PHYSICAL REVIEW VOLUME 168, NUMBER 3 15 APRIL 1968

Infrared Donor-Acceptor Pair Spectra Involving the Deep Oxygen Donor in Gallium Phosphide

P. J. Dean, C. H. Henry, and C. J. Frosch
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 4 December 1967)

We report the infrared radiative recombination of electrons bound to deep O donors with holes bound to C, Zn, or Cd acceptors in GaP. From the transition energies of the discrete no-phonon lines, which can be closely accounted for using a simple Coulomb donor-acceptor interaction energy term, the ionization energy of the O donor is calculated to be 893±2 meV. Aggregation between Zn (or Cd) acceptors and O donors in nearest-neighbor lattice sites produces strong red luminescence not observed in C-doped crystals where the closest possible donor-acceptor pairs are next-nearest neighbors. The infrared pair spectra are broad because of strong phonon-assisted transitions arising from the tight binding of the O donor. Two modes of energy 19.5 and 47.0 meV are prominent in the infrared spectra, whereas only one ~48-meV mode is prominent in the green luminescence due to recombinations between shallow donors and C, Zn, or Cd acceptors in GaP.

I. INTRODUCTION

Until recently, the red luminescence of Zn- and O-doped GaP was believed due to electron-hole recombination at unassociated pairs of oxygen donors and Zn acceptors.[1–3] Recent work has shown that this red luminescence, which is of current practical interest in red electroluminescent GaP diodes, arises at low temperatures: (a) from the recombination of an exciton localized at a complex center involving both Zn and O,[4,5] and (b) from the recombination of electrons bound to this complex with holes trapped at relatively remote Zn acceptors.[5] Mechanism (b) represents a new type of pair recombination process in which the major cause of the dependence of the transition energy upon the pair separation (the Coulomb term) is absent as the electron trap is uncharged. Similar spectra have been observed in Cd-doped GaP.

The properties of the red exciton transition can be understood if the exciton is bound to a nearest-neighbor Zn-O or Cd-O conventional donor-acceptor pair.[4,6] A comparison of the experimental red luminescence spectra corresponding to transitions (a) and (b) above has shown that the electron is bound to the ionized (neutral) Cd-O acceptor-donor pair by almost 0.40 eV.[5] This large binding energy is due to the oxygen donor, and occurs despite the fact that interaction between the electron and the negatively charged nearest-neighbor acceptor ion raises the energy of the electron by ~0.5 eV. The donor-acceptor model of the red exciton transition therefore implies that the ionization energy of the isolated O donor is ~0.9 eV, much larger than previous estimates obtained from a *remote* Cd (or Zn)-O acceptor-donor pair model for the red luminescence.[1–3] This revised value for the ionization energy of the O donor implies that electron-hole recombinations between widely separated Cd(or Zn)-O acceptor-donor pairs should produce *infrared* luminescence. The present paper describes new low-temperature donor-acceptor pair spectra in this spectral region for Zn, Cd and C-doped GaP.[7] These spectra contain many sharp lines and involve hole-electron recombinations between zinc, cadmium, and carbon acceptors and deep oxygen donors, i.e., they are the "conventional" donor-acceptor pair spectra predicted for the deep O donor.[8]

II. EXPERIMENTAL

The GaP crystals were grown by cooling from Ga-rich solutions in sealed evacuated vitreous silica tubes.[9] The acceptors were added as the metal (for Zn and Cd) or by growing the crystals in an ambient of CO. The donor O is usually present inadvertently, but its concentration may be increased through the addition of Ga_2O_3 to the Ga or by growing the crystals in an O_2 ambient.

The photoluminescence was excited by the 4880 Å emission from an Ar^+ laser. The crystals were immersed in liquid He which was pumped below the λ point which reduced the strength of pair transitions from low-lying excited states and led to considerable simplification of the spectra.

III. RESULTS AND DISCUSSION

Figure 1 shows the no-phonon line spectra of crystals containing three different acceptors. The donor O is on P lattice sites, as is the C acceptor, so a type-I pair

---

[1] M. Gershenzon, F. A. Trumbore, R. M. Mikulyak, and M. Kowalchik, J. Appl. Phys. **36**, 1528 (1965).

