tures of both crystals are essentially the same as would occur in strained verisons of their binary analogs.[7]

We mentioned earlier that the model in Fig. 1 was originally proposed[1] to explain the experimental observation that the lowest-energy $\Gamma_7 \rightarrow \Gamma_6$ transition (peak A) was strongly polarized $E \parallel Z$ in $CdSnP_2$. It is at first surprising that the A peak is polarized $E \parallel Z$, since we see on the right-hand side of Fig. 1 that all transitions are either polarized $E \perp Z$ or are allowed for both polarizations. This apparent anomaly is readily explained by the quasicubic model, and is in fact the principal success of the theory. For this model the ratio of the strengths of transitions from a given Γ_7 valence band to the Γ_6 conduction band for light polarized, respectively, parallel or perpendicular to the optic axis is given by

$$I_{\parallel}/I_{\perp} = (2 - 3E/\Delta_{so})^2 , \qquad (2)$$

where E is given by Eq. (1). For the A peak in $CdSnP_2$, $E = -0.08$ eV, $\Delta_{so} = 0.10$ eV, and Eq. (2) predicts that $I_{\parallel}/I_{\perp} = 20$ in good agreement with experiment.[1] Equation (2) is shown as the solid line in Fig. 2, and the points represent the experimental intensity ratios for the A and C peaks of $CdSnP_2$[1] and $ZnSiAs_2$.[6] The quasicubic model quantitatively explains the observed polarization dependences.

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Microwave Phonon Attenuation Measurements in *n*-Type Silicon†

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Microwave phonon attenuation at 9.3 GHz in *n*-type silicon has been measured between 2 and 100 K. The excess attenuation observed in impure samples is attributed to conduction electrons. The intervalley relaxation time is determined from these results for Sb- and As-doped silicon with impurity concentration between 3×10^{17} and 2×10^{19} cm^{-3}. A large excess attenuation, not accounted for by any existing theories, is observed at low temperatures in nondegenerate samples. The discrepancy between experiment and theory is thought to arise from electrons in impurity states. It is suggested that hopping conduction may explain our results at low temperatures. No specific influence of impurity band formation on attenuation is found experimentally.

I. INTRODUCTION

In the last decade, high-frequency ultrasonic techniques have become increasingly useful for studies in solid-state physics.[1,2] One phenomenon that can be investigated in this manner is intervalley scattering in many-valley semiconductors. In conventional transport experiments, the effect of intervalley scattering appears only as a small perturbation on the background of intravalley scattering, which has a much higher probability; thus, the intervalley contribution is difficult to evaluate. Conversely, ultrasonic attenuation in doped material strongly depends on the intervalley relaxation time. The strain-induced variation of their energy causes the electrons to undergo transitions to lower states. This relaxation takes a finite time and, therefore, some power will be lost by the ultrasonic wave to

the electrons.

The best-known many-valley semiconductors are n-type Ge and Si. Extensive acoustoelectric,[3,4] velocity,[5,6] and attenuation[7,8] measurements have been reported in the former. Important parameters in the theory of electron-phonon interactions, the uniaxial deformation potential, and the intervalley relaxation time have been determined. Experiments on n-type silicon have been limited in number and confined to velocity measurements.[6,9,10] In this paper, we report on 9-GHz phonon attenuation measurements in n-type silicon over wide ranges of doping and temperature. Mikoshiba's theory for Ge[11] is readily adapted to the case of Si. It predicts that the attenuation coefficient depends on the square of frequency. This fact makes microwave measurements very attractive. The deformation potential and the intervalley relaxation time in Si are smaller than in Ge. Therefore, the attenuation at 9 GHz is measurable, in contrast to the case of Ge.[7] The intervalley relaxation time is determined from our measurements in Sb- and As-doped Si for impurity concentrations between 3×10^{17} and 2×10^{19} cm^{-3}. However, a large excess attenuation, not accounted for by any existing theories, is observed at low temperatures in nondegenerate samples.

