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Mean-Square Atomic Displacements in HgTe and Their Temperature Dependence

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The mean-square atomic displacements and associated Debye temperature of HgTe have been determined from single-crystal x-ray scattering measurements at 32, 90, and 296 °K. The mean-square displacements of Hg and Te are observed to increase from 0.0064 ± 0.0001 and 0.0055 ± 0.0001 Å^{-2} to $0.029^{+0.011}_{-0.003}$ and $0.0209^{+0.0046}_{-0.0021}$ Å^{-2}, respectively, while the corresponding Debye temperature increases from (73 ± 1) to (101^{+6}_{-13}) °K, over this temperature range. Comparison is made with other similar measurements and with recent theoretical calculations for HgTe; differences are noted and discussed. The results reported here tend to substantiate the experimental work upon which a recently reported failure of the Brooks-Yu theory for HgTe is based.

I. INTRODUCTION

The cause of the positive temperature dependence of the energy band gap in HgTe and in $Cd_xHg_{1-x}Te$ $(x < 0.5)$ alloys remains an open question. Based on the successful application by Keffer, Hayes, and Bienenstock[1,2] of the Brooks-Yu[3] theory to predict the positive band-gap temperature dependence of PbTe and the similarity between the relative masses in PbTe and HgTe, Scott[4] suggested that a similar calculation may be appropriate for HgTe, in spite of the dissimilarity in crystal structures. However, in a recent publication Guenzer and Bienenstock[5] report the failure of this theory to predict the band-gap temperature coefficient for HgTe.

The temperature dependence of the band structure is established in the Brooks-Yu theory by combining the ionic pseudopotential form factors with suitable Debye-Waller factors, values of the Debye-Waller factor being obtained from appropriate scattering experiments. Guenzer and Bienenstock[5] determined the Debye-Waller factors of HgTe from x-ray scattering measurements and used these results in their unsuccessful attempt to predict the band-gap temperature dependence for this material. We note, however, that in a previous x-ray determination of the Debye-Waller factors for HgTe, Bublik, Gorelik, and Kapustina[6] reported values for the mean-square displacements which differ by more than a factor of 2 at room temperature from the results of Guenzer and Bienenstock. Furthermore the Bublik *et al.* results indicate that the mean-square atomic displacement of the heavier Hg atom is only about 4% greater than that of the Te atom, whereas Guenzer and Bienenstock observe the mean-square displacement of Hg to be about 1.4 times greater than that of Te at all temperatures. In addition, Ivanov-Omskii, Kolomiets, Kleshchinskii, and Smekalova[7] have studied the effect of acceptor concentration on the x-ray Debye temperature Θ^M of HgTe. In all cases, they find values of Θ^M which are significantly greater than those reported by Guenzer and Bienenstock and less than those reported by Bublik *et al.*

In consideration of these discrepancies and the apparent failure of the Brooks-Yu theory in this case, it was felt that an independent experimental determination of the Debye-Waller factors of HgTe was in order. It is further believed that the results reported in this work represent an improvement over the previous measurements for the following reasons: (i) Data were collected below the previous low-temperature limit of 77 °K. (ii) All data were corrected for thermal-diffuse-scattering contributions to the measured intensity. (iii) An explicit correction was applied for extinction effects. (iv) The data were collected under conditions which were prechecked to ensure the absence of possible first-order simultaneous multiple-diffraction events.

II. THEORY

The integrated intensity diffracted from an extended face of a mosaic crystal can be expressed as follows:

$$\rho' = C\Omega(\theta) |F_{hkl}|^2 , \qquad (1)$$

where C is a constant containing an unknown intensity scale factor, $\Omega(\theta)$ is a known function of the Bragg diffraction angle only, and F_{hkl} is the modulus of the structure factor. The structure factor for a zinc-blende lattice (space group $F\bar{4}3m$), such as HgTe, can be written as follows:

