spite of the fact that the Q's themselves are slightly lower.

(v) Since the field associated with the whispering modes inside the sphere is limited to the vicinity of the surface, it should suffice if the luminescent centers are present in this surface layer.

(vi) Since the degeneracy of the whispering modes can be removed by introducing any departure from spherical symmetry, further mode selection ought to be possible. This could be done, e.g., by use of a spheroidal shape, by employing a uniaxial host lattice, or by applying a magnetic field.

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Theory for the Photoemission from a Space-Charge Region of a Semiconductor

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A theory is developed for evaluation of the effect of a space-charge region on photoemission from semiconductors. Such effect is shown to be significant in many cases and leads to the conclusions: (1) a "tail" should extend beyond the normal threshold region; (2) the energy of the valence band edge cannot, in general, be inferred from the observed threshold; (3) positive and negative space-charge regions cause effects which may not be symmetrical; (4) power-law fits to photoemission data near the threshold are of doubtful validity. It is shown that several anomalous results appearing in the literature can be explained by the space-charge effect.

INTRODUCTION

IT has long been realized that surface effects might influence the external photoelectric behavior of semiconductors. Such influence may arise from the surface states themselves or from the adjacent space-charge region in which an electrostatic potential alters some of the bulk properties of the material. The latter aspect of the problem will be treated here and the surface states enter only as they affect the space-charge region. The purpose of the work is to evaluate the effect of the presence of a space-charge region on photoemission from semiconductors. It is thus concerned with what is generally called the "volume photoelectric effect," so that the conclusions reached also have a bearing on the question of the relative importance of the volume vs surface photoeffect.

CONVENTIONAL TREATMENT OF PHOTOEMISSION

Because there exists no established theoretical model for photoemission from semiconductors, these calculations are based on the most general expressions which can usefully represent the fundamental processes. The essential conclusions can thus be applied to any of the theories found in the literature. A simple, nondegenerate semiconductor is assumed throughout with Fermi energy E_f, valence band edge E_v, and work function ϕ. It is further assumed that all photoelectrons originate in the valence band so that the photoelectric threshold energy $(h\nu)_t$ corresponds to emission of electrons whose initial energy was E_v. The photocurrent may be written as

$$i=\int_E I(\nu)\sigma(\nu,E)f(E)n(E)t(E+h\nu)dE, \qquad (1)$$

where E is the initial energy of the electron, $h\nu$ the photon energy of the light whose intensity is I, σ the cross section for an absorption capable of producing a photoelectron, f the Fermi occupation function, n the density of states in the semiconductor, and t an escape probability for an excited electron. In keeping with the assumption of nondegeneracy, it will be assumed $f(E)\simeq 1$ in the valence band, although this restriction can be relaxed if necessary.

In the various theories of photoemission, different models are advanced for the dependence on energy of the absorption and escape probabilities. The density of states is normally taken as $n(E)\propto(E-E_v)^{\frac{1}{2}}$ if energy increases for levels lying deeper in the valence band. This approximation should be satisfactory in most cases, particularly for energies near the band edge where surface effects should be most important. Combining the energy dependences of the terms in Eq. (1) results in all cases in a functional dependence on energy having the form

$$i\propto(E-E_v)^l \qquad (2)$$

near the photoelectric threshold. Apker *et al.*[1] used a value

[1] L. Apker, E. Taft, and J. Dickey, Phys. Rev. 74, 1462 (1948).

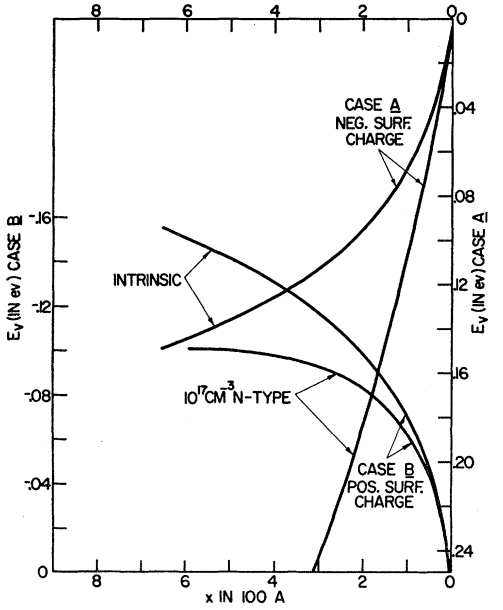

FIG. 1. Calculated shapes of the valence band edge $E_v(x)$ of Ge in several cases. $E=0$ is taken arbitrarily at the level at which the band edge meets the surface. Note the two scales of energy.