Resistivity and other measurements have shown that, as the doping level increases, a semiconductor undergoes a transition from an insulating state to a conducting state at 0 K (the Mott transition) owing to the progressive overlap of neighboring impurity wave functions.[12] At finite temperatures, one observes a region of anomalous conduction called impurity conduction, attributed to electrons hopping from one impurity to another or to electrons in a so-called impurity band within the forbidden energy gap.[13,14] Our ultrasonic attenuation measurements are strongly influenced by these processes. This influence is reported here for the first time in many-valley semiconductors. A similar effect has been noted in CdS.[15] Some correlation between conductivity and ultrasonic attenuation is found, indicating an electronic origin for the latter.

II. EXPERIMENT

The well-known pulse-reflection technique, requiring only one microwave cavity, has been used. Our experimental system is shown in Fig. 1. A 2J51 magnetron provides high-power microwave pulses of $\frac{1}{4}$-μsec duration at a repetition rate of 500 pulses per sec. About 500-mW average power is fed to a reentrant cavity. The high electric field across its gap excites a thin-film CdS electromechanical transducer on a sample. A superheterodyne receiver (channel A) with an over-all sensitivity of about -90 dBm (dB above 1 mW) is used for detecting the small return signal. Because a sweep generator is needed to align the receiver, the same apparatus also serves as the local oscillator. A TR tube and a semiconductor diode switch have been inserted in the signal arm as protection against high-power leakage. A small increase in sensitivity is obtained with a gated integrator. It averages over many cycles the difference between two short samples of the signal taken at any two instants within a period. In practice, one gate is set in the noise long after all echoes have died out and the other gate is positioned on the first echo to obtain a maximum in the dc output. Nonlinearities in the system are bypassed by always reducing the signal to a fixed level with a calibrated attenuator. The relative attenuation is thus directly read in decibels. Channel B is used for the alignment of the receiver.

We obtained our samples from the Monsanto Co. They were cut into 1-cm-long cylinders of $\frac{3}{16}$-in.

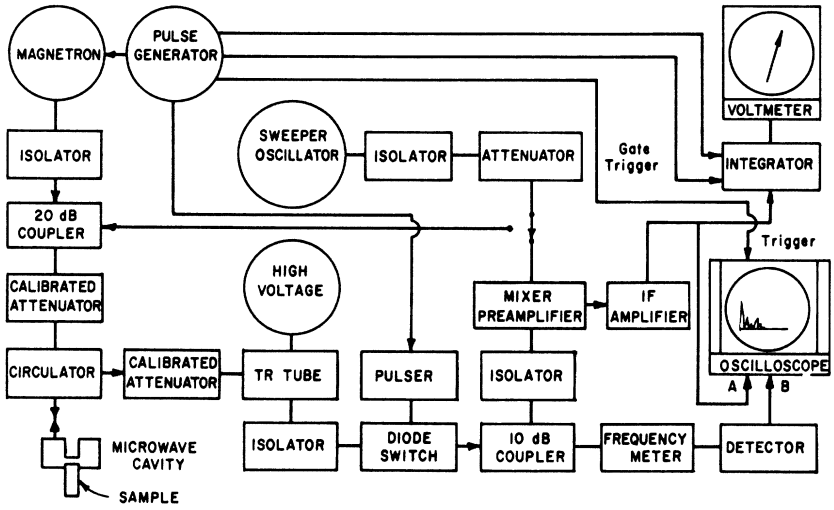

FIG. 1. Block diagram of the experimental system.

diameter and polished by Frank Cooke, Inc.[16] to precise tolerances: both faces parallel to within 5 sec of arc and flat to less than $\frac{1}{10}$ wavelength of sodium light. Their axis was parallel to a ⟨110⟩ direction to within 5 min of arc. Samples for resistivity and Hall measurements were taken from adjacent portions of the ingots. Thin-film resonant CdS transducers were grown simultaneously on three aluminum-plated samples after the method of De Klerk.[17] An aluminum film of at least 8000-Å thickness is needed to keep the microwave fields out of the sample. Without this precaution, the Q of the cavity, and, therefore, the apparent attenuation, changes with temperature in a manner unrelated to the real attenuation in the sample.

