

Effect of Defect Fields on the Optical Absorption Edge

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The electric fields of charged defects in a solid broaden its fundamental optical absorption edge by a mechanism which is an internal analog of the Franz-Keldysh effect. Using this analogy, a semiquantitative calculation is made of such broadening due to impurities in semiconductors having direct absorption edges. Without the use of any adjustable parameters, reasonable agreement is found with published absorption tails of InAs, for both the magnitude of the effect and its dependence on impurity concentration. It is proposed that such effects account for the common Urbach's rule observations, and a qualitative discussion is given for the corresponding effects in insulators.

I. INTRODUCTION

IN recent years, it has become recognized that an applied electric field could shift the fundamental optical absorption edge of a solid to slightly lower energies. This effect, sometimes called the Franz-Keldysh effect for the authors of the theoretical treatments,¹ has been observed² in several solids upon the application of fields of $\sim 10^5$ V/cm. Physically, the effect may be thought of as a consequence of the quantum mechanical penetration of the band states into the energy gap when a strong potential gradient exists. The result is that an ideally sharp, direct, band-band absorption edge acquires a nearly exponential tail at energies less than the gap energy E_G .

The purpose of this paper is to investigate the way in which an absorption edge may be influenced by the corresponding effect due to the electric fields of charged defects in a solid. It will be shown that such effects are significant and can account for the previously unexplained Urbach's rule.³ This discussion will emphasize the effects in semiconductors; insulators will be discussed qualitatively at the end. Among the possible

types of defects which can be charged, only point defects will be treated in detail because they can be shown to be the most important type in ordinary semiconductor crystals. In thin films, however, surface effects warrant serious consideration although they will not be discussed further here. Specifically, this paper attempts to account for the observations of Dixon and Ellis on InAs shown in Fig. 1, taken from their paper.⁴ At photon energy $\hbar\omega$, somewhat higher than shown in this figure, the absorption coefficient follows approximately the relation

$$\alpha \simeq \sqrt{3} \times 10^4 (\hbar\omega - 0.35)^{1/2} \text{ cm}^{-1}. \quad (1)$$

This is consistent with the accepted view of the direct nature of transitions across the gap, and leads to the value $E_G = 0.35$ eV shown dashed in Fig. 1. The unexplained departure of the observed α from relation (1) near the gap energy and the absorption tails below it are typical of a number of materials.⁴ Previous attempts to relate such tails to impurity absorption processes⁵ have been unsuccessful apparently because the effect of the fields of the impurities on the wave functions was not considered. In fact, it should be possible to treat this problem as an impurity absorption process—in the limit of noninteracting impurities—provided the proper wave functions are used. For reasons to be given below, that approach is not taken in this paper.

II. COMPUTATION OF EFFECT OF DEFECT FIELDS

An evaluation of this effect of the fields of charged impurities has been made by invoking the analogy with the Franz-Keldysh effect. This requires making the following two approximations:

1. All transitions are treated as direct, band-to-band transitions to make the Franz-Keldysh relations applicable. Transitions to exciton states are ignored because the exciton binding energies in materials like InAs are less than the amount by which the band edges

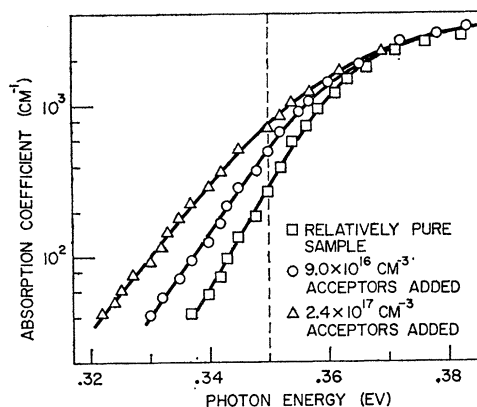


FIG. 1. Absorption edge of InAs of varying purity (from Dixon and Ellis).

¹ W. Franz, Z. Naturforsch. **13a**, 484 (1958); L. V. Keldysh, Zh. Eksperim. i Teor. Fiz. **34**, 1138 (1958) [translation: Soviet Phys.—JETP **7**, 788 (1958)].

² Richard Williams, Phys. Rev. **126**, 442 (1962).

³ F. Urbach, Phys. Rev. **92**, 1324 (1953); W. Martienssen, J. Phys. Chem. Solids **8**, 294 (1959).

