PHYSICAL REVIEW VOLUME 106, NUMBER 1 APRIL 1, 1957

Absorption Coefficients for Exciton Absorption Lines*

G. Dresselhaus†
Department of Physics, University of California, Berkeley, California

(Received November 26, 1956)

The absorption coefficient for excitons is calculated in the effective-mass approximation. The coefficient is shown to be decreased over what one would expect for a collection of free atoms by the factor $\epsilon^{-1}(a_0/a_B)^3$, where ϵ is the dielectric constant and a_0/a_B is the ratio of the lattice constant to the exciton radius. This result seems not inconsistent with the identification of the observed absorption lines in Cu_2O, CdS, HgI_2, PbI_2, and CdI_2 as exciton lines.

I. INTRODUCTION

The optical spectra of a number of insulating solids[1] have revealed sharp absorption lines located near the absorption band edge. These lines have been interpreted by observers as being associated with exciton formation. Unfortunately, most crystals exhibiting these spectra are rather impure, and hence it is difficult to rule out the possibility that impurity atoms or other crystalline defects may be the cause of the absorption lines. An estimate of the absorption coefficients for exciton lines is given below. It is shown that the experimental values are not incompatible with the identification of the observed lines as being due to the optical formation of excitons.

Two formulations of the exciton problem exist in the literature. The original Frenkel-Peierls treatment[2] considers the electronic excitation as a superposition of atomic excitations at the various lattice sites in the crystal. The absorption coefficient associated with the Frenkel-Peierls formulation of the exciton problem is given by Seitz[3] and is identical with that which one would obtain from a collection of free atoms. A treatment of the exciton problem in terms of effective particles was first given by Wannier. The Wannier or effective-mass approximation has recently been extended[4] to include degenerate bands and the energy band extrema located at general positions in the Brillouin zone. The present paper contains a calculation of the absorption coefficient for exciton formation in the Wannier approximation. The coefficient is shown to be reduced from that obtained for a collection of free atoms by the ratio $(a_0/a_B)^3$, where a_0 is the lattice constant and a_B is a measure of the radius of the exciton. The reduction of the absorption coefficient for weakly bound excitons was first discussed by Slater and Shockley[5] for an exciton in a one-dimensional lattice.

II. THEORY

An exciton at wave vector $\mathbf{K}$ is formed from a wave packet in wave vector space of electron and hole states with wave vector $\mathbf{k}_e$ and $\mathbf{k}_h$ such that[4][‡]

$$\mathbf{k}_e+\mathbf{k}_h=\mathbf{K}. \tag{1}$$

Hence for the optical formation of excitons at $\mathbf{K}=0$ one has the selection rule

$$\mathbf{k}_e+\mathbf{k}_h=0. \tag{2}$$

This is also precisely the selection rule for optical transitions from a filled valence state to a conduction state in the crystal. This selection rule corresponds to a vertical electronic transition, since a hole with wave vector $\mathbf{k}_h$ corresponds to a missing electron state at $-\mathbf{k}_h$. One would expect the transition probability for the optical excitation of excitons at $\mathbf{K}=0$ to be proportional to the transition probability for interband transitions at wave vector $\mathbf{k}$ weighted by the amount of admixture of the electron and hole states of wave vector $\mathbf{k}$ contained in the exciton wave packet; this result will emerge from the calculation below.

A quantitative treatment of this simple model is now presented. The two-particle Hamiltonian for the exciton problem may be written

$$H_0=\frac{p_e^2}{2m}+V_p(r_e)+\frac{p_h^2}{2m}+V_p(r_h)+V_{eh}(r_e,r_h), \tag{3}$$

where the electron and hole coordinates and momenta are labeled with subscripts e and h respectively; $V_p(r)$ is the periodic crystalline potential; and $V_{eh}(r_e,r_h)$ is the attractive potential between the electron and hole. In the presence of a radiation field the gauge may be chosen so that the scalar potential and the divergence of the vector potential vanish. The Hamiltonian for the system is then

$$H=H_0-\frac{e}{mc}[\mathbf{p}_e\cdot\mathbf{A}(r_e)+\mathbf{p}_h\cdot\mathbf{A}(r_h)]+\frac{e^2}{2mc^2}[\mathbf{A}^2(r_e)+\mathbf{A}^2(r_h)]. \tag{4}$$

---

[*] The work has been assisted in part by the U. S. Office of Naval Research, the U. S. Signal Corps, and the U. S. Air Force Office of Scientific Research.