[2] D. F. Nelson and K. F. Rodgers, Phys. Rev. **140**, A1667 (1965).

[3] M. Gershenzon, F. A. Trumbore, R. M. Mikulyak, and M. Kowalchik, J. Appl. Phys. **37**, 483 (1966).

[4] T. N. Morgan, B. Welber, and R. N. Bhargava, Phys. Rev. **166**, 751 (1968).

[5] C. H. Henry, P. J. Dean, and J. D. Cuthbert, Phys. Rev. **166**, 754 (1968).

[6] C. H. Henry, P. J. Dean, D. G. Thomas, and J. J. Hopfield, in Proceedings of the Conference on Localized Excitations, Irvine, 1967 (to be published).

[7] Recent evidence, to be published in detail elsewhere, suggests that carbon is the phosphorus site acceptor responsible for the type-I_A pair spectra, rather than silicon as suggested in Ref. 8.

[8] D. G. Thomas, M. Gershenzon, and F. A. Trumbore, Phys. Rev. **133**, A269 (1964).

[9] See, for example, J. F. Miller, in *Compound Semiconductors*, edited by R. K. Willardson and H. L. Goering (Reinhold Publishing Corp., New York, 1962), Vol. 1, Chapter 23.

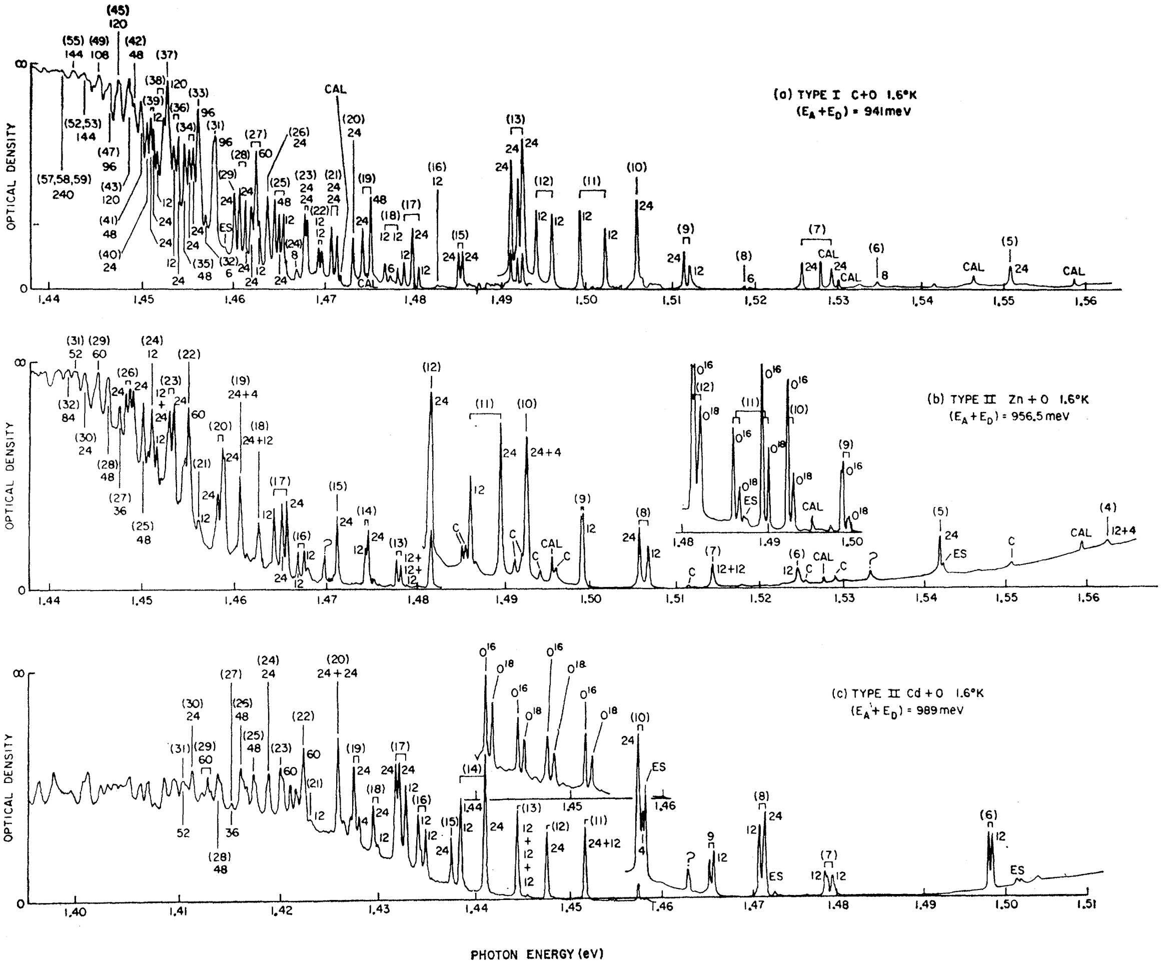

FIG. 1. Densitometer tracings from photographic plates of portions of the infrared luminescence spectra of GaP produced by adding (a) C+O, (b) Zn+O, and (c) Cd+O. Two different exposure times and sometimes different excitation intensities were used in each spectrum to adequately record the relatively weak higher-energy lines. The lines marked C in spectrum (b) are due to transitions at extraneous C acceptors. Calibration lines due to Rb or Ar are denoted by CAL. Recombinations from excited pair states are denoted by ES. The braced integers denote the shell number, m, an index of the donor-acceptor separation ($m=1$ for nearest neighbors, etc.). The unbraced numbers denote the number of pairs within a given shell. Note that there may be two or more inequivalent groups of pairs within a given shell of given pair separation, R, and this can lead to resolvable fine structure. The insets in spectra (b) and (c) show that each discrete no-phonon pair line is replicated by a line ~0.71 meV to higher energy when some of the O^{16} is replaced by the isotope O^{18}. The line widths are limited by instrumental resolution.