of $l=\frac{5}{2}$ in fitting their retarding potential data for Te. Spicer, however, found that $l=\frac{3}{2}$ best fitted his spectral distribution measurements of the highly sensitive alkali antimonides.[2] Some of their data and theoretical curves are shown below. Other values for l have been suggested (always a small, positive number), and it seems likely that different cases will require somewhat different values even in more refined theories. Therefore, expression (2) will be used to represent the energy dependence of the photoemission near the threshold and assignment of a value for l will be left to the specific applications of the resulting theory.

Also of consequence in photoemission from semiconductors is the difference between the work function ϕ and the photoelectric threshold $(h\nu)_t$. This difference should be just $(E_v-E_f)\equiv\delta$ in a flat-band model, but agreement is not found experimentally.[3,4] In the space-charge region of a semiconductor the electrostatic potential causes E_v, hence δ, to vary with position, and the photoemissive properties may be influenced if the photoelectrons originate in a region in which such variation is appreciable. This was pointed out by Bardeen (reference 1, footnote 28). In the light of increasing evidence of the importance of "volume photoemission,"[2,5] the evaluation of the influence of the space-charge region seems worthwhile.

The first and most difficult problem is the source region of photoelectrons. The attenuation of the incident light and range of the excited electrons must both be considered for this purpose. For the light intensity, the normal decay will be assumed so that $I=I_0\exp(-\alpha x)$, where I_0 is the incident intensity, α the absorption coefficient, and x the depth below the surface.

The range of the excited electrons is less well known and is different in different classes of materials, depending on the dominant scattering mechanism.[6] It has been shown, however, that for lattice scattering, the escape probability is well represented by an exponential dependence on depth of the form $t\propto\exp(-\beta x)$, where $1/\beta$ is the mean escape distance.[7] In the absence of the appropriate expressions for t when scattering is dominated by other mechanisms, this exponential form will be used with the understanding that it may be only a first approximation in some cases.

The explicit dependence of photocurrent on depth is then

$$i\propto\exp(-\gamma x), \tag{3}$$

where $\gamma=\alpha+\beta$ and $1/\gamma$ is the mean depth of origin of the photoelectrons. In materials like Cs_3Sb where this formulation should be appropriate, $\beta\simeq 4\times10^5$ cm^{-1}, $\alpha\simeq 1\times10^5$ cm^{-1} near the threshold,[8] giving a mean depth of origin $\sim$200 A. For Ge, $\alpha=1.4\times10^6$ cm^{-1} near the threshold[9] and scattering by pair-producing collisions may suppress the escape depth to a value well under 100 A.[10] Departure from the exponential form of expression (3) may also occur, although the following calculations are based on the assumption that some effective γ can be assigned in all cases.

With the use of relations (2) and (3), it is found that Eq. (1) assumes the form

$$i\propto[E-E_v(x)]^l e^{-\gamma x}. \tag{4}$$

It is readily seen that this is simply the power-law dependence at each depth weighted in proportion to the contribution which electrons from that depth can make to the photocurrent. This expression will be integrated over x once the appropriate function $E_v(x)$ is known.

BAND SHAPE CALCULATIONS

The bending of the energy bands in the region of interest must next be evaluated quantitatively. The established method for such calculations has been used in the particular form appropriate for determining the actual band shapes rather than the surface conductance. A numerical integration of Poisson's equation has been performed with the surface potential ϕ_s, bulk potential ϕ_b, temperature T, and intrinsic Debye length L as

[2] William E. Spicer, J. Appl. Phys. **31**, 2077 (1960).
[3] J. A. Dillon and H. E. Farnsworth, J. Appl. Phys. **28**, 174 (1957).
[4] G. W. Gobeli and F. G. Allen, J. Chem. Phys. Solids **14**, 23 (1960).
[5] Harry Thomas, Z. Physik **147**, 395 (1957) and following papers.
[6] L. Apker, E. Taft, and J. Dickey, J. Opt. Soc. Am. **43**, 78 (1953).
[7] Malcolm H. Hebb, Phys. Rev. **81**, 702 (1951).
[8] W. E. Spicer, Phys. Rev. **112**, 114 (1958).
[9] H. R. Philipp and E. A. Taft, Phys. Rev. **113**, 1002 (1959).
[10] P. A. Wolff, Phys. Rev. **95**, 1415 (1954). This expectation is yet to be reconciled with the observations reported in reference 5 of 300 A depth of origin in alkali metals.

