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Intrinsic Optical Absorption in Single-Crystal Germanium and Silicon at 77°K and 300°K*

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The intrinsic absorption spectra of high-purity single-crystal germanium and silicon have been measured at 77°K and 300°K. The spectral regions studied encompassed a range of absorption coefficient from 0.1 cm^{-1} to 10^5 cm^{-1} for each material. The germanium data may be interpreted as indicating a threshold for direct transitions at 0.81 ev at 300°K and at 0.88 ev at 77°K. The threshold for indirect transitions was placed at 0.62 ev and 0.72 ev for 300°K and 77°K, respectively. For silicon the data were not as readily interpreted However, there is an indication that the threshold for direct transitions should be placed at about 2.5 ev and the threshold for indirect transitions at 1.06 ev and 1.16 ev at 300°K and 77°K, respectively.

INTRODUCTION

RECENT advances in our knowledge of the band structure of germanium and silicon[1-3] have revived interest in the problem of the intrinsic optical absorption process in these materials.[4-6] A theory has been developed by Hall, Bardeen, and Blatt which attempts to relate the optical absorption coefficient to the fundamental parameters of the band structure (e.g., shape and separation of the band surfaces).[7] This theory envisions two processes to account for the absorption. In the first process, absorption of the photon takes place with k-vector being conserved within the electron system itself (i.e., vertical transitions). For this "direct" process, the low-energy threshold for absorption would occur at the photon energy corresponding to the minimum energy separation, measured vertically on a reduced zone plot, between valence and conduction band states. This minimum separation is probably located at the origin of the Brillouin zone for both germanium and silicon.

For the second process, the indirect process, k-vector is not conserved within the electron system, but rather conservation is obtained by the emission or absorption of phonons. The process is pictured as a diagonal transition on a reduced zone plot. The threshold energy for the indirect transitions would correspond to the minimum energy separation, without restriction, between valence and conduction bands, less the energy of a phonon having the required k vector.

If the two thresholds are well separated, one might expect to see a separation of the absorption spectrum into two regions, one in which the absorption process is dominated by direct transitions, the other for which indirect transitions would be dominant.

Previous measurements of the absorption coefficient in single crystal silicon and germanium were restricted to absorption coefficients less than about 10^3 cm^{-1} because of problems of sample thickness.[4-6] By using evaporated films, it was possible to study higher absorption coefficients.[5] Some early optical investigations indicated to us that the values obtained from such films were not characteristic of single-crystal material. In view of the theoretical interest in the subject, it seemed worthwhile to develop methods that would allow for as complete a study of absorption coefficients in single crystal materials as could be made. Accordingly the study described below was undertaken.

EXPERIMENTAL

Samples of high-purity germanium and silicon with resistivities in excess of 20 ohm-cm were cut to an appropriate thickness with a diamond saw. The faces were ground with successively finer grades of carborundum and then polished with aluminum oxide polishing powder on a bee's wax lap. For samples whose thickness was 100 microns or less, special pains were necessary to obtain samples that were of uniform thickness and free from pinholes. For these samples one face was first ground and polished so that no scratch marks were visible under a low-powder microscope. This face was then pressed in contact with a glass plate on which a resin had been spread. Thus mounted, the samples were ground and polished down to the desired thickness. Alkanex, a thermosetting resin, was used for samples 0.5μ to 2μ thick. Glycol phthalate, a thermoplastic resin, was used for samples 2μ or thicker. The latter had the advantage of permitting the sample to be freed from the backing for the measurement.

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* A preliminary report of this work was presented at the 1955 New York Meeting of the American Physical Society [Phys. Rev. **98**, 1536(A) (1955)].

[1] F. Herman, Phys. Rev. **88**, 1210 (1952); F. Herman and Callaway, Phys. Rev. **89**, 518 (1953); F. Herman, Phys, Rev. **93**, 1214 (1954); F. Herman, Phys. Rev. **95**, 847 (1954); F. Herman, Physica **20**, 801 (1954).

[2] Dresselhaus, Kip, and Kittel, Phys. Rev. **92**, 827 (1953); Dresselhaus, Kip, and Kittel, Phys. Rev. **95**, 568 (1954); C. Kittel, Physica **20**, 829 (1954).