In order to eliminate as much as possible the attenuation due to phonon-phonon collisions,[18] we have to work at low temperatures. A conventional double Dewar cryogenic system is used. A copper can encloses the sample region, preventing liquid helium from entering the microwave cavity. The temperature can be set at any point between 2 and 20 K by either pumping on the helium bath or by controlling the current through a high-resistivity wire wound around the sample holder. It can be similarly controlled between 45 and 100 K with nitrogen in the interior Dewar. The temperature is monitored by a calibrated germanium resistor to within ±0.5 K.

It was found that the results do not depend on which echo is monitored. Therefore, all our data represent the change in the amplitude of the first echo. The attenuation in the purest sample (No. 1) at low temperatures has been arbitrarily taken as zero and all other measurements are relative to this point. The accuracy of our data for any given sample is ±0.5 dB/cm. The error in the relative position of the curves for different samples is about ±2 dB/cm; this was established by removing the transducers and fabricating new ones several times. Our results on pure silicon agree within experimental uncertainties with those of Pomerantz[18] obtained with ferromagnetic thin-film transducers.

III. EXPERIMENTAL RESULTS

The resistivity and Hall coefficient in our samples are plotted in Figs. 2 and 3. Three samples exhibit impurity conduction, the onset of which is characterized by a maximum in the Hall coefficient and a break in the resistivity curves. At high temperatures, the observed activation energy is the donor ionization energy ϵ_1. The impurity concentration in sample 2 is probably too low for an impurity band to form.[12] Hopping conduction is observed at low temperatures. The activation energy in this region is usually labeled ϵ_3. Samples 3 (Sb doped) and 5 (As doped) are in the intermediate doping region[12] in which impurity band conduction is also present. In this region an activation energy ϵ_2 is observed. Sample 4 is degenerate over the whole temperature range.

Our ultrasonic measurements are shown in Fig. 4. The attenuation observed in the purest sample (No. 1) is entirely due to three-phonon collisions.[18] The deviation from the theoretical T^4 dependence is within the experimental error. No contribution from conduction electrons is expected since, below 100 K, their number is extremely small.

In germanium, for comparable doping levels, a small attenuation has been observed at low temperatures[19] and interpreted as being due to inelastic phonon scattering and thermally assisted absorption by neutral donors.[20] Since, in silicon, the valley-orbit splitting is nearly ten times larger than in germanium, a much smaller effect is predicted. Experimental data showing this effect on the slow shear wave propagating along a ⟨110⟩ direction in P-doped silicon with an impurity concentration of 6×10^{15} cm^{-3} have been recently reported.[21] The increase in attenuation is less than 3 dB. For longi-

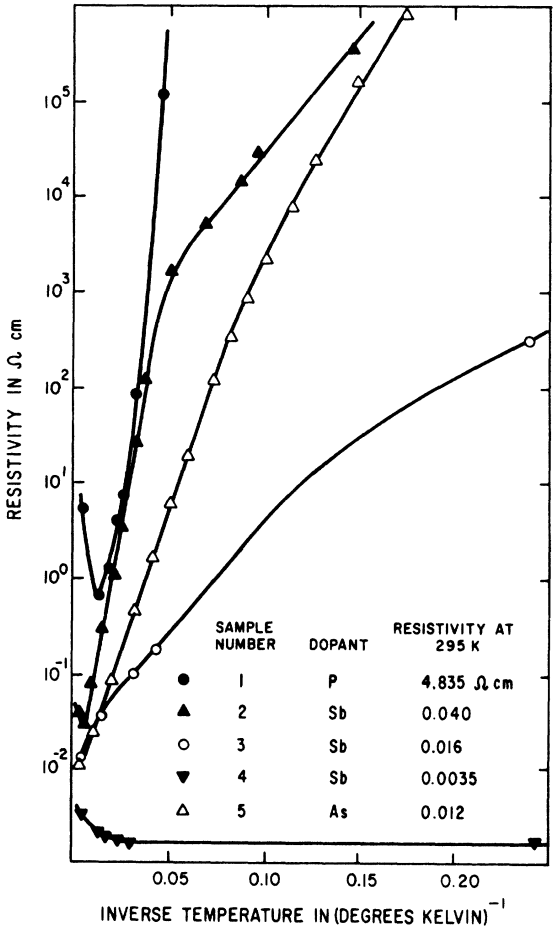

FIG. 2. Resistivity versus reciprocal of absolute temperature.