spectrum is anticipated for these impurities.[8] In the type-II spectra, the impurities are on opposite lattice sites as expected for Zn-O and Cd-O pairs. Inspection of Fig. 1 shows that the Zn-O and Cd-O spectra are relatively similar (note, for example, the low strength observed for line 21 as anticipated for type-II spectra) whereas the C-O spectrum is different. The relative intensities of adjacent lines in the C-O spectrum are in good agreement with the indicated strengths, which are calculated on the assumption that the donors and acceptors are distributed at random and that the luminescence intensities are directly proportional to the number of possible sites at a given donor-acceptor separation R. In addition, most of the clearly resolved transitions exhibit, for a given shell, substructure of multiplicity consistent with expectation for a type-I spectrum. This substructure arises from the fact that the donor-acceptor lattice separation which defines a given shell can in general be derived from more than one inequivalent set of direct lattice vectors (**k**,**l**,**m**). For each such set, the environment of the donor and acceptor is different. This difference causes the donor-acceptor interaction energy, and hence the pair transition energy [see Eq. (1) below], to differ slightly for each distinct set (**k**,**l**,**m**). These facts, together with the absence of lines at shell numbers $m=14$ and 30 in Fig. 1(a), confirm that these donors and acceptors are substitutional and on the same lattice site.

The agreement of the Zn-O and Cd-O spectra with similar predictions for type-II spectra is acceptable but less dramatic. There are three unidentified lines in the Zn-O spectrum and one in the Cd-O spectrum. On the other hand, some other lines show unexpected small splittings, for example line 9 in both spectra and line 6 in the Cd-O spectrum. Line 13 shows fewer components than anticipated, as it does in the green Zn-S and Cd-S pair spectra.[10,11] It is possible that many of these detailed differences arise because the splitting of some of the transitions for the deeper acceptors is larger than the energy separation between transitions at adjacent shells.

