decrease steadily, and seem to correspond to a singularity less steep than $(1-\kappa)^{-\frac{1}{3}}$.

It is interesting to look at the corresponding expansions for the f.c.c. lattice for the Heisenberg model. Fewer terms are here available, and corresponding to (1) we now have

$$C_v/R=18K^2+108K^3+90K^4-840K^5+6750K^6. \quad (5)$$

The Curie point can be estimated from high-temperature susceptibility data as given[3] by $kT_c/12J=0.695$. The reduced specific heat expansion corresponding to (3) is now

$$C_v/R=0.2588\kappa^2(1+0.7194\kappa+0.07188\kappa^2 -0.08044\kappa^3+0.07750\kappa^4). \quad (6)$$

It will be seen from the term outside the parentheses that the tail is considerably larger than for the Ising model. However the terms inside the parentheses do not show steady behavior, are much smaller, and are not all of the same sign. They seem to be consistent with a much less steep behavior near the Curie point, and possibly a finite value at the Curie point.

PHYSICAL REVIEW VOLUME 108, NUMBER 6 DECEMBER 15, 1957

Conductivity Mobilities of Electrons and Holes in Heavily Doped Silicon

GERHARD BACKENSTOSS
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received August 8, 1957)

Electron and hole mobilities in silicon have been determined in a region in which ionized impurity scattering is predominant. Resistivities were measured by a four-point probe and impurity concentrations were obtained with radioactive tracers or from thermal neutron activation analysis. Measurements were taken with several Group III and Group V impurities up to concentrations of 6×10^{19} (cm^{-3}) and 6×10^{18} (cm^{-3}) for n- and p-type silicon, respectively. The conductivity mobility can be calculated from these data by considering the percentage of ionized impurities. The electron mobility approaches 80 cm^2/v-sec and the hole mobility 60 cm^2/v-sec for the highest impurity concentrations. The comparison with measured Hall mobilities leads to a ratio μ_H/μ_c which agrees with theory. A comparison with the existing theory of impurity scattering yields better agreement for n-type silicon than for p-type. In the latter the measured mobilities are considerably smaller than the theoretical values.

INTRODUCTION

DRIFT mobilities in semiconductors have been theoretically calculated by several authors. Values of the drift mobility in the higher concentration range can be obtained from the theories of impurity scattering by Conwell-Weisskopf[1] and Brooks-Herring.[2] In addition to this, several independent theoretical treatments of the ratio of Hall mobility to drift mobility for nondegenerate semiconductors are available.[3–5] All treatments yield a ratio greater than unity. In the degenerate case this ratio approaches unity since the averaging of τ over energy becomes unimportant.

Various measurements of Hall mobilities are published for n- and p-type silicon.[6–8] They cover a wide range of impurity concentrations and are generally in agreement.

Drift or conductivity mobilities have been measured by Prince,[9] Cronemeyer,[10] and Horn.[11] Only the data of Horn include the high-concentration range above 10^{17} (cm^{-3}), but they are restricted to boron-doped silicon. His mobilities are higher than the reported Hall mobilities but smaller than theoretical mobilities. However, according to Carlson[8] the reliability of the chemical calibration involved in this method appears to be doubtful. Carlson applies a correction which leads to lower mobilities.

The present investigation gives additional data for conductivity mobilities in the higher concentration range. Radioactive tracers or thermal neutron activation analysis have been used to determine impurity concentrations. This method was applied to several donor and acceptor elements.

METHOD

In heavily doped silicon the contribution of the minority carriers to the conductivity is negligible. Therefore, the conductivity mobility μ is obtained from the resistivity ρ by the relation

$$\mu=1/q\rho n, \quad (1)$$

where n is the charge carrier density and q the magnitude of the electronic charge. In the present experiments the resistivity was measured by a four-point