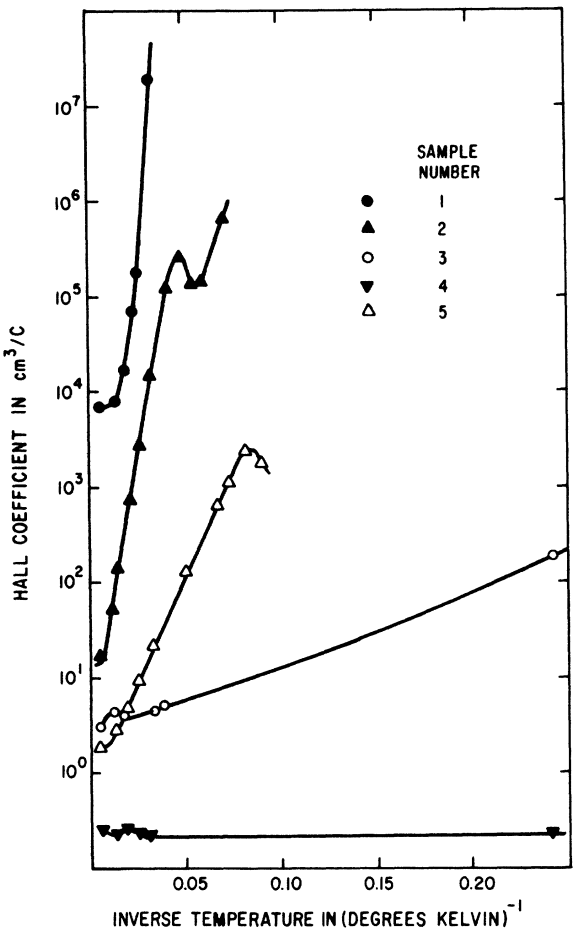

FIG. 3. Hall coefficient versus reciprocal of absolute temperature. (The symbols refer to the same samples as in Fig. 2.)

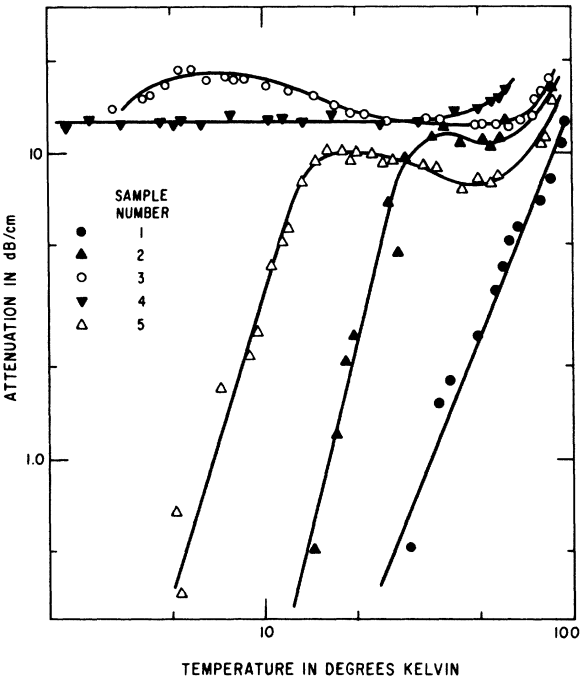

FIG. 4. Temperature dependence of longitudinal microwave phonon attenuation in n-type silicon at 9.3 GHz. (The symbols refer to the same samples as in Fig. 2.)

tudinal waves propagating along the same direction it should be considerably smaller.

The attenuation in sample 1 was thus taken as a base line. At a given temperature, any increase above this level is assumed to be due to electrons. This difference has been plotted in Figs. 5–8. The arrows denote presumed transitions from one conduction process to another.