[†] Now at Department of Physics, Cornell University, Ithaca, New York.

[1] Gross, Zakharchenya, and Reinov, Doklady Akad. Nauk U.S.S.R. **99**, 231 (1954); J. Apfel and L. Hadley, Phys. Rev. **100**, 1689 (1955); Nikitine, Perny, and Sieskind, Compt. rend. **238**, 67 (1954); E. Gross and M. Jakobsen, Doklady Akad. Nauk U.S.S.R. **102**, 485 (1955); S. Nikitine, Helv. Phys. Acta **28**, 307 (1955); E. F. Gross and A. Kaplianski, Zhur. Tekh. Fiz. **25**, 2061 (1955); E. F. Gross, Nuovo cimento **3**, Suppl. 4, 672 (1956).

[2] J. Frenkel, Phys. Rev. **37**, 17, 1276 (1931); R. Peierls, Ann. Physik **13**, 905 (1931).

[3] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 647.

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

[5] J. C. Slater and W. Shockley, Phys. Rev. **50**, 718 (1936).

[‡] *Note added in proof.*—See also the paper of H. J. G. Meyer, Physica **22**, 109 (1956).

Only first-order processes are to be considered; hence the terms in the square of the vector potential can be dropped. The calculation is also to be restricted to electric dipole transitions, so that only the time dependence of the vector potential need be considered. The problem is tractable without these assumptions; however, the calculation embraces a particularly simple form under the above conditions. The Hamiltonian (4) is thus written

$$H=H_0-(e/mc)e^{-i\omega t}\mathbf{A}_0\cdot(\mathbf{p}_e+\mathbf{p}_h), \tag{5}$$

where $\mathbf{A}=\mathbf{A}_0e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\cong\mathbf{A}_0e^{-i\omega t}$. Eigenfunctions of (5) can be expressed as a linear combination of products of Bloch functions for the electron and hole, i.e.,

$$\Phi=\sum_{m,n,k_e,k_h}\Psi_{mn}(k_e,k_h)\psi_m(k_e,r_e)\psi_n(k_h,r_h). \tag{6}$$

The expansion (6) represents a wave packet in $\mathbf{k}$ space with an envelope function $\Psi_{mn}(k_e,k_h)$. This treatment corresponds to the introduction of the crystal momentum representation discussed by Adams.[6] Substitution of (6) into the Schrödinger equation,

$$H\Phi=i\hbar\partial\Phi/\partial t, \tag{7}$$

yields the matrix equation for $\Psi_{mn}(k_e,k_h)$:

$$\{\mathfrak{H}_0-(e/mc)e^{-i\omega t}\mathbf{A}_0\cdot[\mathfrak{P}_e(k_e)+\mathfrak{P}_h(k_h)]\}\boldsymbol{\Psi}=i\hbar\partial\boldsymbol{\Psi}/\partial t, \tag{8}$$

where

$$\boldsymbol{\Psi}=\begin{bmatrix}\Psi_{11}\\ \Psi_{12}\\ \vdots\\ \Psi_{21}\\ \Psi_{22}\\ \vdots\end{bmatrix},\quad \mathfrak{P}_e(k)=\begin{bmatrix}\mathbf{P}_{11} & \mathbf{P}_{21} & \cdots & 0 & 0 & \cdots\\ \mathbf{P}_{12} & & & 0 & & \\ \vdots & & & \vdots & & \\ 0 & 0 & \cdots & \mathbf{P}_{11} & \mathbf{P}_{21} & \cdots\\ 0 & & & \mathbf{P}_{12} & & \\ \vdots & & & \vdots & & \end{bmatrix},$$

$$\mathfrak{P}_h(k)=\begin{bmatrix}\mathbf{P}_{11} & 0 & \cdots & \mathbf{P}_{21} & 0 & \cdots\\ 0 & \mathbf{P}_{11} & & 0 & \mathbf{P}_{21} & \\ \vdots & & & \vdots & & \\ \mathbf{P}_{12} & 0 & \cdots & \mathbf{P}_{22} & 0 & \cdots\\ 0 & \mathbf{P}_{12} & & 0 & \mathbf{P}_{22} & \\ \vdots & & & \vdots & & \end{bmatrix},$$

$$\mathfrak{H}_0=\begin{bmatrix}E_1(k_e)-E_1(k_h) & 0 & \cdots\\ 0 & E_1(k_e)-E_2(k_h)+V_{eh} & \cdots\\ \vdots & & \end{bmatrix}, \tag{9}$$