$$F_{hkl}=4(f_{\mathrm{Hg}}e^{-x\langle u^2_{\mathrm{Hg}}\rangle}\pm f_{\mathrm{Te}}e^{-x\langle u^2_{\mathrm{Te}}\rangle})\quad\begin{cases}+\text{ if } h+k+l=4n\\ -\text{ if } h+k+l=4n\pm 2\\ (h,k,l\text{ all even})\,,\end{cases}\tag{2}$$

$$F_{hkl}=4(f_{\mathrm{Hg}}\,e^{-x\langle u^2_{\mathrm{Hg}}\rangle}\pm if_{\mathrm{Te}}\,e^{-x\langle u^2_{\mathrm{Te}}\rangle})\quad\begin{cases}+\text{ if } h+k+l=4n+1\\ -\text{ if } h+k+l=4n-1\\ (h,k,l\text{ all odd})\\ n=1,2,3,\ldots\,,\end{cases}\tag{3}$$

$$F_{hkl}=0\quad(h,k,l\text{ mixed indices}),\tag{4}$$

where

$$x=8\,(\pi\sin\theta/\lambda)^2\,.$$

The exponential terms in Eq. (2) and (3) represent the Debye-Waller factors for the two constituent atoms; $\langle u^2_{\mathrm{Hg}}\rangle$ and $\langle u^2_{\mathrm{Te}}\rangle$ are the mean-square displacements of the two atoms; f_{Hg} and f_{Te} are the respective atom scattering factors; all other terms have their standard meaning (as defined in the *International Tables for X-Ray Crystallography*). In principle, measurement of the intensity of any two independent reflections is sufficient to determine $\langle u^2_{\mathrm{Hg}}\rangle$ and $\langle u^2_{\mathrm{Te}}\rangle$ to within an unknown scale factor. In this work, data were collected from a number of reflections belonging to the two classes: $h+k+l=4n$ and $h+k+l=4n\pm 2$, the so-called superlattice and sublattice reflections, respectively. The values of the two mean-square displacements were determined by a least-squares procedure as described below.

Within the quasiharmonic approximation, the mean-square displacements for a cubic, diatomic lattice are related to the frequency spectrum of the lattice $G(\omega)$ through the Debye-Waller theory as follows:

$$m_{\mathrm{Hg}}\langle u^2_{\mathrm{Hg}}\rangle+m_{\mathrm{Te}}\langle u^2_{\mathrm{Te}}\rangle=\frac{1}{2\pi^2}\,\frac{\int G(\omega)\,\overline{E}(\omega)\,\omega^{-2}\,d\omega}{\int G(\omega)\,d\omega}\,,\tag{5}$$

where $\overline{E}(\omega)$ is the mean energy of an oscillator of frequency ω; m_{Hg} and m_{Te} are the respective atomic masses; the integrations are performed over all frequencies.[8] If the Debye frequency distribution function is substituted for $G(\omega)$, the mean-square displacements can be expressed in terms of the x-ray Debye temperature Θ^M:

$$m_{\mathrm{Hg}}\langle u_{\mathrm{Hg}}\rangle+m_{\mathrm{Te}}\langle u_{\mathrm{Te}}\rangle=6\,\hbar^2\,T[\Phi(X)+\tfrac{1}{4}X]/k(\Theta^M)^2,\tag{6}$$