adjustable parameters. One treatment assumed (1) complete ionization of impurities, (2) nondegenerate statistics, and (3) thermal equilibrium, and is thus appropriate for most Ge or Si at room temperature.[11] In other cases the more general form of these calculations was applied, requiring only equilibrium conditions.[12]

In Fig. 1 are shown several calculated band shapes for Ge at room temperature based on reasonable bulk and surface conditions. In each case, the allowed valence band states lie below the appropriate curve for E_v. For p-type material the band shapes are simply mirror images of those for n-type material with opposite surface charge. It will be noted that energy increases deeper in the valence band and the zero of energy is taken at $E_v(0)$ in each case. It is evident from these curves that E_v may vary by significant amounts ($\sim$0.1 ev) over the region of origin of photoelectrons. From this it may be concluded that (1) the space-charge region can play an appreciable role when volume photoemission occurs, and (2) values of δ inferred from photoemission are not generally significant.

INTEGRATION OF THE PHOTOCURRENT

Using functions for $E_v(x)$ obtained in this manner, expression (4) has been integrated over x in a number of cases using a computer program which accepts arbitrary values for l, γ, and temperature as well as bulk and surface properties of the material. Before presenting some results, the following points should be made (see Fig. 2). First, the exponential weighting factor destroys the symmetry between situations with negative surface charge (case A) and those with positive surface charge (case B), because only for the former cases are the highest-lying valence band states at the surface where they are weighted most heavily. Consequently, n-type and p-type materials are no longer symmetrical in general, since n-type materials can support a larger negative surface charge than can p-type materials. Also, the limits of integration are different for these two types of cases because some valence band states are confined near the surface in case A but not in case B.

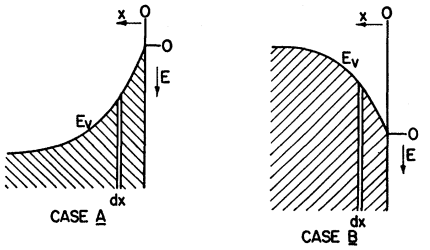

FIG. 2. Illustration of the asymmetry of the two types of cases: Negative surface charge is called case A; positive surface charge, case B.

[11] G. C. Dousmanis and R. C. Duncan, Jr., J. Appl. Phys. **29**, 1627 (1958).

[12] Ruth Seiwatz and Mino Green, J. Appl. Phys. **29**, 1034 (1958).

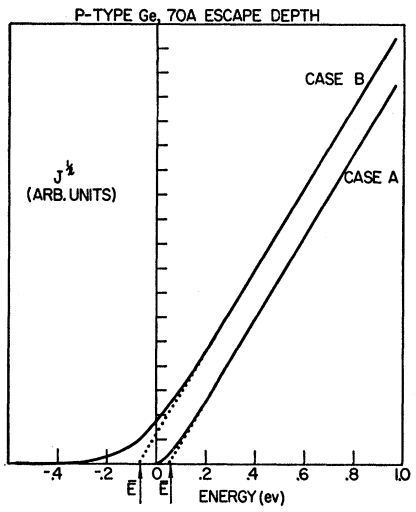

FIG. 3. Calculated photocurrent J (plotted as the $1/l$ power) vs energy including space-charge effect. Dotted extrapolation corresponds to flat-band, power-law theory. Acceptor concentration 10^{17} cm^{-3}. In this example $l=\frac{5}{2}$.

The results of these calculations are illustrated by Figs. 3 and 4 in which the integrated photocurrent J is compared with the behavior expected from the conventional, flat-band theory. It may be seen that J follows the original power-law dependence for energies away from the threshold. If, however, the simple power-law behavior is extrapolated to locate a "threshold" (as in Fig. 3), the value so obtained, $\bar{E}$, does *not* represent the level of the valence band edge, contrary to