The role of O in these infrared pair spectra is proved by the addition of O^{18} to the crystals. Figure 1(b) and (c) shows that each pair line is then replicated by a similar line 0.71±0.02 meV to higher energy. This energy shift is only slightly larger than observed in the red exciton (nearest neighbor Cd-O pair) transition.[4,6] Since the resolved phonon structure in the red and infrared spectra is quite different (see below) this similarity is consistent with the observation that the isotope shift of the no-phonon line is not primarily determined by energy changes of any of the resolved phonons in the Cd-O exciton spectrum.[6]

Neglecting terms which may be important at small donor-acceptor separations, such as arise from mutual polarization of the neutral impurities, the pair transition energy $h\nu$ is[8]

$$h\nu = E_g - (E_A + E_D) + e^2/\epsilon R. \tag{1}$$

The energy gap of GaP, E_g, is 2.339±0.002 eV at 0°K.[11] Figure 2 shows that the observed values of $h\nu$ are closely described by Eq. (1) for both types of spectrum over the ranges of m identified in Fig. 1. This was not true for the green pair spectra in GaP. The better fit of Eq. (1) to the infrared pair spectra arises partly because a recently revised larger value of the low-frequency dielectric constant ϵ was used in Fig. 2 ($\epsilon = 11.1$).[12] In addition, the effect of polarization interactions are expected to be small when one of the electronic particles is very tightly bound (here the O donor). The agreement is surprisingly good for the nearest-neighbor pair, since Eq. (1) predicts $e^2/\epsilon R_{\mathrm{NN}} = 550$ meV, whereas the no-phonon lines of the Cd-O and Zn-O excitons are 553 and ~600 meV above the $R = \infty$ transition energies obtained from Fig. 2. This close agreement for the $m=1$ transition energy is fortuitous, since the observed energies for the $m=3$ and $m=4$ C—O transitions are appreciably larger than predicted from Eq. (1). The observed energy intervals $5 \rightarrow 4$ and $4 \rightarrow 3$ are 54 and 47 meV, whereas only ~18 and ~26 meV are predicted from Eq. (1). The identification of these transitions is again supported by the relative intensities of adjacent lines, and the fact that the $m=4$ transition is a singlet while the $m=3$ transition is a close doublet as predicted from the shell analysis.

In the first shell of the type-II spectrum, the impurities are on nearest-neighbor (NN) lattice sites ($R = 2.36$ Å) and chemical bonding between them is possible. We presume that this accounts for the excess population of NN type-II pairs which is responsible for the strong red luminescence in Zn and Cd-doped GaP.[4,5] The low-energy tail of this red luminescence can be seen at high energies in Fig. 1(b) and (c). This tail prevents the observation of the relatively weak luminescence from pairs of lower shell number (excluding $m=1$) than are shown in Fig. 1(b) and (c). No such red luminescence is present in C-doped GaP, where the impurities are on next nearest-neighbor sites in the first shell of the type-I pair spectrum ($R = 3.86$ Å), and a direct chemical bond is impossible. The $m=1$, 2 pair transitions have not been observed in the C—O spectrum presumably because the probability of formation of the close pairs is very small when the donors and acceptors are distributed at random on the lattice sites and preferential pairing is insignificant.

From the fitted data in Fig. 2 ,$(E_A)_{\mathrm{Cd}} - (E_A)_{\mathrm{Zn}} = 32.5$ meV and $(E_A)_{\mathrm{Zn}} - (E_A)_C = 15.5$ meV, in good agreement with the green pair spectra,[10] thus confirming that these substitutional acceptors are involved in the infrared pair spectra. Since the absolute values of these acceptor ionization energies are known,[13] $(E_D)_{\mathrm{O}}$ may be calculated from Fig. 2, and is 893±2 meV.

The no-phonon recombinations at relatively widely separated pairs collectively form well-defined bands (NP in Fig. 3) at very low-excitation intensities (unsaturated spectra). Phonon replicas of these bands are observed at lower energies involving phonons of energy 19.5±1.0 meV and 47.0±0.5 meV. Only one series of phonon replicas associated with a ~48-meV optical (O) phonon has been reported in the green pair spectra.[8] The ~20-meV (LOC) replica is significantly broader than the O replica. No significant shift of this phonon replica, or of the 47-meV optical replica, was observed between crystals in which ~85% of the oxygen was O^{18} compared with those with 100% O^{16}. The ~1-meV shift of the broad replica expected if the kinetic energy of the 20-meV mode was entirely due to motion of the oxygen ion should just have been detectable. We conclude that coupling to the phonons resolved in Fig. 3 are not primarily responsible for the oxygen isotope shift in the infrared no-phonon pair lines. A similar conclusion was obtained in Ref. 6 concerning the red exciton spectrum involving Cd acceptors. The greater breadth of the spectra in Fig. 3 compared with the green pair spectra (e.g.,

---

[10] F. A. Trumbore and D. G. Thomas, Phys. Rev. **137**, A1030 (1965).