where

$$\Phi(X)=(1/X)\int_{z=0}^{X}z\,(e^z-1)^{-1}\,dz,\quad X=\Theta^M/T\,.$$

III. EXPERIMENTAL PROCEDURE

The crystal used for all measurements was supplied by Dr. J. L. Schmit of Honeywell, Inc. Hall measurements on a sample cut from the same ingot from which the present sample was obtained indicated an acceptor concentration of $3.3\times10^{17}\ \mathrm{cm}^{-3}$.[9] Prior to experiment the sample was mechanically polished and etched in a 10% methanol bromide solution. The crystal mosaicity was characterized by determining the value of the Zachariasen[10,11] extinction coefficient r^*, which was found to be 4.96×10^{-5} cm at room temperature. The crystal was mounted in a Cryogenics Associates cryostat (model No. CI-36) which, in turn, was mounted on a General Electric XRD-6 x-ray diffractometer. All data were collected from the $(h00)$ reflections, and each measured reflection was analytically tested for the possibility of extraneous first-order simultaneous reflections. $K\alpha$ radiation from a Ag x-ray tube was selected with a LiF crystal monochromator and the intensities were measured with a NaI(Tl) detector followed by a pulse-height discriminator. The intensity of each reflection was measured in the $\omega/2\theta$ scan mode over a range which varied from about 1.6° to 3.2° at a scanning speed of 0.2° min^{-1}. The angular height and width of the detector window were 7.9° and 4.2°, respectively. Data were collected on all $(h00)$ peaks which could be detected above the background radiation: The highest order of the superlattice and sublattice measured reflections were, respectively, the (16 00) and (12 00) at room temperature and the (20 00) and (14 00) at 32 °K.

Low temperatures were achieved by passage of a controlled, cold gas stream (N_2 or He) through a large Cu block containing the sample. The temperatures were measured with an Au(Fe)-chromel thermocouple; low-temperature measurement and control are believed to be accurate to within 5 °K.

IV. RESULTS AND DISCUSSION

A number of standard corrections were applied to the measured integrated intensities. Correction for background scattering was made by the standard linear-extrapolation procedure. The data were also corrected for first-order acoustical-mode thermal-diffuse scattering (TDS). The usual assumption was made that the smaller optical-mode contributions to the TDS vary slowly under the Bragg peak and are therefore approximately accounted for in the background correction. The TDS correction was evaluated for all reflections using the procedure of Skelton and Katz[12] and the elastic-constant data of Alper and Saunders.[13] It was noted, however, that this correction was quite large for some of the higher-order reflections; e.g., calculations indicate that at 296 °K 43.8% of the background-corrected intensity of the (16 00) reflection is due to TDS. In consideration of the unusually large size of this correction, the TDS intensity was recalculated for all room-temperature data with the use of the more refined procedure of Walker and Chipman.[14] (The Walker and Chipman procedure to compensate for primary-beam divergence was not employed.) The largest difference between the two calculations was about 1% of the measured intensity; i.e., the Walker and Chipman procedure yielded a value of 42.7% for the same (16 00) measurement. On the other hand, the TDS correction for the lower-order reflections is very small; e.g., at 296 °K only 0.02% of the (200) peak and 0.12% of the (400) peak are attributed to TDS. We observe that despite the large TDS correction for the higher-order reflections, omission of this correction causes a decrease of less than 6% in the mean-square displacements and an increase of less than 2% in the Debye temperature. The relatively small effect of the TDS correction seen here is probably explained by the fact that our analysis is based on all the measurable (h00) reflections, rather than just the higher-order peaks.

The data were also corrected for Lorentz and absorption effects and Azaroff's[15] expressions were used to account for the polarization of the radiation diffracted from the crystal monochromator. Extinction corrections were applied using the general formulas of Zachariasen[10] in the manner described below.

The observed structure factor F_0, taken to be the square root of the corrected intensities (to within a scale factor), can be expressed for an (h00) reflection in terms of the mean-square displacements in the following manner:

$$\ln F_0 = \ln C' + \ln(4 f_{\mathrm{Hg}}) - x\langle u^2_{\mathrm{Hg}}\rangle + \ln(|1 \pm g\, e^{-x\Delta u}|), \quad \begin{cases} + \text{ if } h = 4n \\ - \text{ if } h = 4n \pm 2 \end{cases} \tag{7}$$

where

$$g = f_{\mathrm{Te}}/f_{\mathrm{Hg}} \text{ and } \Delta u = \langle u^2_{\mathrm{Te}}\rangle - \langle u^2_{\mathrm{Hg}}\rangle ;$$

