit time in an energy density of incident radiation given by $\rho(\nu)$ as a function of frequency ν, is

$$\frac{1}{\hbar\nu^2}|\langle 0|\sigma|\mathbf{K},n\rangle|^2\delta(E_0-E_{\mathbf{K},n}+h\nu)\rho(\nu) \tag{3.1}$$

between the ground state and excited state $|\mathbf{K},n\rangle$. Here $\sigma=e^{i\mathbf{q}\cdot\mathbf{r}}\boldsymbol{\xi}\cdot\mathbf{j}$, where $\mathbf{j}$ is the current operator acting on electron states, and $\mathbf{q}$, $\boldsymbol{\xi}$ are the photon wave and polarization vectors. For the linear combination (2.1) of hole-electron pair states,

$$|\langle 0|\sigma|\mathbf{K},n\rangle| =\left[\sum_{\mathbf{K}_e,\mathbf{K}_h,j,j'}\Psi_{\mathbf{K}_e,\mathbf{K}_h,j,j'}{}^{\mathbf{K},n}\int\psi_{\mathbf{K}_e,j}{}^*e^{i\mathbf{q}\cdot\mathbf{r}}\frac{ie\hbar}{m}\boldsymbol{\xi}\cdot\boldsymbol{\nabla}\psi_{-\mathbf{K}_h,j'}\right]. \tag{3.2}$$

Because of momentum conservation we have effectively $\mathbf{K}_e=-\mathbf{K}_h$ so that the only transitions which can take place are to $\mathbf{K}=0$. There will therefore be a line spectrum from the $\mathbf{K}=0$ states of the exciton bands, followed by a continuous absorption. The f values for the lines are given by

$$f_n=\frac{2m}{he^2\nu}|\langle 0|\sigma|0,n\rangle|^2. \tag{3.3}$$

In the continuous absorption a sum over the quantum numbers n describing the relative motion [which are here conveniently taken as $\mathbf{k}$ and l as in (2.10)], gives

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[9] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), second edition, p. 52.

an absorption coefficient

$$\kappa=\frac{2\pi}{\nu c}|\langle 0|\sigma|0,n\rangle|^2 s_n(E), \tag{3.4}$$

where s_n is the density of states $|0,n\rangle$ per unit energy range at energy E.

There are two cases which will be considered separately.

(a) Allowed Transitions

In this case the integral in (3.2) is finite when $\mathbf{K}_e$ represents the band edge, which for convenience we take at the center of the Brillouin zone. Since only a small range of $\mathbf{K}_e$ is important in the sum (3.2), it may be assumed as a first approximation that the integrals are independent of $\mathbf{K}_e$. It is convenient to write

$$\langle 0,j|\sigma|0,j'\rangle=2\pi\nu e\mathbf{x}_{jj'}\cdot\xi, \tag{3.5}$$

where in the tight-binding approximation $ex_{jj'}$ is the dipole moment between the atomic functions which make up the Bloch functions in bands j and j'. It will always be of the order of magnitude of an atomic dipole moment.

Equation (3.2) therefore becomes

$$\begin{aligned}\langle 0|\sigma|0,n\rangle&=\sum_{\mathbf{K},j,j'}2\pi\nu e\mathbf{x}_{jj'}\cdot\xi\Psi_{\mathbf{K},-\mathbf{K},j,j'}\\&=\sum_{jj'}2\pi\nu e\mathbf{x}_{jj'}\cdot\xi(NB)^{\frac{1}{2}}\phi_{j,j'}{}^{0,n}(0),\end{aligned} \tag{3.6}$$

where we have used definition (1.3). Considering unpolarized radiation, we obtain

$$f_n=NBg|\textstyle\sum_{jj'}x_{jj'}\phi_{jj'}{}^{0,n}(0)|^2, \tag{3.7}$$

where $gx_{jj'}{}^2$ is the f value of a transition with dipole moment $ex_{jj'}$.

For the simple case of two spherical bands of masses m_e and m_h, $\phi(0)$ is nonzero only for s states, where

$$|\phi^{0,n}(0)|^2=(\pi a^3n^3)^{-1}. \tag{3.8}$$

A series of lines is therefore predicted at energy

$$h\nu=E_{\text{gap}}-G/n^2, \tag{3.9}$$

with intensity falling like n^{-3}. The f value per atom in the first line is of order (atomic radius/exciton radius)^3. As the absorption edge is approached, the infinite number of lines will overlap so that it may be considered as a continuum. The density of states is

$$\frac{1}{B}\left(\frac{\partial E}{\partial n}\right)^{-1}=\frac{G^{\frac{1}{2}}}{2BE^{\frac{3}{2}}}\quad(E=E_{\text{gap}}-h\nu)$$

giving

$$\kappa=8\pi^2N\nu x^2\epsilon/a^2c, \tag{3.10}$$

independent of energy.