[11] P. J. Dean and D. G. Thomas, Phys. Rev. **150**, 690 (1966).

[12] A. S. Barker, Jr. (private communication).

[13] The ionization energies of the three shallow acceptors C, Zn' and Cd used in the present analysis are 2 meV larger than tabulated by P. J. Dean, J. D. Cuthbert, D. G. Thomas, and R. T. Lynch, Phys. Rev. Letters **18**, 122 (1967). This change is due to the combined effect of reductions in the ionization energies of shallow donors in GaP by 5 meV as a result of a recent move, detailed analysis of the "two-electron" luminescence spectra made by R. A. Faulkner, and decreases in the values of $E_A + E_D$ by −3 meV due to the use of the recent larger value of ϵ in a reanalysis of the shallow green pair spectra in GaP. These developments will be reported in detail elsewhere.

Fig. 4 of Ref. 8) arises from the tight binding of the electron to the O donor.

These infrared pair spectra broaden very rapidly with increase in excitation intensity, causing the phonon replicas to become ill-defined (Fig. 4). This effect has been extensively discussed in connection with the green pair luminescence in GaP.[8] It is due to saturation of the (low-energy) transitions at relatively remote pairs under high-excitation intensity, which causes the relatively close pairs with higher recombination energy and transition probability to play a greater role in the recombination process. The no-phonon transitions shown in Fig. 1 were obtained from a high-resolution study of the high-energy tail of the N.P. bands, which are prominent under high-excitation intensity as shown in Fig. 4. The infrared pair bands could be saturated much more readily than the green Cd (or Zn)-S acceptor-donor pair bands in the same crystals under identical conditions. This difference is probably due mainly to the significant decrease in the radiative transition probability with decrease in the transition energy between these two spectral regions.

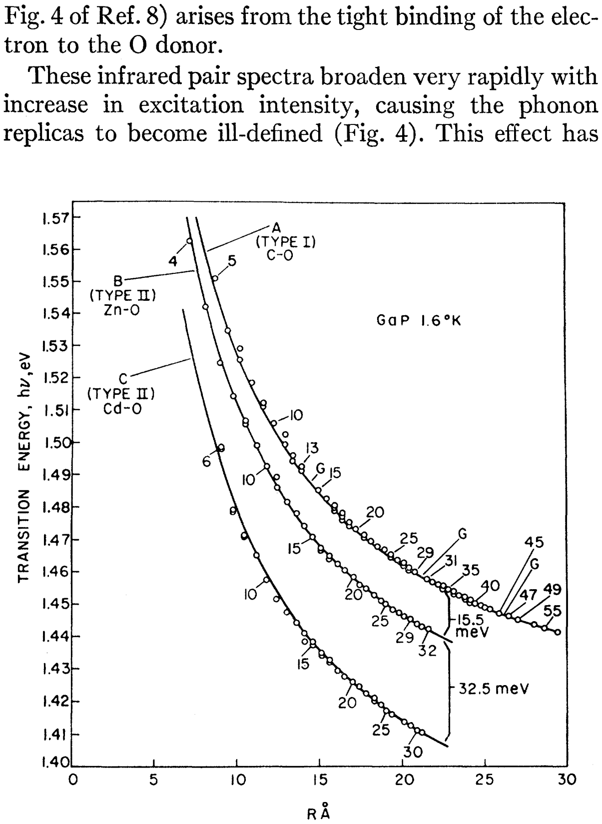

FIG. 2. The energies of the discrete infrared pair no-phonon lines in GaP plotted against the pair separations in Å. The experimental points follow Eq. (1) in each spectrum with $\epsilon=11.1$, $(E_D)_O=893$ meV and $(E_A)_C=48.5$ meV, $(E_A)_{Zn}=64$ meV and $(E_A)_{Cd}=96.5$ meV. The shell numbers of some of the lines are indicated. Predicted gaps in the type-I spectrum are denoted by *G*.