and

$$\mathbf{P}_{ij}(k)=\int\psi_i(k,r)\mathbf{p}\psi_j(k,r)d\mathbf{r}. \tag{10}$$

The term

$$\mathfrak{H}'=-(e/mc)e^{-i\omega t}\mathbf{A}_0\cdot[\mathfrak{P}_e(k_e)+\mathfrak{P}_h(k_h)] \tag{11}$$

is to be treated by time-dependent perturbation theory. The unperturbed problem,

$$\mathfrak{H}_0\boldsymbol{\Psi}_0=E\boldsymbol{\Psi}_0, \tag{12}$$

gives the solutions of the exciton problem discussed in reference 4.

The diagonal terms in $\mathfrak{H}'$ induce intraband exciton transitions, i.e., transitions for which the electron and hole remain in the same band. The diagonal term,

$$\mathfrak{H}'_{mn,mn}=-(e\hbar/c)e^{-i\omega t}\mathbf{A}_0\cdot[\boldsymbol{\nabla}_{k_e}E_m(k_e)+\boldsymbol{\nabla}_{k_h}E_n(k_h)], \tag{13}$$

is identical with what one would obtain from the first term in a Taylor's series expansion of the energy functions in the Wannier equation:

$$\left[E_m\left(\mathbf{k}_e-\frac{e}{\hbar c}\mathbf{A}\right)-E_n\left(\mathbf{k}_h-\frac{e}{\hbar c}\mathbf{A}\right)+V_{eh}\right]\boldsymbol{\Psi}_{mn}=i\hbar\frac{\partial}{\partial t}\boldsymbol{\Psi}_{mn}. \tag{14}$$

The intraband transition probability per exciton for a hydrogenic exciton (an exciton formed by a hole and an electron on spherical energy surfaces) is given by

$$w=\frac{4\pi^2e^2}{\epsilon\hbar^2c}I(\omega_{kn})|(\mathbf{r})_{kn}|^2, \tag{15}$$

where ϵ is the dielectric constant, $I(\omega_{kn})$ is the intensity of the electromagnetic field at the angular frequency $\omega_{kn}=(E_k-E_n)\hbar^{-1}$, and $(\mathbf{r})_{kn}$ is the matrix element of the radius vector between the exciton states k and n. The usual f-sum rule applies for the intraband transition probabilities. The matrix element $(\mathbf{r})_{kn}$ is of the order of magnitude of the exciton radius, a_B; hence a weakly bound exciton with a large orbit has a large transition probability due to the large dipole moment. It seems unlikely however that intraband transitions could be of experimental importance because of the large exciton density which would be required for their observation.

On the other hand, the interband transitions, i.e., transitions for which the electrons or the hole change bands, have presumably been observed experimentally. The calculation of the interband transition probability involves perturbation theory using the off-diagonal terms in $\mathfrak{H}'$. Consider a transition in which an electron changes band while the hole remains in the same band. The perturbation matrix element connecting these states is

$$\mathfrak{H}'_{mn,m'n}=-(e/mc)e^{-i\omega t}\mathbf{A}_0\cdot\mathbf{P}_{mm'}(k_e). \tag{16}$$

---

[6] E. N. Adams, J. Chem. Phys. **21**, 2013 (1953).

The solutions of the unperturbed problem in the crystal momentum representation are denoted $\Psi_{0mn}{}^{(\mathbf{K},s)}(k_e,k_h)$ where m and n label the electron and hole bands, **K** the exciton wave vector; and s is the quantum number or set of numbers used to denote the state within the "center of mass" of the exciton. The transition probability from a state $\Psi_{0mn}{}^{(\mathbf{K},s)}$ to a state $\Psi_{0m'n}{}^{(\mathbf{K}',s')}$ is given by

$$w_{m'n,\,mn}{}^{(\mathbf{K}',s')(\mathbf{K},s)} \cong \frac{4\pi^2e^2I(\omega_{m'm})}{\epsilon m^2\hbar^2\omega_{m'm}{}^2c} \times\left|\int d\mathbf{k}_e d\mathbf{k}_h \Psi_{0m'n}{}^{(\mathbf{K}',s')}P_{m'm}{}^{\alpha}(k_e)\Psi_{0mn}{}^{(\mathbf{K},s)}\right|^2, \quad (17)$$

where P^α is the matrix element of the component of the momentum along the vector potential and $\omega_{m'm} = \hbar^{-1}[E_{m'}(0)-E_m(0)]$. The dielectric constant enters into the denominator of (17) because in a solid the intensity of the electromagnetic radiation is related to the vector potential by[7]

$$\epsilon|A_0|^2=\frac{2\pi c}{\omega^2}I(\omega)\Delta\omega.$$

An approximate evaluation of (17) can be made for transitions from a filled valance band to a simple hydrogenic exciton state. The results should be indicative of what is to be expected in the case of a more involved exciton spectrum.