In the true continuum where $h\nu-E_{\text{gap}}=E>0$, one obtains from (2.10):

$$|\phi(0)|^2=\frac{\pi\alpha e^{\pi\alpha}}{(NB)\sinh(\pi\alpha)}, \tag{3.11}$$

and

$$s(E)=(NE^{\frac{1}{2}}/2\pi^2)(2\mu/\hbar)^{\frac{3}{2}},$$

so that

$$\kappa=8\pi^2N\nu e^2x^2\alpha e^{\pi\alpha}(2\mu)^{\frac{3}{2}}E^{\frac{1}{2}}/c\hbar^3\sinh(\pi\alpha). \tag{3.12}$$

This is continuous with the exciton absorption at $E=0$ when $\alpha\rightarrow\infty$. For $E\gg G$ where $\alpha\rightarrow 0$, κ becomes proportional to $E^{\frac{1}{2}}$ in agreement with the calculation of Hall, Bardeen, and Blatt[7] who neglected the electron-hole interactions.

(b) Forbidden Transitions

In this case the integral in (3.2) is zero at $\mathbf{K}_e=0$ but for small values of $\mathbf{K}$ will be proportional to K.

$$\langle\mathbf{K},j|\sigma|\mathbf{K},j'\rangle=2\pi\nu e(\xi\cdot\mathbf{K})x_{jj'}{}^2, \tag{3.13}$$

where x^2 is a quantity which is roughly the square of the atomic radius. Therefore

$$\begin{aligned}\langle 0|\sigma|0,n\rangle&=\sum_{\mathbf{K},j,j'}2\pi\nu e(\xi\cdot\mathbf{K})x_{jj'}{}^2\Psi_{\mathbf{K},-\mathbf{K},j,j'}{}^{0,n}\\&=\sum_{jj'}2\pi\nu ex_{jj'}{}^2\frac{\partial\phi_{jj'}{}^{0,n}(0)}{\partial r_\xi},\end{aligned} \tag{3.14}$$

when one uses definition (1.3). The gradient of ϕ at the origin is taken in the direction of polarization. For unpolarized incident radiation, therefore,

$$f_n=NBg\left|\sum_{jj'}x_{jj'}{}^2\frac{\partial\phi_{jj'}{}^{0,n}(0)}{\partial r}\right|^2, \tag{3.15}$$

where $gx_{jj'}{}^2$ is the f value of an atomic transition with dipole moment $ex_{jj'}$.

For the simple hydrogenic model used before,

$$\left|\frac{\partial\phi^{0,n}(0)}{\partial r}\right|^2=\frac{n^2-1}{3\pi n^5a^5}, \tag{3.16}$$

only p states giving a nonzero result. A series of exciton lines thus occurs at energies (3.9) except that the first line is now missing. For small values of n, the intensity does not fall off so rapidly as in case (a). The f values are smaller, being of the order of (atomic radius/exciton radius)^5 per atom. At large n values the lines overlap to give a continuum with

$$\kappa=(8\pi^2N\nu x^4\epsilon/3a^4c)[1+(h\nu-E_{\text{gap}})/G]. \tag{3.17}$$

In the true continuum, where $h\nu-E_{\text{gap}}=E>0$, we have from (2.10)

$$\left|\frac{\partial\phi(0)}{\partial r}\right|^2=\frac{\pi_\alpha(1+\alpha^2)e^{\pi\alpha}k^2}{3NB\sinh(\pi\alpha)}, \tag{3.18}$$

so that

$$\kappa=8\pi^2 N\nu e^2 x^4(1+\alpha^2)\alpha e^{\pi\alpha}(2\mu)^{\frac{5}{2}}E^{\frac{3}{2}}/3c\hbar^3 \sinh\pi\alpha. \tag{3.19}$$

This is again continuous with (3.17) and varies like $E^{\frac{3}{2}}$ well away from the edge, in agreement with reference 7.

The spectrum is on the whole weaker by the factor (atomic radius/exciton radius)^2 than in case (a).