C' is an unknown scale factor. Values of the atomic scattering factors were taken from the calculations of Cromer and Waber[16] for Te and from those of Doyle and Turner[17] for Hg. In order to evaluate the extinction correction, the mean radius of the crystallite domains and their relative misalignment must be known: These two parameters can be expressed in terms of a single constant, denoted as r^* by Zachariasen.[11] In addition foreknowledge of the results (in this case $\langle u^2_{\mathrm{Hg}}\rangle$ and $\langle u^2_{\mathrm{Te}}\rangle$) is needed in order to calculate the structure factor and hence the extinction correction. The values of C', r^*, $\langle u^2_{\mathrm{Hg}}\rangle$, and $\langle u^2_{\mathrm{Te}}\rangle$ were determined in the following manner: Since the extinction correction for each of the two classes is largest for the lowest-order peaks, the (200) and (400) data were initially ignored. The remaining data were analyzed to find the values of $\langle u^2_{\mathrm{Hg}}\rangle$, $\langle u^2_{\mathrm{Te}}\rangle$, and C' which minimized the square of the difference between the two sides of Eq. (7). These provisional values of $\langle u^2_{\mathrm{Hg}}\rangle$, $\langle u^2_{\mathrm{Te}}\rangle$, and C' were then used in conjunction with the (200) and (400) data to determine r^*, after which a provisional extinction correction was applied to all data. A new set of values of $\langle u^2_{\mathrm{Hg}}\rangle$, $\langle u^2_{\mathrm{Te}}\rangle$, and C' were determined in the manner described above and the cycle repeated. This procedure was continued until the change in the mean-square displacements was less than 0.01%; convergence was achieved within ten iterations for all cases. The mean-square displacements and corresponding Debye temperatures are shown in Fig. 1 and 2, respectively; smooth curves (solid lines) have been drawn through our results. The upper and lower error limits on our results were estimated by rerunning the data reduction program with the input intensities increased and decreased, respectively, by an amount equal to the standard deviation in the net intensity. One reason for the significant increase seen in the estimated experimental errors at room temperature is that the peak-to-background intensity ratio of the higher-order reflections is small and therefore the uncertainty in the integrated intensities is large, e.g., the relative standard deviation for the (16 00) reflection is about 18% at 296 °K as compared with 1.5% at 32 °K.

The results of our measurements are compared with appropriate published values in Figs. 1 and 2. We note that within our estimated error, our results are substantially in agreement with the work of Guenzer and Bienenstock.[5] On the other hand, we find disagreement between our results and the measurements of Bublik *et al.*[6] This discrepancy, which varies from 40 to 66% over our common temperature range, may not be significant, since Bublik *et al.* have not reported their experimental error. Furthermore, the mean-square displacements determined by these authors were based on high-angle data which apparently had not been corrected for TDS. As noted above, this correction can be significant for HgTe at large diffraction angles.

We mentioned previously that there is also a significant discrepancy between published values of the relative difference in the mean-square displacement of the two atoms: Based on the results of Bublik *et al.*,[6] the ratio $\langle u^2_{\mathrm{Hg}}\rangle/\langle u^2_{\mathrm{Te}}\rangle$ remains essentially constant at 1.03 ± 0.02 over the temperature range $77 \le T \le 295$ °K; on the other hand, the mean-square displacements reported by Guenzer and Bienenstock[5] indicate that the ratio remains constant at about 1.4. We support the latter work; i.e., we find the ratio to be 1.45 at 90 °K and 1.39 at 296 °K. We note however that the ratio does decrease with decreasing temperature, dropping to 1.16 at 32 °K.