At sufficiently high temperatures, attenuation by electrons in the conduction band is expected to dominate. It is straightforward to adapt the theory of attenuation by intervalley relaxation to the case of a longitudinal wave propagating along a ⟨110⟩ direction in Si.[22] We find

$$\alpha = \frac{1}{20}\,\frac{n_0 \Xi_u^2}{\rho s^3 kT}\,\frac{F'_{1/2}(\eta)}{F_{1/2}(\eta)}\,\frac{4\tau_R}{3\tau_{iv}}\,\frac{\omega^2\tau_R}{1+\omega^2\tau_R^2}\,, \qquad (1)$$

where $1/\tau_R = 4/3\tau_{iv} + \omega^2/\omega_d$ and $\omega_d = s^2/D$. Here, s is the sound velocity and D is the diffusion coefficient.

In our case, diffusion is negligible, i.e., $\omega^2/\omega_d \ll 4/3\tau_{iv}$ and $\omega^2\tau_{iv}^2 \ll 1$. Thus, Eq. (1) can be simplified to

$$\alpha = \frac{3}{80}\,\frac{n_0 \Xi_u^2}{\rho s^3 kT}\,\frac{F'_{1/2}(\eta)}{F_{1/2}(\eta)}\,\omega^2\tau_{iv}\,. \qquad (2)$$

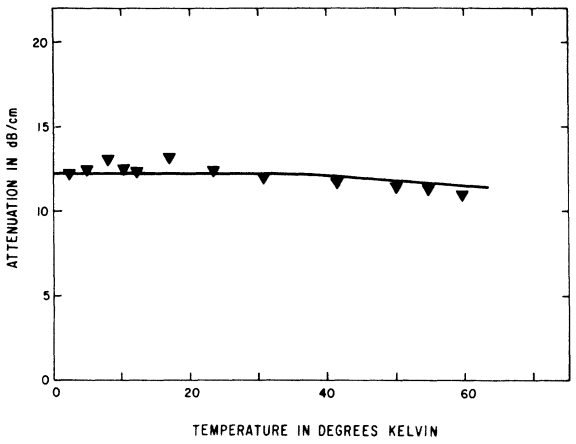

FIG. 5. Attenuation by conduction electrons in sample 4 (degenerate). The continuous line represents the theoretical prediction of Eq. (2).

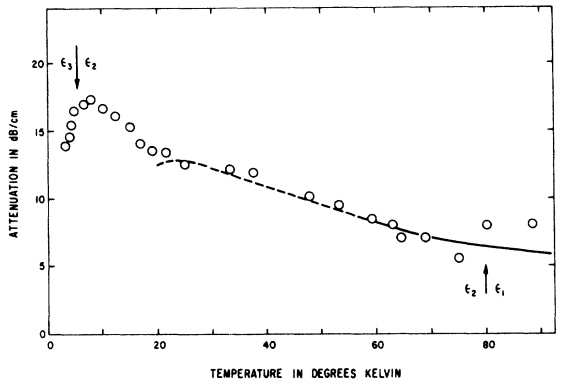

FIG. 6. Attenuation by conduction electrons in sample 3. The continuous and broken line represents the theoretical prediction of Eq. (2) (see text).

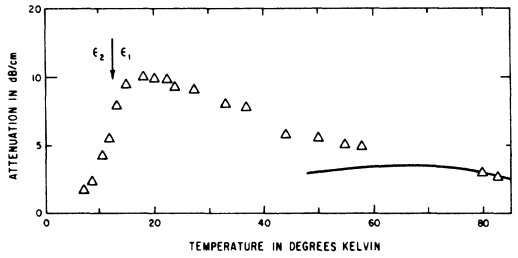

FIG. 8. Attenuation by conduction electrons in sample 5. The continuous line represents the theoretical prediction of Eq. (2).