For a filled band,

$$\Psi_{0mn}{}^{(0,0)}(k_e,k_h)=\delta(k_e+k_h)\delta_{mn}, \quad (18)$$

and for a 1s state

$$\Psi_{0m'n}{}^{(\mathbf{K},s)}=\frac{1}{(2\pi)^6}\int d\mathbf{r}_e d\mathbf{r}_h e^{-i\mathbf{k}_e\cdot\mathbf{r}_e}e^{-i\mathbf{k}_h\cdot\mathbf{r}} \times e^{\frac{1}{2}i\mathbf{K}\cdot(\mathbf{r}_e+\mathbf{r}_h)}\phi_{1s}(r_e-r_h)$$
$$=\delta(k_e+k_h-K)\Phi_{m'n}{}^{1s}\left(\frac{k_e-k_h}{2}\right), \quad (19)$$

where ϕ_{1s} is the wave function of an atomic 1s state;

$$\Phi_{m'n}{}^{1s}(K)=-\frac{2a_B{}^{\frac{3}{2}}}{(2\pi)^3}\frac{1+Ka_B}{(1+K^2a_B{}^2)^2}; \quad (20)$$

and a_B is the radius of the 1s orbit. The transition probability (17) is given approximately by

$$w_{mn,\,nn}{}^{(00)(00)}\approx\frac{N4\pi^2e^2I(\omega_{mn})}{\epsilon m^2\hbar^2\omega_{mn}{}^2c}\left(\frac{a_0}{a_B}\right)^3|P_{mn}(0)|^2 \quad (21)$$

where a_0 is the lattice constant and $N=a_0{}^{-3}$ is the number of atoms per unit volume. In deriving (21) the dependence of the momentum matrix element on wave vector and factors of the order of magnitude of unity have been neglected. It can be shown that the order of magnitude of the result is unaffected by the inclusion of the wave vector dependence of the momentum matrix element unless the transition is forbidden at the center of the zone. The integration reduces to an integral over the exciton wave packet. Hence the result expected qualitatively is obtained by the somewhat more quantitative treatment. If the exciton is tightly bound, having a radius of the order of magnitude of the lattice constant, the absorption coefficient is the same as that for a collection of free atoms. Hence, when the binding is such that the atomic orbital approximation given in reference 3 is the more correct treatment of the problem, the effective-mass calculation of the transition probability has the correct limiting value.

III. DISCUSSION

In the observations of exciton lines cited in reference 1, accurate determinations of the absorption coefficients have not been made. However, one would expect theoretically to have the absorption coefficient for excitons (bound with about 0.01 ev) decreased by about five orders of magnitude over the absorption coefficient for a collection of free atoms. This value is not inconsistent with the experimental results. The possibility of using careful absorption coefficient measurements to identify the source of the absorption lines should be emphasized.

The exciton lifetime should also be about five orders of magnitude longer than the lifetime of an excited atomic state, ~10^{-3} sec.

A way of viewing this decrease in absorption coefficient is that a large exciton wave function in space implies a sharply defined exciton in wave vector space, and hence the excitation of only a very few Bloch functions will be effective in exciton formation.

The creation of excitons in excited states has a smaller transition probability owing to the increased wave packet size associated with such an exciton state. For a hydrogenic exciton the transition probability falls off as $n^{-\frac{3}{2}}$, where n is the principal quantum number of the exciton. One has the further selection rule that only $J=1$ states may be excited by photon absorption. The possible spin states for a simple hydrogenic exciton are $S=0$, 1; hence only $L=0$, 1 orbital states can be observed by optical transitions.

The author is indebted to Professor C. Kittel for discussions related to this problem and to the Berkeley solid state group for their hospitality during the summer of 1956. He would like to acknowledge the financial support rendered by the National Carbon Research Laboratories.

---

[7] M. Lax, J. Chem. Phys. **20**, 1752 (1952).