[3] Lax, Zeiger, Dexter, and Rosenblum, Phys. Rev. **93**, 1418 (1954); Dexter, Zeiger, and Lax, Phys. Rev. **95** 557 (1954); Dexter, Lax, Kip, and Dresselhaus, Phys. Rev. **96**, 222 (1954); R. N. Dexter and B. Lax, Phys. Rev. **96**, 223 (1954); Lax, Zeiger, and Dexter, Physica **20**, 818 (1954).

[4] H. Y. Fan and M. Becker, in *Semiconducting Materials* (Butterworth Publications, London, 1951), p. 132; Fan, Sheppard, and Spitzer, Atlantic City Photoconductivity Conference, November, 1954 (to be published).

[5] W. H. Brattain and H. B. Briggs, Phys. Rev. **75**, 1705 (1949).

[6] H. B. Briggs, J. Opt. Soc. Am. **42**, 686 (1952).

[7] Hall, Bardeen, and Blatt, Phys. Rev. **95**, 559 (1954); also Atlantic City Photoconductivity Conference (unpublished).

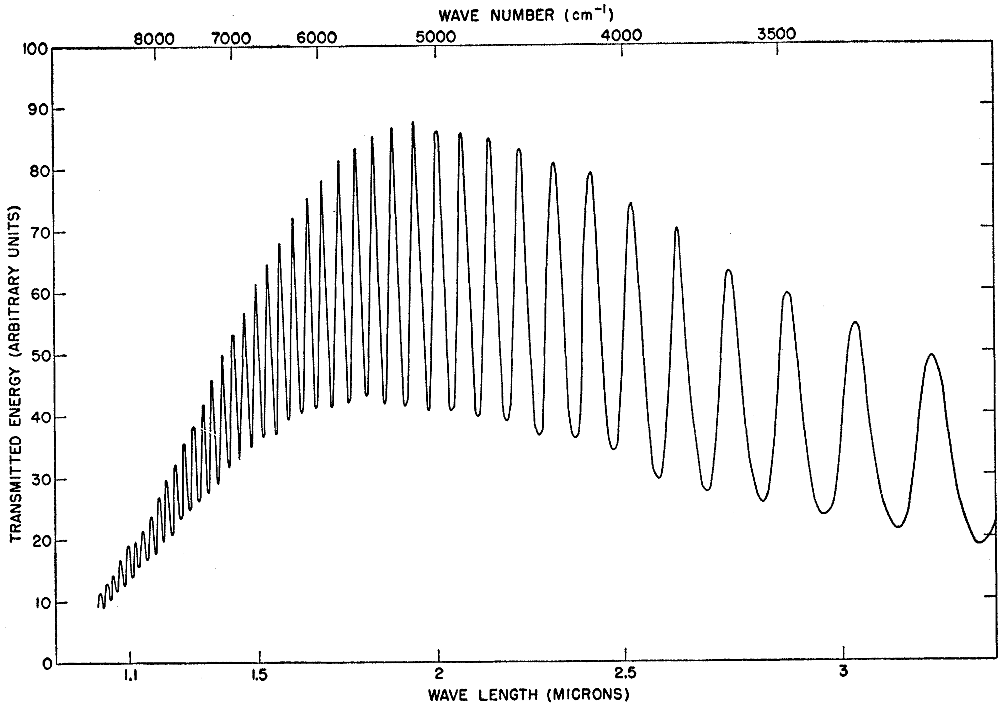

FIG. 1. Interference fringe pattern for a silicon sample 9.2μ thick and about 5×5 mm in area.

Thickness was measured, variously, by direct measurement with a dial gauge (0.1 mil/division), weighing, or measurement of the interference fringe spectrum. The last method gave the most reliable results for thin samples and also some measure of the nonuniformity of the samples. If, for example, a nonuniformity in thickness can be described by saying that the sample consists of two sections of equal area, one of which is thicker than the other by an amount δ, then it is possible to calculate very simply the quantity δ from the intensity pattern of the interference fringes.[8] For one sample of silicon of mean thickness equal to 9.2μ and an area of about 5×5 mm, a δ of $\sim$0.07μ was calculated from the fringe pattern which is shown in Fig. 1. In practice, nonuniformities in thickness of about 5 percent are unimportant in the absorption constant measurements. Samples used for these measurements were well within this tolerance.