The concentration of electrons in the conduction bands n_0 is determined from Hall measurements (Fig. 3). Note that below the temperature at which it reaches a maximum, the Hall coefficient no longer gives the concentration of electrons in the conduction band. In that region we are overestimating the attenuation due to free electrons. This is particularly important in sample 3. Below about 60 K the actual theoretical curve should deviate somewhat from the curve we have plotted (broken line in Fig. 6). The value of the uniaxial deformation potential Ξ_u is 8.6 eV in Si.[10] ρ and kT represent density and average thermal energy, respectively. $F_{1/2}$ is the Fermi integral and $\omega = 2\pi f$, where f is the ultrasonic frequency. The intervalley relaxation time τ_{iv} is assumed to be temperature independent and is determined by fitting Eq. (2) to the experimental data at high temperatures (Fig. 9). Some results previously reported by Mason[23] are shown for comparison. Qualitatively, the same trend as in Ge is observed.[8] Up to about 10^{18} cm^{-3}, τ_{iv} decreases nearly as the inverse of impurity concentration; at high doping, it approaches a constant value which is somewhat lower than in Ge. τ_{iv} varies approximately as the inverse of valley-orbit splitting from one dopant species to another. This lends some support to the compound capture-reemission model proposed by Weinreich.[3]

Although the intervalley relaxation time can be determined from our data, Eq. (2) does not properly predict their variation at low temperatures in some cases (Figs. 6–8). In the samples in which impurity conduction is observed, there is a large extra attenuation that cannot be explained by existing models. Despite the differences noted in the transport data, the attenuation in all these samples behaves very similarly. There is a shallow maximum at a temperature T_m below which the attenuation drops sharply. No specific influence of impurity band formation is observed.

In an effort to relate ultrasonic attenuation and

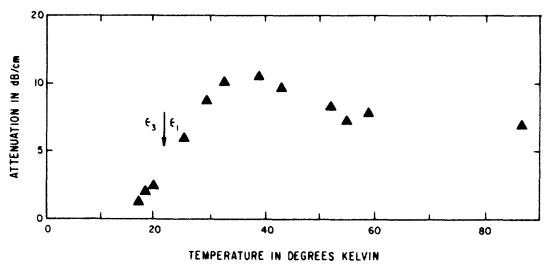

FIG. 7. Attenuation by conduction electrons in sample 2. In this case, the theoretical curve is fitted to an extrapolation of the experimental results above 100 K and has been omitted.

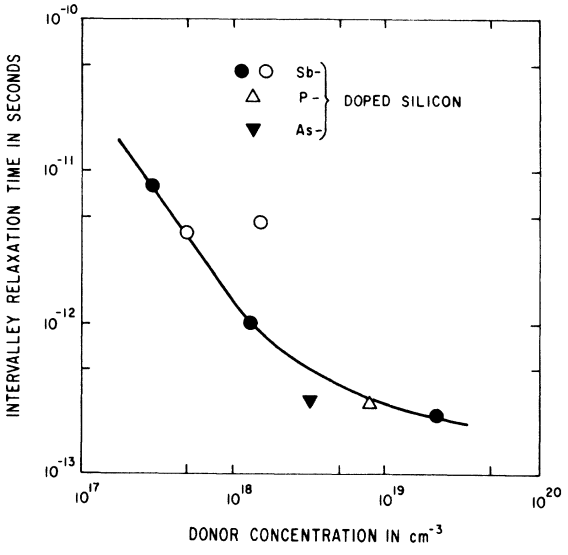

FIG. 9. Dependence of the intervalley relaxation time on impurity concentration [open symbols represents Mason's results (Ref. 23)].

conductivity analytically, we assume that all electron energy levels are equally affected by a strain, in other words, that the relation

$$U = \Xi S \tag{3}$$

between the change U in electron energy and strain S is valid throughout the crystal. Ξ is the deformation potential. Note that for electrons in the conduction band, Ξ has to reflect crystal symmetry and varies from one valley to another. For simplicity and for lack of better knowledge, we shall assume that Ξ is constant in the impurity conduction region. It is then straightforward to derive the relation[2,22]

$$\alpha = \frac{\Xi^2 \sigma}{\rho s^5 e^2} \frac{\omega^2}{1 + (4\pi\sigma/\omega\epsilon)^2}, \tag{4}$$

where diffusion has again been neglected; e is the electron charge. The conductivity σ in Eq. (4) should reflect the effect of ac conduction. It has been shown experimentally that σ increases dramatically with frequency at low temperatures, where hopping conduction is predominant.[24,25]

Equation (4) predicts that there is a maximum in α at a temperature T_m' such that $\sigma = \omega\epsilon/4\pi$. In Si at 9 GHz, this occurs at a resistivity of about 15 Ω cm. In the absence of ac conductivity data in this region, we assume that ac conduction becomes important only below T_m'. Tanaka and Fan's results in p-type Si[25] lend some support to this assumption. Accordingly, we can read T_m' directly off Fig. 2. The agreement between the theoretical value T_m' and the experimental value T_m is quite good (Table I) in view of the crudeness of this model. Thus, we have a strong suggestion that attenuation at low temperatures is an electronic effect.