(c) Discussion

In an actual crystal the spectrum may be expected to differ in detail from the simple model calculated above. In the case of degeneracy at one band edge the exciton states will also be degenerate and ϕ will be a solution of a more complicated equation. It may, however, be expected that there will be two classes of exciton spectra corresponding to the two cases given above.

This broad classification does seem to have some application in practice although no f values have been reported in the literature to the author's knowledge. HgI_2, PbI_2 for example have one very intense line.[10] Cuprous oxide,[2] on the other hand, agrees very well with the theory of the second kind. Two exciton series have been reported arising from a near degeneracy in either of the bands. Just such a small splitting of otherwise degenerate bands may be caused by spin-orbit coupling.[11] If the highest valence-band edge has wave functions built from triply degenerate d functions, this splitting will be $\frac{3}{2}\lambda$ (where λ is the spin-orbit coupling constant), giving a single band higher and a doubly-degenerate one lower. In atomic Cu^{++},[12] $\lambda=828$ cm^{-1} giving reasonable agreement with the observed splitting of 1050 cm^{-1}.

At the center of the zone in this cubic crystal single bands are spherical, and the conduction band is presumably single (probably a Cu s band). The low-energy (yellow) series should therefore be correctly treated by a hydrogen-like model and indeed the exciton series agrees to within experimental error with

$$h\nu=E_{\text{gap}}-(G/n^2),$$

for $n=2, 3\cdots 9$. The $n=1$ line is however very weak while the intensity of the others appears in qualitative agreement with (3.16) on the evidence of the figure given by Apfel and Hadley.[13] Thus the picture of forbidden transitions gives good agreement and it would be interesting to see if the absorption coefficient on the edge has the predicted $E^{\frac{3}{2}}$ dependence. The higher energy (green) series has a similar behavior. If the above interpretation of the band splitting is correct, the excitons should have a double degeneracy like the valence band. The energy surfaces in this band must however be nearly spherical, although in principle "fluting" would be allowed as observed[14] in the valence bands of Si and Ge. The weak $n=1$ line is at considerably lower energy than the hydrogen model predicts. This is paralleled by a similar effect in impurity states,[4] and is due to the breakdown of the effective-mass approximation at small r where $V(r)$ is no longer slowly varying. The effect is appreciable only in s states where $\phi(0)$ is large. Other weak lines observed by Gross may be other s states, but it seems that the exciton spectrum of Cu_2O is actually more complex than the above model predicts in spite of the excellent agreement with the predominant features.

Germanium would provide an interesting case of the first kind since the lowest energy *direct* transitions occur probably at $\mathbf{K}=0$ and are allowed according to theoretical predictions.[15] The experiment is difficult since the main line is only about 5×10^{-3} ev away from the continuum, but preliminary measurements at R.R.E. indicate that the absorption rises here much more rapidly than $E^{\frac{1}{2}}$.

4. INDIRECT TRANSITIONS

Transitions to exciton states with $\mathbf{K}\neq 0$ may take place with simultaneous creation or destruction of a phonon. The transition probability (3.1) is now proportional to

$$\left|\sum_i \frac{\langle 0;\, n_{\mathbf{K}}|\sigma|0,i;\, n_{\mathbf{K}}\rangle\langle 0,i;\, n_{\mathbf{K}}|\mathcal{H}_p|\mathbf{K},n;\, n_{\mathbf{K}}\pm 1\rangle}{E_f-E_{0,\,i}}\right|^2 \times\delta(E_{\mathbf{K},\,n}-E_0\pm\hbar\omega_{\mathbf{K}}-h\nu), \tag{4.1}$$

where the sum is over all intermediate states. $\mathcal{H}_p$ is the electron-phonon interaction operator which changes the phonon population number $n_{\mathbf{K}}$ by one. The alternative signs refer to creation and destruction. Momentum conservation in the second matrix element restricts the phonons taking part to have wave vectors $-\mathbf{K}$ in creation and $\mathbf{K}$ in destruction.

Expanding the states in Bloch functions as in (2.1) the second matrix element may be written

$$\sum_{\mathbf{q},j'',j'''} \Psi_{\mathbf{q},-\mathbf{q},j'',j'''}{}^{0,i} \times[\Psi_{\mathbf{q},\mathbf{K}-\mathbf{q},j'',j'}{}^{\mathbf{K},n}\langle -\mathbf{q},j'''|\mathcal{H}_p|\mathbf{K}-\mathbf{q},j'\rangle +\Psi_{\mathbf{K}+\mathbf{q},-\mathbf{q},j,j'''}{}^{\mathbf{K},n}\langle \mathbf{q},j''|\mathcal{H}_p|\mathbf{K}+\mathbf{q},j\rangle], \tag{4.2}$$

since the phonon interaction operator has a similar form for all electrons and therefore can change either the hole or the electron state but not both simultaneously.