The optical measurements were made on a Perkin-Elmer 112 double-pass spectrometer using a CaF_2 prism. Room temperature measurements were made with samples mounted at either the entrance or exit port. No difference was observed between the two measurements. The liquid nitrogen measurements reported were made with the samples mounted in a transparent dewar flask and immersed in the refrigerant. It was found that this method gave as reliable data as more elegant methods and had the further advantage of insuring that the samples were at temperature, a far from trivial point in the case of the very thin samples.

Depending on the spectral region being studied, a thermocouple, a PbS cell, or a photomultiplier was used as a detector. Where overlapping data points were available, the agreement between different measurements was good.

Absorption measurements were made by the usual sample-in, sample-out technique correcting for the reflectance of the samples. Reliable absorption coefficients could usually be obtained with the measured transmission in the range from about 0.3 to 10^{-3}. For very low transmissions it was necessary to check for stray light signals and nonlinearity in the over-all detection system. In some instances, absorption coefficients, which subsequently proved to be reliable, were obtained from transmissions as low as 10^{-6}. Because our measurements were made in the low-transmission range, the corrections for the effects of sample backing described by Brattain and Briggs[5] were unimportant. Data taken on a given sample with and without its backing gave identical absorption coefficients.

An important aspect of the work was concerned with determining to what extent the thinnest samples had the properties of bulk single-crystal material. To this end, two experiments were performed. The first was to obtain an x-ray diffraction picture and observe whether the thinnest material was still single crystal and to what extent it was disordered. Back-reflection Laue photographs of samples $\sim$1μ thick indicated single-crystal patterns which, to the resolution of the x-ray camera, were indistinguishable from the patterns for bulk single crystals.

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[8] M. Born, *Optik* (Verlag Julius Springer, Berlin, 1933), p. 122.

The second experiment was perhaps a more sensitive test of the crystalline perfection of the thin samples. It consisted of a measurement of the Hall effect in some of these samples. A germanium sample of 2μ in thickness was found to be *p*-type with a hole mobility at room temperature of about 600 cm^2/volt sec. After an annealing treatment, the mobility increased to about 2500 cm^2/volt sec. The hole mobility in the parent material, which was *p*-type, was also about 2500 cm^2/volt sec. A silicon sample 2μ thick, which had been cut from a *p*-type crystal, was found to be *n*-type with a mobility of about 500 cm^2/volt sec at room temperature. The electron mobility in good silicon is of the order 1500 cm^2/volt sec. The effect of annealing was not measured on this sample. No difference was observed optically between other annealed and unannealed samples at either 300°K or 77°K.

Summarizing the results given above, we conclude that the thin samples are single crystal, although probably not of the perfection of the bulk material. We have, unfortunately, no good way of judging how the imperfections will affect the absorption coefficient. For this reason, we would regard the data obtained from the very thin samples (i.e., absorption coefficients $>10^4$) as still subject to some small uncertainty. From the lack of an annealing effect and from the cross checking of data points obtained from samples differing in thickness by about a factor of 5, it would appear that this uncertainty would be less than 20 percent in the value of the absorption coefficient.

RESULTS

The absorption spectra for germanium at room temperature and liquid nitrogen temperature are shown in Figs. 2 and 3, those for silicon in Fig. 4. Figure 2 is a plot of a portion of the germanium data on an expanded horizontal scale.

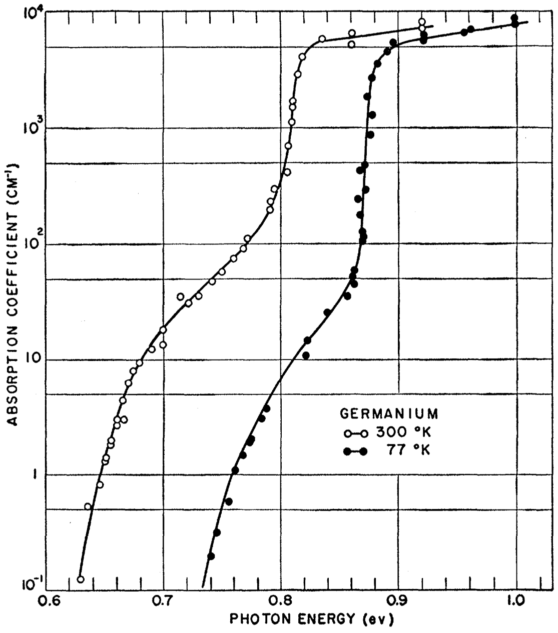

FIG. 2. Absorption spectra of single-crystal germanium at 77°K and 300°K.