The magnitude of α predicted by Eq. (4) is, in general, quite small unless σ or Ξ is very large. This may well be the case in the region of hopping conduction.

TABLE I. Comparison of experiment and theoretical prediction [Eq. (4)] of temperature of maximum attenuation.

Sample No.	T_m' (K)	T_m (K)
2	31	36
3	8	7
5	17	18

IV. SUMMARY

Microwave phonon attenuation at 9 GHz has been measured in n-type Si over a wide range of impurity concentrations. There is good agreement between the theory of Mikoshiba and our experimental data in the degenerate case, in which conduction electrons play a dominant role throughout the temperature range, but there is a large excess attenuation in the impurity conduction region. The discrepancy is attributed to electrons in impurity states. A simple model relating ultrasonic attenuation and conductivity is proposed. It is shown that hopping conduction may explain our results at low temperatures. Discrepancies between this model and details of the observed behavior remain.

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Application of the Method of Tight Binding to the Calculation of the Energy Band Structures of Diamond, Silicon, and Sodium Crystals*

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The method of tight binding is used to calculate the energy band structure of the diamond, silicon, and sodium crystals. The wave functions of the valence and conduction bands of diamond are expanded in terms of Bloch sums constructed from the 1*s*, 2*s*, and 2*p* Hartree-Fock atomic orbitals, and two different crystal potentials [the muffin-tin and the overlapping atomic potential (OAP)] were used. With the muffin-tin potential, the tight-binding and the augmented-plane-wave (APW) method yield nearly identical valence band structure, and their conduction bands show only minor differences. When the OAP is used, the results of the tight-binding scheme differ appreciably from those of Bassani and Yoshimine by the method of orthogonalized plane waves (OPW), the discrepancy being attrubuted to incomplete convergence of the latter calculations. The tight-binding structures of the valence band derived from the two different potentials agree quite well with each other, but considerable deviations are found in the conduction band. The x-ray form factors calculated by means of the tight-binding wave functions are in good agreement with experiment and represent a considerable improvement over a simple superposition of atomic charges. The convergence of the tight-binding method with respect to the higher atomic orbitals has been examined. It is found that addition of 3*s*, 3*p*, and 3*d* Bloch sums to the wave functions of diamond has only small effects on the energy of the valence and conduction bands. A similar tight-binding calculation has been performed for the band structure of silicon using OAP, and the results are in good agreement with those of a modified scheme of the method of OPW using as basis functions 609 OPW's as well as the Bloch sums of the core states. For the base of sodium, the method of tight binding gives conduction-band energies in good agreement with the APW-type calculations of Schlosser and Marcus. Generalization of the method of tight binding by using single-Gaussian Bloch sums is discussed, and the use of this scheme leads to substantial improvements for the case of diamond.

I. INTRODUCTION

A few years ago it was shown that the method of tight binding for calculating electronic energy band structure of crystals, which, hitherto, was used largely for qualitative purposes, is capable of giving energies in very good agreement with those obtained by methods based on modified plane-wave-type expansion.[1] The difficulty of evaluating the multicenter integrals, which had been the bottleneck of any quantitative application of the method of tight binding, was circumvented by the use of the Gaussian transformation. In a more recent paper,[2] it was pointed out that if the atomic wave functions were expressed in terms of the Gaussian-type orbitals (instead of the Slater-type orbitals), all the multicenter integrals occurring in the band-structure calculations can be reduced to analytic forms, and the computational procedure is greatly simplified.

In both Refs. 1 and 2, we have seen that when the overlap between atomic wave functions at all sites are properly taken into consideration and the summation over the crystal sites in the computation of matrix elements is carried out to convergence, the method of tight binding is even applicable