⁴ J. R. Dixon and J. M. Ellis, Phys. Rev. **123**, 1560 (1960). This was chosen because it is the most extensive data of this type available.

⁵ D. M. Eagles, J. Phys. Chem. Solids **16**, 76 (1960).

are blurred by the fields. More important, this approximation implies that the "bound states" of the impurities are treated as states of the adjacent band. This can be partially justified by two facts: (a) These "bound states" are really derived from the adjacent band. (b) Overlap effects among adjacent impurities in semiconductors like InAs are so great that none of the "bound states" (with the possible exception of the lowest one) is actually bound or discrete in energy. This latter is also one of the reasons that the impurity absorption approach is not used for this problem.

2. The electric field strength is regarded as uniform in every small—but macroscopic—volume element of the crystal. The validity of this assumption rests on the estimate that, for the most part, the relative field strength does not vary greatly over a distance of the order of the penetration distance of the wave functions into the gap ($\sim 10^{-7}$ cm). Aside from this question of the variation in magnitude of the fields, there remains the question of the variation in direction. This will be mentioned later.

Using these approximations, the local absorption coefficient due to any field value F is computed as in the Franz-Keldysh effect. The total absorption coefficient is then found by integrating over all field strengths, weighting each value by its probability of occurrence $W(F)$:

$$\alpha(\omega) = \int_0^{\infty} A(\omega, F) W(F) dF, \quad (2)$$

where $A(\omega, F)$ is the expression describing the (local) absorption coefficient for frequency ω in the presence of field F . The range of integration extends to infinity even though this formulation is not valid at very high fields, because the integral converges fairly rapidly in that range. That is, the very high-field regions contribute little to Eq. (2). Also, any choice of a maximum field would be subject to several uncertainties.

The field distributions can be represented by moderately screened, Holtzmark distributions as described in the preceding paper.⁶ For the present purposes, however, the "nearest ion distribution" is used instead because (a) it is the only one having a closed form; (b) it happens to be a good approximation to the correct distributions for impurity concentrations of most interest.⁶ Thus, the probability distribution function for fields of magnitude F is taken to be

$$W(F) dF = \frac{3}{2F} \left(\frac{F_0}{F}\right)^{3/2} \exp\left[-\left(\frac{F_0}{F}\right)^{3/2}\right] dF, \quad (3)$$

where the "normal field" is

$$F_0 = 2.6(e/\epsilon)N^{2/3}, \quad (4)$$

ϵ is the static dielectric constant, e the magnitude of the

electronic charge, and N the concentration of charged impurities.

It is convenient to consider this calculation in two parts: (a) the magnitude of the absorption at the gap energy $\hbar\omega_1 = E_G$, the highest energy for which the ideal crystal should not absorb; (b) the slope of the (nearly) exponential tail away from the gap energy. At $\omega = \omega_1$ Franz' expression (25) for the relative absorption, $A(\omega, F)$, becomes simply¹

$$A(\omega_1, F) = [\Gamma(3/2)/3\Gamma(7/6)](\omega_F)^{1/2}, \quad (5)$$

where

$$\omega_F = (e^2 F^2 / I 2 \hbar m^*)^{1/3}, \quad (6)$$

and m^* is twice the reduced effective mass of the valence and conduction bands. To convert the $A(\omega, F)$ to absolute absorption coefficient for purposes of comparison with experiment, all that is needed is to multiply it by the appropriate numerical factor found from the absorption at energies greater than E_G . In the case of InAs this factor is obtained from Eq. (1) as $\sim \sqrt{3} \times 10^4$. Thus, using (3) and (5) in Eq. (2) and including this factor, we find

$$\alpha(\omega_1) = \sqrt{3} \times 10^4 \times [\Gamma(3/2)\Gamma(7/9)/3\Gamma(7/6)](\omega_{F_0})^{1/2} \quad (7)$$

where ω_{F_0} is just ω_F evaluated at $F = F_0$. Using $\epsilon = 12$ and $N = 2.4 \times 10^{17}$ cm⁻³ in Eq. (3) for comparison with the highest curve of Fig. 1, this leads to $\alpha(\omega_1) \sim 520$ cm⁻¹ compared to the observed value of ~ 700 cm⁻¹. It also follows from Eq. (7) that $\alpha(\omega_1)$ should vary as $N^{2/9}$ which is to be compared with the estimated $N^{1/3}$ dependence relating the experimental values of $\alpha(\omega_1)$ in the upper two curves of Fig. 1.