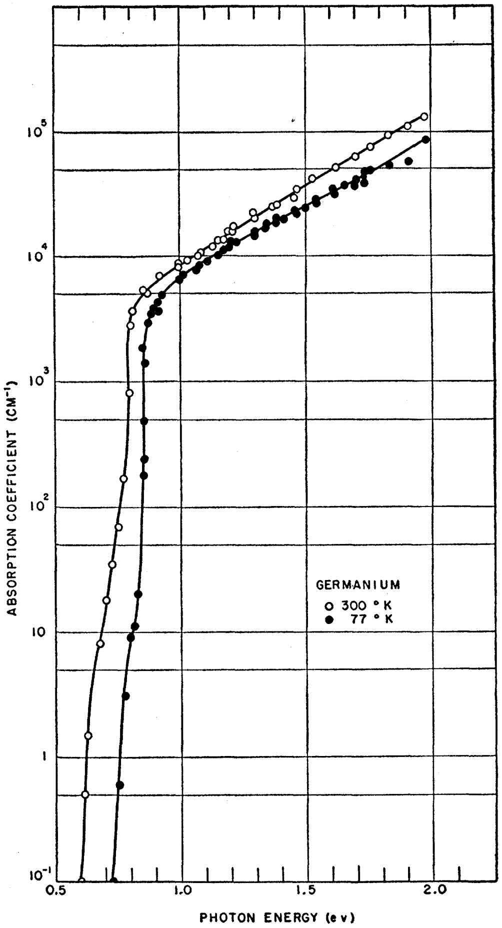

FIG. 3. Absorption spectra of single-crystal germanium at 77°K and 300°K.

It is of interest to see if the observed data can be interpreted in terms of the theoretical model suggested by Hall, *et al.*[7] Let us first consider the case for germanium. Starting at the high-energy end and going toward lower energies, there is a gradual decrease in the absorption coefficient from order 10^5 to 10^4 cm^{-1} down to an energy of 0.81 ev at room temperature and 0.88 ev at liquid nitrogen. At these points there is a very abrupt and rapid decrease in absorption coefficient from about 5×10^3 to about 10^2 cm^{-1}. (See Fig. 3.) One can interpret the absorption on the high-energy side of these "knees" as resulting largely from direct transitions and the knees themselves as indicating the approximate low-energy thresholds for these direct transitions. This view is supported by the magnitude of the absorption coefficient in the high-energy region. For example, assume that the oscillator strength for the transition is of order 3 and that the valence and conduction bands are of order 10 ev wide with a constant density of states. One

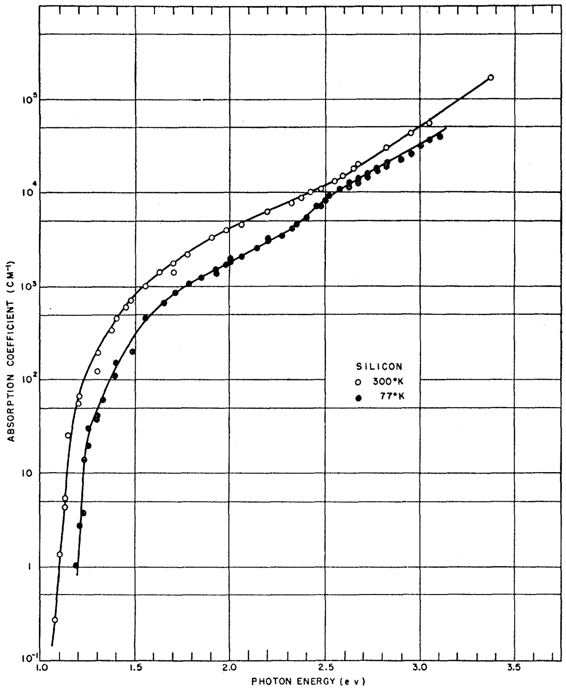

FIG. 4. Absorption spectra of single-crystal silicon at 77°K and 300°K.

can then naively calculate that the absorption coefficient should be of order 10^6 cm^{-1}.[9] These assumptions overestimate the absorption coefficient for photon energies within one or two ev of the threshold. Hence the observed coefficients in the high-energy region are in the expected range.