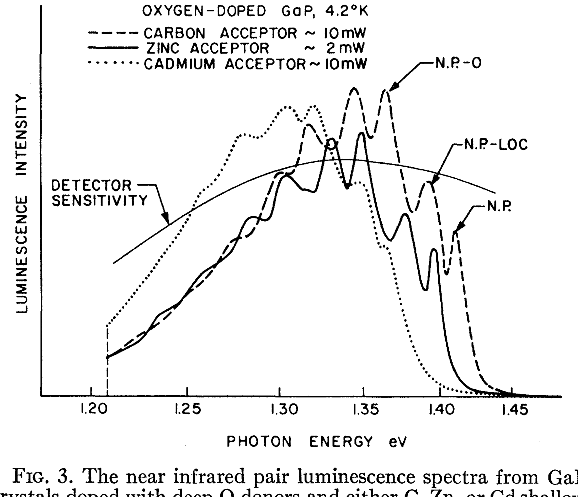

FIG. 3. The near infrared pair luminescence spectra from GaP crystals doped with deep O donors and either C, Zn, or Cd shallow acceptors. These spectra were recorded photoelectrically under the lowest usable excitation intensities so that the bands due to unresolved no-phonon pair transitions (N.P.) were as narrow as possible. These pair transitions are strongly coupled to two phonons (LOC and O). The spectra are found to be mutually displaced by the differences in acceptor ionization energy noted in Fig. 2.

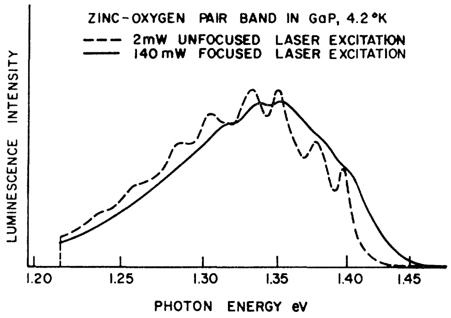

FIG. 4. Near infrared donor-acceptor pair luminescence in Zn, O-doped GaP recorded photoelectrically for two widely different excitation intensities. The poor resolution of the phonon structure at high-excitation intensities arises from broadening of the no-phonon band near the high-energy limit of the spectrum due to saturation of the (lower-energy) transitions at remote pairs.

IV. SUMMARY

Infrared luminescence bands due to recombinations between electrons trapped on deep O donors and holes trapped on Zn, Cd, or C acceptors have been observed in GaP. Transitions between pairs with many different separations have been mutually resolved and identified, both in the type-I and type-II lattice site configurations. Analysis of the energies of these lines provides an accurate estimate of the ionization energy of the deep O donor, 893±2 meV. The identification with O is proved by the observation of an isotope shift in the discrete pair no-phonon lines in crystals grown in contact with O^{18}. These infrared pair spectra exhibit prominent ~20- and ~47-meV phonon replicas at low-excitation intensities. The ~20-meV replica is far from the density of states maxima for vibrations of the unperturbed GaP lattice, but does not appear to involve entirely independent motion of the O ion.

An important conclusion from the present work is that, in contrast to earlier speculations,[1,2] structure due to transitions at separate shells in conventional donor-acceptor pair spectra is resolvable even when one of the impurities produces a deep (here nearly 1 eV or $\sim$0.4 E_g) bound state. It is likely that such structure may be observable in other semiconductors. If so, the ionization energies of deep centers may be accurately determined from the low-temperature pair luminescence spectrum alone.

ACKNOWLEDGMENTS

The authors are indebted to D. G. Thomas and F. A. Trumbore for advice and encouragement in the analysis of the pair transitions. Thanks are due to R. B. Zetterstrom and M. Kowalchik for providing many of the solution-grown crystals and to E. I. Gordon for the Ar$^+$ laser tube.