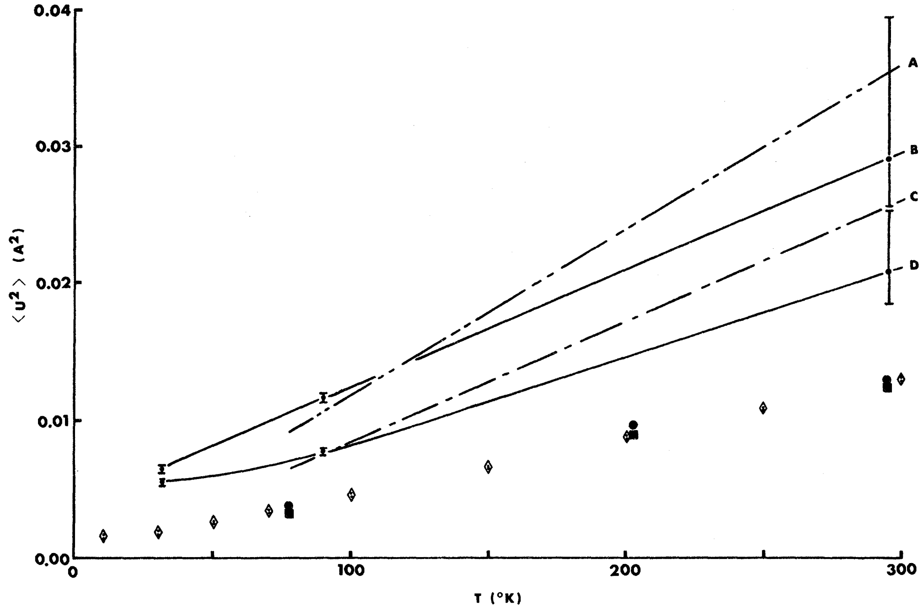

FIG. 1. Temperature dependence of the mean-square displacement of Hg and Te in HgTe. Curves A and C: $\langle u^2_{\mathrm{Hg}} \rangle$ and $\langle u^2_{\mathrm{Te}} \rangle$, respectively, from Guenzer and Bienenstock (Ref. 5); curves B and D: $\langle u^2_{\mathrm{Hg}} \rangle$ and $\langle u^2_{\mathrm{Hg}} \rangle$, respectively, from this work; circles and squares: $\langle u^2_{\mathrm{Hg}} \rangle$ and $\langle u^2{}_{\mathrm{Te}} \rangle$, respectively, from measurements of Bublik *et al.* (Ref. 6); diamond: mean-square displacement calculations of Vetelino *et al.* (Ref. 20); where distinguishable, the upper and lower points refer to $\langle u^2_{\mathrm{Te}} \rangle$ and $\langle u^2_{\mathrm{Hg}} \rangle$, respectively.

We find excellent agreement between our room-temperature results and recent measurements of Rusakov, Vekilov, and Kadyshevich,[18] who measured the temperature dependence of the specific heat of HgTe and have analyzed their data in terms of the moments of the phonon spectrum. The high-temperature limiting value of Θ^M, as computed from their analysis, is 102 °K; this compares very favorably with the value of (101^{+6}_{-13}) °K computed from our room-temperature mean-square displacements using Eq. (6). (Values of 91 and 82 °K are computed from the Guenzer and Bienenstock[5] and Bublik *et al.*[6] data, respectively.)

Ivanov-Omskii *et al.*[7] have examined the effect of varying the acceptor concentration level in HgTe on Θ^M. Their results indicate that, as the carrier concentration increases from 8×10^{14} to 3×10^{18} cm^{-3}, Θ^M decreases from (130 ± 5) to (110 ± 5) °K. Our result of (101^{+6}_{-13}) °K for Θ^M is to be compared with their value of (120 ± 5) °K determined from a sample with a carrier concentration of 3×10^{17} cm^{-3}. A possible explanation for the 19% discrepancy in Θ^M between our results and those of Ivanov-Omskii *et al.* is the following: They computed Θ^M from measurements of only the (200) and (400) reflections at 77 and 293 °K. Their method of analysis is based on the procedure discussed by Startev and Aronova[19] in which Θ^M is computed from the angular dependence of the high- and low-temperature intensity ratios and, by the way, in which it is tacitly assumed that Θ^M is thermally invariant. Since Ivanov-Omskii *et al.* only measured two reflections at each of the two temperatures, errors in the corrected intensity could have a significant effect on the computed value of Θ^M. We point out that extinction effects are largest for the most intense reflections, usually the low-angle data; e.g., the multiplicative extinction-correction parameters computed in this work decrease from 1.177 and 1.502, for the (200) and (400) peaks, respectively, to 1.000 026 and 1.000 000 for the (10 00) and (12 00) peaks, respectively. Ivanov-Omskii *et al.* have not applied a correction for extinction to their data and do admit that "there is no assurance of the absence of a contribution of extinction."