The computation of the absorption tail below the gap is considerably more difficult and must be performed numerically. Furthermore, the unlimited range of fields used in the integration precludes the use of any of the approximate formulae for the Franz-Keldysh effect. In fact, to obtain an expression for $A(\omega, F)$ usable in Eq. (4) it was found necessary to reformulate⁷ Franz' result, giving

$$A(\omega, F) = (\omega_F)^{1/2} \int_{(\omega_1 - \omega)/\omega_F}^{\infty} |\text{Ai}(z)|^2 dz, \quad (8)$$

where $\text{Ai}(z)$ is the Airy function.⁸ A value of A is found at each ω by integrating Eq. (8) numerically and using the result in Eq. (2) which is then evaluated numerically, also. The curve of $\alpha(\omega)$ so obtained is nearly exponential over the range of frequencies comparable to those of Fig. 1. But the slope of the absorption tail calculated using the parameters appropriate to the highest curve of Fig. 1 was found to be too small by a factor of ~ 2.6 .

This disagreement may be reduced greatly by the following qualitative considerations. The second as-

⁷ K. Tharmalingam (unpublished).

⁸ Jeffreys and Jeffreys, *Methods of Mathematical Physics* (Cambridge University Press, New York, 1956).

⁶ D. Redfield, preceding paper [Phys. Rev. **130**, 914 (1963)].

sumption made at the beginning of this section was that the fields be considered locally uniform in magnitude and direction. Such fields convert normal Bloch wave functions to Houston functions.⁹ If, however, the fields arise from potentials with spherical symmetry, Coulomb functions would result.¹⁰ These functions are attenuated more strongly in the gap—in fact, by an amount which would increase the calculated slope by a factor of 2.4 and, thus, nearly account for the discrepancy. This rough argument has some support from the fact that the absorption away from the gap (at lower energies) must be dominated by the relatively high-field regions. It is just these regions, close to the charges, which should actually have the most nearly spherical potential symmetry.¹¹ Furthermore, the use of Coulomb wave functions would not be expected to alter the results obtained at ω_1 . The reason, of course, that this entire calculation has not been attempted in a form utilizing the Coulomb functions, is their complexity.

III. DISCUSSION

In view of the fairly good results of this simple treatment and the fact that no adjustable parameters were needed, it is felt that this effect offers a satisfactory explanation for the Urbach rule absorption tails.¹² It is, therefore, in order to examine some further implications of this model. First, it is obvious why attempts to assign “effective temperatures” to such exponential tails in semiconductors led to erratic values.⁴ Furthermore, it is now reasonable to expect that optical measurements of energy gaps and their temperature de-

pendence can be interpreted more accurately. It should be mentioned, however, that indirect absorption edges are probably less sensitive to the defect fields, although this remains to be shown.

It also follows from this model that at temperatures low enough to freeze out the free carriers of semiconductors, the absorption tails should vanish. If, however, both donor and acceptor impurities are present they remain charged at low temperatures and the tails should persist. Both of these expectations have recently been confirmed in work on GaSb.¹³

In treating the related questions for insulators several changes must be made. First, there are no free carriers; charge compensation is maintained by defects with both signs of charge. Some of these may associate and produce dipolar fields. More important is that the binding energy of excitons is no longer smaller than the band edge blurring. Thus, the edge shape should be considered in terms of a field-perturbed exciton transition. It is probable that the effect of defect fields will be qualitatively the same as for band-to-band transitions; this is being considered at present.

The most important aspect of insulators is that vibrations of their ionic lattices provide an additional source of electric fields.¹⁴ Such fields appear to offer an explanation for the strong temperature dependence of Urbach tails in ionic crystals. This expectation is consistent with the very weak temperature dependence in semiconductors. Further work on this subject is in progress.

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⁹ W. V. Houston, *Phys. Rev.* **57**, 184 (1940).

¹⁰ P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953).

¹¹ In spite of this reference to high-field regions, these considerations do not require the participation of the very close-in regions where use of the static dielectric constant is severely in error.

¹² A number of attempts to explain Urbach's rule in insulators are summarized in a forthcoming review: R. S. Knox, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York), Vol. 15 (to be published).

¹³ E. J. Johnson and H. Y. Fan, *Bull. Am. Phys. Soc.* **7**, 185 (1962).

¹⁴ The author is indebted to R. S. Knox for pointing out the pertinence of this fact.