PHYSICAL REVIEW VOLUME 168, NUMBER 3 15 APRIL 1968

Quantum Theory of Transport in Narrow Channels

C. B. Duke
General Electric Research and Development Center, Schenectady, New York 12301*
and
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois

(Received 1 December 1967)

The electrical conductivity in a semiconductor surface channel or a thin film is written in terms of integrals over a retarded current-current correlation function and evaluated using a Green's-function formulation of perturbation theory. The perturbation theory exhibits four new features. (1) The boundary conditions at the surfaces of the channel are expressed in terms of a fluctuation potential rather than a Fuchs reflectivity parameter. (2) The quantization of the eigenvalues for motion normal to the channel is explicitly incorporated into the theory. (3) The averaging procedure used to obtain the diagrammatic definition of the propagators and correlation functions is extended to include the effects both of screening and of graded interface impurity doping by permitting summation of multiple-scattering effects within planes of impurities parallel to the surface prior to the consideration of interference between these planes. (4) The propagators and conductivity are evaluated at arbitrary temperatures, using the Matsubara formalism. The conductivity is calculated explicitly in the quantum limit that the energy spacings ΔE between the eigenvalues for motion normal to the surface satisfy $\Delta E \gg kT$ for the occupied eigenstates. The approximations needed to reproduce the Boltzmann-equation analysis by Stern and Howard of the extreme quantum limit are delineated. The effects of dispersion and quantized-state mixing are examined for a δ-function model of the fluctuation potential. They are found to be significant if a quantized eigenvalue is near the Fermi energy or if the doping in the channel is highly nonuniform.

I. INTRODUCTION

The theory of transport in thick films and semiconductor surface channels is an old and venerable topic, which is usually discussed within the framework of solving the Boltzmann equation, using classical or semiclassical carrier dynamics.[1–4] Although the possible importance of quantization effects in narrow channels or very thin films has been recognized for at least 10 years,[5] serious theoretical consideration of these effects has been given only in the past year.[6–10] The origin of this delay lies in the fact that although a variety of experiments have been interpreted as suggesting the importance of surface-induced quantization effects,[11–17] only recently have transport experiments[18] on (100) silicon surfaces convincingly demonstrated the existence of the two-dimensional energy bands associated with a narrow *n*-type inversion channel on *p*-type silicon.

The space-charge potential of an accumulation region at a planar *n*-type semiconductor interface is illustrated schematically in Fig. 1. Each quantized state for motion normal to the interface leads to a two-dimensional con-

---

[*] Permanent address.

[1] See, e.g., A. Many, Y. Goldstein, and N. B. Grover, *Semiconductor Surfaces* (North-Holland Publishing Co., Amsterdam, 1965), Chap. 4.

[2] R. F. Greene, Surface Sci. **2**, 101 (1964).

[3] R. F. Green, Phys. Rev. **141**, 687 (1966); **141**, 690 (1966).

[4] R. F. Greene and R. W. O'Donnell, Phys. Rev. **147**, 599 (1966).

[5] J. R. Schrieffer, in *Semiconductor Surface Physics*, edited by R. H. Kingston (University of Pennsylvania Press, Philadelphia, 1957), p. 68.

[6] C. B. Duke, Phys. Letters **24A**, 461 (1967).

[7] C. B. Duke, Phys. Rev. **159**, 632 (1967).

[8] D. J. BenDaniel and C. B. Duke, Phys. Rev. **160**, 679 (1967).

[9] F. Stern and W. E. Howard, Bull. Am. Phys. Soc. **12**, 275 (1967).

[10] F. Stern and W. E. Howard, Phys. Rev. **163**, 816 (1967).

[11] P. Handler and S. Eisenhouer, Surface Sci. **2**, 64 (1964).

[12] N. St. J. Murphy, Surface Sci. **2**, 86 (1964).

[13] F. Proix and P. Handler, Surface Sci. **5**, 81 (1966).

[14] F. F. Fang and W. E. Howard, Phys. Rev. Letters **16**, 797 (1966).

[15] A. P. VanGelder, Phys. Letters **22**, 7 (1966); T. W. Nee and R. E. Prange, *ibid.* **25A**, 582 (1967).

[16] S. Kawaji and Y. Kawaguchi, J. Phys. Soc. Japan Suppl. **21**, 336 (1966).

[17] S. Kawaji and H. C. Gatos, Surface Sci. **6**, 362 (1967); **7**, 215 (1967).

[18] A. B. Fowler, F. F. Fang, W. E. Howard, and P. J. Stiles, Phys. Rev. Letters **16**, 901 (1966); J. Phys. Soc. Japan Suppl. **21**, 331 (1966).