We have also compared our results with a very

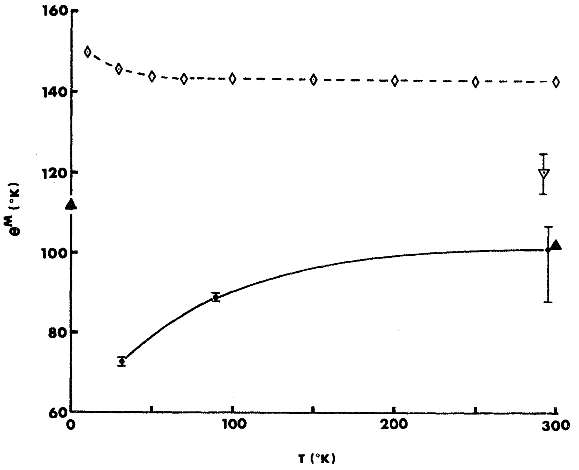

FIG. 2. Temperature dependence of the x-ray Debye temperature Θ^M of HgTe. Solid curve: this work; diamond: our calculations based on results of Vetelino *et al.* (Ref. 20); open triangle: measurements of Ivanov-Omskii *et al.* (Ref. 7); closed triangle: measurements and calculations of Rusakov *et al.* (Ref. 18).

recent lattice-dynamical force-model calculation of Vetelino, Gaur, and Mitra.[20] Using a modified rigid-ion model these workers have calculated the mean-square displacements for a number of zinc-blende crystals. There is over-all disagreement between our measurements and these force-model calculations. (We have divided the total mean-square displacements reported by Vetelino *et al.* by a factor of 3 in order to compare them with the directional mean-square displacements reported here.) The differences in $\langle u_{\mathrm{Hg}}^2\rangle$ and $\langle u_{\mathrm{Te}}^2\rangle$ decrease with increasing temperature from 72 and 62% to 55 and 37%, respectively, over the common temperature range from 32 to 296 °K. The high-temperature experimental data may be significantly affected by anharmonicity, however, and since the force model is based on essentially quasiharmonic theory, discrepancies of the order seen here at high temperatures are not unreasonable. On the other hand, this reasoning would also lead one to expect the difference between theory and experiment to decrease with decreasing temperature, contrary to what is observed.

The calculations of Vetelino *et al.*[20] also disagree with experiment in another important respect. Based on calculations for thirteen zinc-blende compounds, they find that the mean-square displacement of the lighter atom is greater than that of the heavier atom at all temperatures. Although the difference in the two mean-square displacements is predicted to be small for HgTe, the sign is opposite to that observed experimentally by all workers. It is noted, however, that the magnitudes of the mean-square displacements obtained from the force-model calculations appear to agree with the values reported by Bublik *et al.*[6]

We have also used the computed mean-square displacements of Vetelino *et al.*[20] in Eq. (6) to determine the associated values of Θ^M; these results are shown in Fig. 2. We note that with increasing temperature, the force model predicts a monotonically decreasing $\Theta^M(T)$ curve, whereas our experimental results indicate that Θ^M monotonically increases with temperature. Furthermore, it is clear that a low-temperature extremum in Θ^M must exist in order for either the experimental or the calculated value of Θ^M to agree at 0 °K with the limiting value of 112 °K, as computed from the thermodynamical-data analysis of Rusakov *et al.*[18] The existence of such an extremum is contrary to the monotonic temperature dependence of Θ^M seen for most substances.