If we accept the premise that we are seeing direct transitions in the high-energy region, then the temperature effects on absorption coefficients in this region should, in first approximation, merely correspond to the change in band gap. That is, the curves in this range should be superposable by a horizontal shift. This is only roughly the case. There is a suggestion that the curves at the two temperatures are not strictly parallel. The horizontal shift required to bring the curves into superposition (in the direct transition region) ranges from 0.07 to 0.12 ev. The shift in the (threshold) region just below the knees is 0.07 ev. These data would indicate a temperature coefficient of band gap of from -3 to -5×10^{-4} ev/°K, the low value corresponding to the shift at the threshold.

Herman's most precise calculation of the band structure of germanium[10] indicated that the lowest states of the conduction band near $k=0$ are of S character, whereas the highest states for the valence band are of P character. If this is true, the theory for the direct transitions indicates that the energy dependence of the absorption coefficient should be as $(\nu-\nu_{\text{threshold}})^{\frac{1}{2}}/\nu$. This expression results from an application of a constant-effective-mass approximation. The observed absorption coefficient indicates a stronger energy dependence. This could result from an inapplicability of the effective mass approximation over the range of our data. In view of our knowledge of the bands, particularly the complex character of the conduction band, this seems a reasonable hypothesis. It is also possible that the lowest states of the conduction band near $k=0$ are of P character, in which case the absorption coefficient would go as $(\nu-\nu_{\text{threshold}})^{\frac{3}{2}}/\nu$. This would be a closer representation of the data but still far from a satisfactory one.

Referring to the germanium data again, it is observed that on the low-energy side of the knees, shoulders are developed in the curves at absorption coefficients of order 10^2 cm^{-1}. These are most clearly shown in Fig. 2. As the energy is further decreased the absorption coefficient again becomes a very rapidly decreasing function of energy. The absorption in the shoulders can be attributed to indirect transitions. The thresholds for these processes are presumably indicated by the regions of very rapid change of absorption coefficient with energy. As such, we would place these thresholds at $\sim$0.62 ev and at $\sim$0.72 ev for 300°K and 77°K, respectively.

The absorption due to indirect transitions should be temperature dependent in two ways. First, there should be a change in band gap and second a change due to an altered phonon interaction. The former process would result in a horizontal shift, the latter in a vertical shift of the absorption curves. We have found that the best superposition of the absorption curves in the range from 10^2 to 10^{-1} cm^{-1} is obtained by a horizontal shift of 0.10 ev and a vertical shift of about a factor of 2 (i.e., multiply 77°K data by 2). This matching procedure appears unique. The horizontal shift suggests a temperature coefficient of band gap of -4.5×10^{-4} ev/°K. The theory for the indirect transitions indicates that the absorption coefficient curve should show a vertical shift factor that would lie somewhere between the ratio of temperatures (i.e., 4 for present data) and unity. The factor of 2 from the above interpretation is, therefore, in the predicted range.

It is of interest to note that the slight difference in the temperature coefficients of the thresholds for direct (-3×10^{-4} ev/°K) and indirect (-4.5×10^{-4} ev/°K) transitions may suggest a temperature dependence of order 1×10^{-4} ev/°K for the energy separation of the various minima of the conduction band.

The curves for silicon do not lend themselves to analysis as readily as those for germanium. That is, there seems no point at which one can make a clear-cut division between absorption due to direct and indirect processes. There is some suggestion from the curves, particularly that for 77°K, that this division may occur at about 2.5 ev.

It is noteworthy that in the low-absorption coeffi-

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[9] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), p. 103.

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

cient region it is possible to get an excellent superposition of the curves for the two temperatures by a single horizontal plus vertical shift. The matching process, which again appears unique, consists of a horizontal shift of 0.10 ev and a vertical shift factor of 1.7 (i.e., multiplying 77°K data by 1.7). This gave a superposition of curves from $\sim 5\times 10^3$ to ~ 0.5 cm^{-1} (lower limit of data). The horizontal shift gives a temperature coefficient of band gap of -4.5×10^{-4} ev/°K. The vertical shift is again of the order of magnitude predicted by theory.