Exact calculations of (3.1) are clearly quite complicated and it is convenient at this stage to make approximations and consider a more specific model. We assume the maximum in the valence band is at $\mathbf{K}=0$ and is doubly degenerate, the minimum in the conduc-

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[13] J. Apfel and L. N. Hadley, Phys. Rev. **100**, 1689 (1955).

[14] Dresselhaus, Kip, and Kittel, Phys. Rev. **98**, 368 (1954); Dexter, Zeiger, and Lax, Phys. Rev. **104**, 637 (1956).

[15] F. Herman, Physica **20**, 801 (1954).

tion band at $\mathbf{K}=\mathbf{K}_0$ and nondegenerate. The lowest exciton states will therefore have $\mathbf{K}=\mathbf{K}_0$ and for consideration of the band edge we are concerned only with states of $\mathbf{K}$ close to this value. For weak electron-hole interaction such states are built predominantly from hole and electron states close to the extrema. Therefore $\Psi_{\mathbf{K}_e,\mathbf{K}_h;j;j'}{}^{\mathbf{K},n}$ are only large if $\mathbf{K}_e\sim\mathbf{K}_0$, $\mathbf{K}_h\sim 0$; $j=c_0$ and $j'=v_1$, v_2 enumerating the bands.

To calculate the summation over intermediate states in (4.1) the energy denominator is neglected for the moment. The intermediate states can therefore be chosen to be simple hole-electron pairs for specific pairs of bands and the first Ψ in (4.2) is unity. Because of the form of $\Psi^{\mathbf{K},n}$ only intermediate states with pairs of $\mathbf{K}\sim 0$ or $\mathbf{K}\sim K_0$ give an appreciable contribution. For each of these groups of pairs the energy denominator will not vary greatly, and it may be considered constant—so justifying its neglect in the summation. Only those groups of pairs for which optical transitions are allowed will give an important effect so that the first matrix element in (4.1) may be considered constant for each group, and from (3.5) is put equal to

$$2\pi\nu e x_{cv}{}^{0} \quad\text{and}\quad 2\pi\nu e x_{cv}{}^{\mathbf{K}_0} \tag{4.3}$$

for pairs in valence band v, conduction band c at point 0 and $\mathbf{K}_0$, respectively. The second matrix element may also be considered roughly constant over these small regions. Considering for simplicity only phonon destruction

$$\langle 0,c|\mathcal{H}_p|\mathbf{K},c_0\rangle \simeq A_{cc_0} n_{\mathbf{K}_0}{}^{\frac{1}{2}} \tag{4.4}$$

$$\langle \mathbf{K},v|\mathcal{H}_p|0,v_l\rangle \simeq B_{vv_l} n_{\mathbf{K}_0}{}^{\frac{1}{2}} \tag{4.5}$$

where l denotes the two valence bands v_1 and v_2. Creation processes are obtained by replacing $n_{\mathbf{K}_0}{}^{\frac{1}{2}}$ by $(n_{\mathbf{K}_0}+1)^{\frac{1}{2}}$. Thus the summation in (4.1) becomes a summation over bands and the matrix element is

$$\sum_{l=1,2}\left[\sum_c \frac{A_{cc_0}x_{cv_l}{}^{0}}{E_c(0)-E_{c0}(\mathbf{K}_0)}+\sum_v \frac{B_{vv_l}x_{c_0v}{}^{\mathbf{K}_0}}{E_{v_l}(0)-E_v(\mathbf{K}_0)}\right] \times n_{\mathbf{K}_0}{}^{\frac{1}{2}}\sum_q \Psi_{\mathbf{q},\mathbf{K}-\mathbf{q},c_0,v_e}{}^{\mathbf{K},n}. \tag{4.6}$$

The first sum represents creation of hole-electron pairs at $\mathbf{K}=0$ and scattering of the electron to $\mathbf{K}=\mathbf{K}_0$; the second represents creation of pairs at $\mathbf{K}_0$ and scattering of the hole to $\mathbf{K}=0$.