V. CONCLUSIONS

Our results tend to substantiate those of Guenzer and Bienenstock,[5] although we disagree with the results found by Bublik *et al.*[6] The differences noted above may be attributable to lack of proper consideration of TDS effects or possibly to differences in the acceptor concentration in the samples used in the various measurements. However the large difference between $\langle u_{\mathrm{Hg}}^2\rangle$ and $\langle u_{\mathrm{Te}}^2\rangle$ seen by Guenzer and Bienenstock and, perhaps more importantly, the sign of this difference, are essentially confirmed by this measurement. In contrast to the situation noted by Keffer *et al.*[2] for PbTe, Guenzer and Bienenstock report that the temperature dependence of the HgTe band gap, as determined from the Brooks-Yu theory, is not very sensitive to the values used for the mean-square displacements. It would seem to follow, therefore, that the conclusions reached by Guenzer and Bienenstock regarding the failure of the Brooks-Yu theory for HgTe would not be affected by the results reported here.

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Influence of Phonons on the Impurity Photoconductivity Spectrum of Phosphorus-Doped Silicon[†]

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The impurity photoconductivity spectrum of phosphorus-doped silicon has been determined at 4 °K between 300 and 650 cm^{-1} for phosphorus concentrations ranging from 4.6×10^{16} to 1.2×10^{18} cm^{-3}. The curves reveal minima which, for most of them, have been attributed to a competitive absorption by lattice vibrations. The phonons are identified by comparison with the optical-absorption spectra. The minimum at 574 cm^{-1} is associated with the electron intervalley scattering with emission of a LA phonon of 26.2 meV.

I. INTRODUCTION

In 1953, Burstein *et al.*[1] reported photoconductivity measurements carried out at liquid-helium temperature between 0.8 and 38 μm on an *n*-type silicon sample containing 4×10^{15} carriers/cm^3 at room temperature. Between 8 and 24 μm, dips in the photoconductivity spectrum appeared, the frequencies of which corresponded to those of the optical-absorption peaks. It was therefore supposed that two absorption mechanisms are competing at these frequencies: One is the optical absorption by phonons and the other one the impurity photoionization. However, no identification of the vibration modes involved has been done.

Since then, a large number of papers, theoretical as well as experimental, have been published concerning the infrared optical properties of doped silicon (see the review article by Newman[2]). The optical-absorption mechanisms (two phonons, single phonon activated by the presence of impurities, impurity resonant modes, and impurity localized modes) have been clarified and a comparison between the infrared absorption spectra and the extrinsic photoconductivity spectra is now possible. These comparisons should help to determine the vibrations responsible for the photoconductivity minima.

In the present work, comparisons have been made of the data for phosphorus-doped silicon samples. An explanation of the experimental results of the photoconductivity associated with a donor level is presented which justifies the existence of minima in the spectrum.

II. ANALYSIS OF THE PHOTOCONDUCTIVITY ASSOCIATED WITH A DONOR LEVEL

It will be assumed that two types of localized states are present in the forbidden gap: one from a group-V donor, the other from a group-III acceptor. Let N_D be the total density of donor states, N_D^+ the density of ionized donors, N_A the density of acceptor states, and n the density of conduction electrons. Since all our samples are n type, only electrons will take part in photoconductivity.

A. Density n_0 of Free Electrons in the Absence of Modulated Illumination

The kinetic equation for the evolution of the carrier density n_0 in absence of "voluntary" illumination can be written

$$\frac{dn_0}{dt}=\frac{\gamma}{g}\,(N_D-N_D^+)\,N_C\,e^{-E_D/kT}+n_p-n_0\gamma N_D^+\ ,$$

where γ is the capture coefficient of an electron by an empty donor state per unit time, g is the degeneracy factor (it is 2 for donors such as phosphorus in silicon), E_D is the ionization energy of donors, n_p the density of conduction electrons generated by stray light per unit time, and $N_C=2(2\pi m^*kT/\hbar^2)^{3/2}$ is the effective density of states in the conduction band. The first term represents the number of electrons thermally ionized from the donor level D to the conduction band, the second term takes account of the effect of stray light, and the last term gives the number of electrons trapped by the ionized donors; all these terms are per unit time.