ACKNOWLEDGMENTS

We are greatly indebted to L. Keifer and J. H. McTaggart for their painstaking work in the preparation of the samples. We should also like to thank A. G. Tweet for the Hall measurements on the thin samples. We have profited from discussion with E. O. Kane of the theoretical aspects of this work. We are indebted to H. Brooks for comments on the manuscript prior to publication.

Note added in proof.—Since the preparation of this manuscript, MacFarlane and Roberts [Phys. Rev. **97**, 1714 (1955); **98**, 1865 (1955)] have presented data for germanium and silicon in the low-absorption coefficient range (i.e., α less than 100 cm^{-1}). Their data differ in detail from those presented here. The latter are, however, in very good agreement in the overlapping range with data previously presented.[4,6]

MacFarlane and Roberts analyze their data in terms of the indirect transition model of Hall, *et al.*,[7] taking the phonon contribution explicitly into account. This they do by plotting the square root of the absorption coefficient as a function of photon energy and decomposing the resultant curve into two straight line sections. The section at low energies is ascribed to a process in which a phonon is absorbed, the section at higher energies to one in which a phonon is emitted. From their data they estimate that the phonon required is characterized by a temperature of 260°K for Ge and 600°K for Si.

Our data do not show as obvious a resolution into two such linear sections when plotted after the manner of MacFarlane and Roberts. An analysis of our data in terms of vertical and horizontal shifts with temperature, as described in the body of our paper, would suggest phonons characterized by temperatures of $\sim$300°K for Ge and 500°K for Si. However, as Brooks has pointed out to us, there is a temperature dependence in the term $(E_{c0}-E_{c(111)})^{-2}$ (see reference 7 for definitions) which appears in the theoretical expression for the absorption coefficient. This dependence is comparable to the temperature dependence explicitly expressed by the phonon population. Consequently, any analysis based solely on a phonon population effect is probably not too meaningful.

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Surface Barrier Analysis for Metals by Means of Schottky Deviations*

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The transmission coefficient for the mirror-image barrier at a metal surface is applied to the case of photoelectric emission. The distribution over which the coefficient is averaged is that given by Fowler for energies normal to the emitter surface, and is altered by the Schottky barrier lowering. The average differs from unity by an amount the major part of which is a periodic function of the accelerating field, giving a periodic deviation from the photoelectric Schottky effect which differs from the thermionic deviation only in amplitude. A refinement in the computation of the unaveraged periodic transmission coefficient brings the theory for thermionic deviations into agreement with that of Miller and Good. The improved form of the thermionic deviation is applied to experimental data to evaluate the complex reflection coefficient μ characterizing the potential form in the immediate vicinity of the surface. The values of $|\mu|$ so obtained for the highly refractory metals are of the order of 0.4, as compared with 0.2 predicted on the basis of the box model.

I. INTRODUCTION

ELECTRONS emitted through a metallic surface into an accelerating field undergo reflection at the surface itself and at the maximum of the mirror-image barrier. The interference resulting from this double reflection manifests itself in periodic deviations from the Schottky effect.[1] In a previous publication,[2] there was formulated a transmission coefficient characteristic of the metallic barrier shape and suitable for the discussion of any emission process involving electrons of low average escape energies. A particular application was made to the case of thermionic emission. In the present work, the parallel case of photoelectric emission will be considered. In the early stages of this work, it was found that the periodic part of the transmission coefficient could be expressed in better form.[3] The only effect of this refinement is to increase the theoretical amplitude of the periodic Schottky deviation; the basic conclusions found previously[2] remain unchanged. The revised transmission coefficient will be described here, and its effects on the interpretation of thermionic data will be discussed before applying it to the formulation of the photoelectric theory.

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[*] This research was sponsored by the U. S. Atomic Energy Commission.

[1] E. Guth and C. J. Mullin, Phys. Rev. **59**, 575 (1941); **59**, 867 (1941).

[2] Juenker, Colladay, and Coomes, Phys. Rev. **90**, 772 (1953).

[3] The author is indebted to Dr. Conyers Herring for pointing out the suitable process in a private communication.