[1] E. M. Conwell and V. F. Weisskopf, Phys. Rev. **77**, 388 (1950).
[2] H. Brooks, Phys. Rev. **83**, 879 (1951).
[3] H. Jones, Phys. Rev. **81**, 149 (1951).
[4] V. A. Johnson and K. Lark-Horovitz, Phys. Rev. **82**, 977 (1951).
[5] F. J. Blatt, Phys. Rev. **105**, 1203 (1957).
[6] F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954).
[7] P. P. Debye and T. Kohane, Phys. Rev. **94**, 724 (1954).
[8] R. O. Carlson, Phys. Rev. **100**, 1075 (1955).
[9] M. B. Prince, Phys. Rev. **93**, 1204 (1954).
[10] D. C. Cronemeyer, Phys. Rev. **105**, 522 (1957).
[11] F. H. Horn, Phys. Rev. **97**, 1521 (1955).

probe.[12] The carrier density was not measured directly. The experimentally determined quantity was the impurity concentration N. This was determined by using as dopants either radioactive isotopes[13] or inactive elements which were later activated with thermal neutrons.

The carrier density can be obtained from the impurity concentrations by calculating the fraction of ionized donors or acceptors. For this calculation the effective masses published by Dresselhaus *et al.*[14] were used. Taking the average of the angular dependent values, one obtains for electrons $m_{\text{eff}}/m=0.27$. For holes the weighted average, taking into account the population ratio of light to heavy holes, yields $m_{\text{eff}}/m=0.39$. The ionization energies E_D and E_A were taken from Morin[15] taking into account that these energy levels depend on the impurity concentration.[16,17]

MEASUREMENTS

The measurements on n-type crystals have been made with donor concentrations between 10^{17} and 10^{20} (cm^{-3}). Three crystals grown with different donor elements were used. An antimony (Sb^{124}) doped crystal for concentrations between 10^{17} and 10^{18} (cm^{-3}); an arsenic (As^{76}) doped crystal for concentrations between 10^{18} and 10^{19} (cm^{-3}) and a phosphorus-doped crystal for donor concentrations between 10^{19} and 10^{20} (cm^{-3}). The antimony- and arsenic-doped crystals were grown with radioactive tracers,[18] while the phosphorus-doped crystal was grown with inactive phosphorus; it was then bombarded in a neutron reactor and subjected to an activation analysis. For absolute calibration the impurity or a suitable compound was simultaneously activated. Calcium phosphate was used for calibration in this case. The resistivity and impurity concentration were measured in approximately twenty identical samples from each crystal.

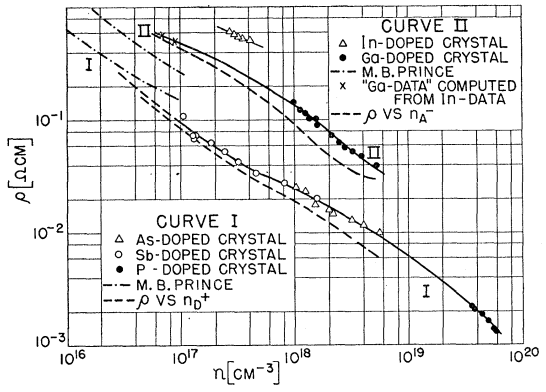

FIG. 1. Resistivity *vs* impurity density, for (I) n-type silicon, (II) p-type silicon. The dashed curves give resistivity *vs* density of ionized impurities.

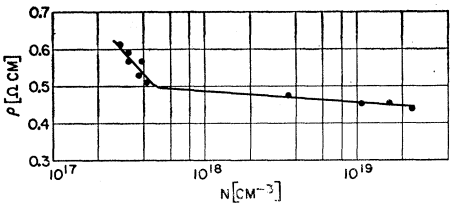

FIG. 2. Resistivity *vs* impurity density for indium-doped silicon.

The hole mobility has been determined, using indium and gallium as doping agents, which are the only group III elements with suitable radioactive isotopes. In both cases the impurity was activated in the grown crystal. Pure indium and gallium were used for calibration. Since gallium has a relatively short half-life, the measurements have to be made shortly after irradiation. A more detailed analysis of the decay curve was necessary since some unknown activities were present. Consequently, gallium crystals give less accurate results in concentration ranges below 10^{18} (cm^{-3}).