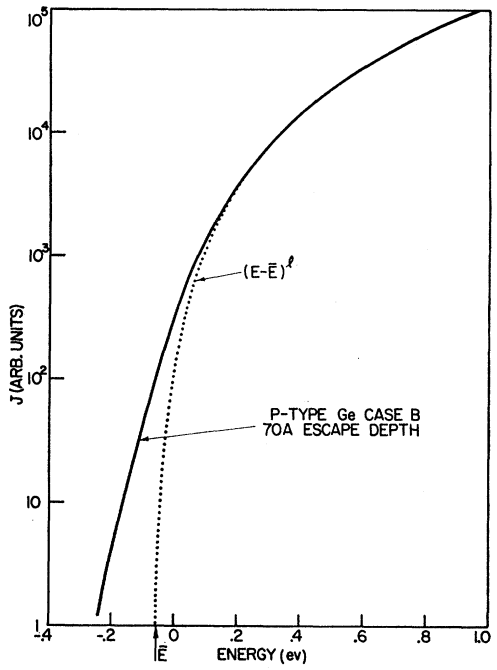

FIG. 4. Semilogarithmic plot of data from Fig. 3 shown for comparison with experimental observations in Figs. 5 and 6.

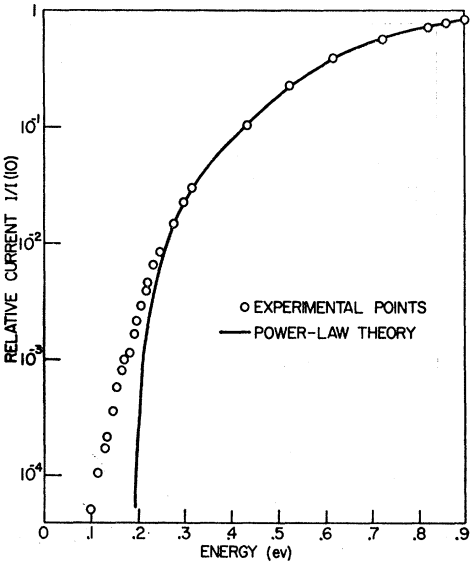

FIG. 5. Retarding potential data on Te at room temperature and the power-law curve (from reference 1).

previous interpretations based on flat-band models. It can readily be shown that $\bar{E}$ is the weighted average of $E_v(x)$, and to first order is independent of the value used for l. The other significant feature of these curves is the appearance of a "tail" extending beyond the expected threshold for all cases in which there is a space charge. The magnitude of the tail emission and its range of energies, however, are sensitive to the material parameters as well as to the values of l, γ, and temperature, so that quantitative application of this method will require more detailed data on these factors than are presently available. Attempts are being made to reverse this procedure and evaluate some of these parameters by curve-fitting techniques.

On the basis of the information presented, it is suggested that some previously observed anomalies can be explained by the effect of the space-charge region. Figure 5 shows some retarding potential data on Te as they were fitted with a theoretical, power-law curve for which $l=\frac{5}{2}$ near the threshold (from reference 1).

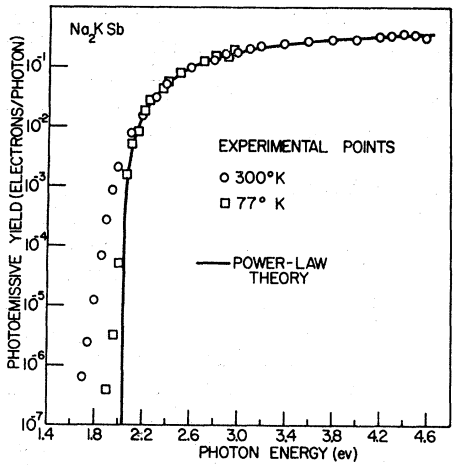

FIG. 6. Spectral distribution of photoemissive yield typical of the alkali antimonides (from reference 2).

It can be seen that the departure of the data from the power-law theory is of the same type as produced in Fig. 4 by the calculated space-charge effect. Similarly, in Fig. 6, typical spectral distribution data on the alkali antimonides from reference 2 are seen to depart from the power-law curve used therein having $l=\frac{3}{2}$ near the threshold. In these latter materials, the wide energy gap and long electron range both favor a pronounced space-charge effect, and some direct observations of an appreciable space-charge region in Cs_3Sb have been reported.[13] The temperature dependence of the tail in Fig. 6 also follows naturally from the great increase in the depth of the space-charge region as low temperature freezes out the free carriers. If this explanation of such observations is correct, they may then be regarded as clear evidence for volume photoemission.

ACKNOWLEDGMENTS

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[13] Frederick O. Wooten, Bull. Am. Phys. Soc. 6, 17 (1961).