Thus in this approximation, when the sum of $\mathbf{q}$ is performed as in (3.6), the matrix element can be written

$$\Sigma_l C_l \phi_{c_0v_l}{}^{\mathbf{K},n}(0) n_{\mathbf{K}_0}{}^{\frac{1}{2}}, \tag{4.7}$$

where C_l represent the complicated factors in (4.6).

Indirect transitions to exciton states give rise to a continuous absorption since phonons may be found to give transitions to all $\mathbf{K}$ values. For the simple case of nondegenerate bands on both sides of the gap, the resultant formulas are simple. There is only one term in (4.7) and $\phi'(0)$ as defined in (2.6) is independent of $\mathbf{K}$. The density of states in a single exciton band is

$$\left(\frac{2M_n}{\hbar^2}\right)^{\frac{3}{2}}[E_{\text{ex}}{}^{n}(\mathbf{K}-\mathbf{K}_0)]^{\frac{1}{2}}, \tag{4.8}$$

where M_n is the "density of states" effective mass. The resulting absorption is proportional to

$$D(2M_n/\hbar^2)^{\frac{3}{2}}|\phi'(0)|^2(h\nu-E_{\text{gap}}+E_{\text{ex}}{}^{\mathbf{K}_0,n}\pm\hbar\omega_{\mathbf{K}_0})^{\frac{1}{2}} \times(n_{\mathbf{K}_0}+\tfrac{1}{2}\pm\tfrac{1}{2}) \tag{4.9}$$

for phonon destruction and creation, respectively. Thus there are two contributions beginning at different energies and with a different temperature dependence given by

$$n_{\mathbf{K}_0}=[\exp(\hbar\omega_{\mathbf{K}_0}/kT)-1]^{-1}. \tag{4.10}$$

Each branch of the phonon spectrum will give a contribution with a different intensity, determined by the different phonon matrix elements occurring in C, and with a different $\omega_{\mathbf{K}_0}$.

The simple assumption of spherical bands centered at $\mathbf{K}=0$ and $\mathbf{K}_0$ is not so realistic in this case since even in a cubic crystal the band at $\mathbf{K}_0$ will be anisotropic. Nevertheless, it will be used to give an indication of some of the effects because of its analytical simplicity. The contribution from each exciton band has relative magnitude given by $|\phi'(0)|^2\propto n^{-3}$ [see (3.8)], and begins at energies $E_{\text{gap}}-G/n^2\mp\hbar\omega_{\mathbf{K}_0}$. After the first few have been superimposed, the total absorption is

$$\sim(G+E)^{\frac{3}{2}}/3G, \qquad E<0 \tag{4.11}$$

$$[(G+E)^{\frac{3}{2}}-E^{\frac{3}{2}}]/3G, \qquad E>0 \tag{4.12}$$

where $E=h\nu-E_{\text{gap}}\pm\hbar\omega_{\mathbf{K}_0}$. The first exciton band alone gives a contribution proportional to $(G+E)^{\frac{1}{2}}$ as may be obtained from (4.9).

Beyond the series limit, i.e., for $E>0$, there is further absorption from the continuum. Using (4.7) and (2.10) the absorption coefficient is obtained by summing contributions proportional to (3.11) over all values of the relative motion $\mathbf{k}$ and over all motion $\mathbf{K}$ subject to the restriction

$$\hbar^2K^2/2M+\hbar^2k^2/2\mu=E. \tag{4.13}$$

If we change variables to E and $X=\hbar^2K^2/2M-\hbar^2k^2/2\mu$, the absorption coefficient is

$$\kappa=D\int_0^E \frac{\pi\alpha e^{\pi\alpha}n_{\mathbf{K}_0}}{\sinh\pi\alpha}\left(\frac{2(m_em_h)^{\frac{1}{2}}}{\hbar^2}\right)^3(E^2-X^2)^{\frac{1}{2}}dx, \tag{4.14}$$

where $\alpha=G(E-X)^{\frac{1}{2}}$. If $E\gg G$, the first factor is unity and the usual result for pairs is reproduced:

$$\kappa=D(n_{\mathbf{K}_0}+\tfrac{1}{2}\pm\tfrac{1}{2})\left(\frac{2(m_em_h)^{\frac{1}{2}}}{\hbar^2}\right)^3 \times(h\nu-E_{\text{gap}}\pm\hbar\omega_{\mathbf{K}_0})^2. \tag{4.15}$$

At general E the integral (4.14) has no analytic solution, but as E tends to zero it has a linear dependence.

For an actual crystal it is probably not valid to use this simple theory to give anything but crude estimates of $|\phi(0)|^2$ (the probability of electron and hole being on the same atom) and the density of states.

In general, the form of the absorption edge will begin like $(E+G)^{\frac{1}{2}}$ for each phonon contribution, have a rather complicated dependence when $E\sim 0$ and become like E^2 when $E\gg G$. At large E, however, the result will be affected by second-order effects neglected in the preceding calculations.

For degenerate bands, however, the form of the absorption is more difficult to predict, since the energies of the exciton bands will not be given even approximately by the above model and $\phi(0)$ will not be independent of $\mathbf{K}$. Thus the initial $(E+G)^{\frac{1}{2}}$ law will only hold when $(E+G)\ll G$. The E^2 will hold as before at larger E.

Indirect transitions may also take place if the extrema are at the same $\mathbf{K}$ values, producing weak continuous absorption beginning close to the energy of the direct transition line and increasing with photon energy.[16]

5. DISCUSSION

Macfarlane *et al.*[6] have observed structure in detailed examination of the absorption in germanium which may be interpreted in the light of these results. There are two contributions to the spectrum arising from each of two phonon branches. The exciton energies so determined, about 5×10^{-3} ev are in rough agreement with a spherical band model with mean effective masses substituted.

In the general theory developed above, it was shown that in principle all phonon branches should give a contribution so that if the extrema in Ge were at general points in $\mathbf{K}$ space there would be six. The evidence of cyclotron resonance[14] shows that the valence-band maximum is at $\mathbf{K}=0$, and the conduction-band minima in the (111) directions. The actual position of these minima was uncertain. When one uses[6] the new accurate measurement of energy gap, the intrinsic conductivity indicates that the minima are at the edge of the zone at point L. The occurrence of only two phonon effects is further strong evidence for this.

A selection rule can be obtained using group-theoretical arguments showing which phonons can actually scatter the electrons and holes in the required way. The argument can be stated simply in this case since the wave functions at L have parity with respect to the inversion operation in the unit cell. Herman's[15] theoretical calculation of the band structure indicates that the wave functions at these minima transform like irreducible representation L_1^+ (L_6^+ if spin-orbit effects are included[11]) of the group of L. The wave functions at the valence band maximum are also even, transforming like Γ_8^+. A hole-electron pair created by a photon must have odd over-all parity so that the intermediate state in (4.1) must have odd parity. But the final electron-hole pair has even parity $L_6^+\times\Gamma_8^+$ so the phonon interaction must change the parity of the state. Only the longitudinal and degenerate transverse acoustic phonons which transform like L_2^-, L_3^- can do this—the optical modes are even. The exciton functions also transform according to L and this selection rule thus holds for them as well as for simple pairs. The selection rule is relaxed away from the actual extrema, but transition probabilities are still zero to first order in the preceding theory. If the minima were away from the edge the optical modes could take part; for example, in Si four phonon effects are to be expected.

It has not been possible to make detailed calculations of the absorption expected for germanium, because of the complicated form of Eq. (2.5) arising from the degenerate valence bands, but qualitatively it agrees with the theory discussed above. The two contributions from the longitudinal phonons begin like $(\Delta E)^{\frac{1}{2}}$ and vary like E^2 at larger E values, exactly as predicted. The contributions from the transverse phonons are weaker, and the exciton contribution is weaker relative to the continuum than it is in the longitudinal case. For single bands these contributions have the same relative intensity [see (4.9) and (4.15)], but if there is degeneracy this is no longer true. The relevant factor in the theory is $|\sum_{l=1,2}C_l\phi_{c0vl}{}^{\mathbf{K},n}(0)|^2$ from (4.7). The C_l are different for each phonon species and the weighting in the continuum $C_1^2+C_2^2$ is therefore different than that for the exciton.

The energy dependence of the transverse phonon contributions is also different being roughly $(\Delta E)^{\frac{3}{2}}$. This is possible theoretically if (4.7) is very small when $\mathbf{K}=\mathbf{K}_0$ so that the major contribution is proportional to $\mathbf{K}-\mathbf{K}_0$. No group-theoretical selection rule seems possible to give this result and it must be attributed to a numerical effect which can only be checked by detailed calculation. In general all contributions should begin like $(\Delta E)^{\frac{1}{2}}$, and this appears to be the case in silicon from preliminary results of Macfarlane *et al.*

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[16] This is in disagreement with a contention of Dresselhaus[5] that this mechanism produces a line width.