EXPERIMENTAL RESULTS

The solid curves in Fig. 1 show resistivity as a function of total impurity concentration for all impurities used. Good agreement between antimony- and arsenic-doped crystals is apparent in the common range. The statistical error introduced by the measurements of resistivity and activity lead to a scattering around the plotted curves of about 5%. Careful consideration was given to possible sources of systematic errors, particularly those due to the calibration. Repeated calibrations indicate that the systematic error can be assumed smaller than 10%.

An interesting feature was observed in connection with the indium measurements. Figure 2 shows resistivity *vs* impurity density in this case. For concentrations greater than 4×10^{17} (cm^{-3}), a change of impurity concentration of two orders of magnitude results in a very small change of resistivity. Indium precipitation was suspected in this range. To check this assumption radiograms of wafers of different indium content were taken. When the indium concentration was greater than 4×10^{17} many black spots were apparent, indicating occluded indium particles in the silicon while wafers with indium concentration smaller than 4×10^{17} (cm^{-3}) showed a homogeneous distribution of radioactive material (Fig. 3). Only the data obtained in the low-concentration range were used in the analysis.

[12] L. B. Valdes, Proc. Inst. Radio Engrs. **42**, 420 (1954).
[13] Pearson, Struthers, and Theuerer, Phys. Rev. **77**, 809 (1950).
[14] Dresselhaus, Kip, and Kittel, Phys. Rev. **98**, 368 (1955).
[15] Morin, Maita, Shulman, and Hannay, Phys. Rev. **96**, 833 (1954).
[16] F. J. Morin, (private communication).
[17] It should be mentioned that this calculation may introduce errors somewhat beyond the experimental ones when the impurity concentration approaches degeneracy.
[18] The author is indebted to J. D. Struthers of Bell Telephone Laboratories who supplied these crystals and measured their impurity density.

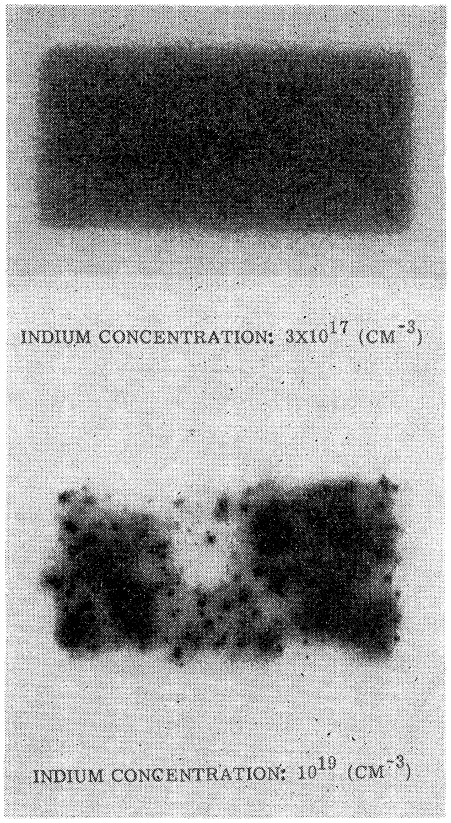

FIG. 3. Radiograms of indium-doped silicon wafers.

DISCUSSION

At the lower concentrations the resistivity as a function of impurity concentration (solid curves Fig. 1) agrees satisfactorily with Prince's data who extrapolated his measurements up to impurity concentrations of 10^{17} (cm^{-3}). The data published by Horn disagree with the present results. These data were obtained by density measurements whereby a chemical analysis served as calibration. According to Carlson[8] the calibration published in Horn's original paper has to be revised in such a direction as to lead to a better agreement.

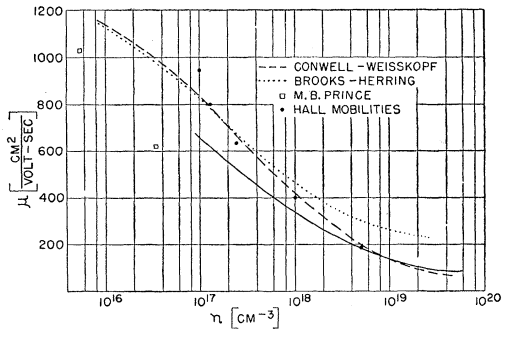

FIG. 4. Conductivity mobility μ in n-type silicon as a function of ionized impurity density.

Since the resistivity is primarily a function of the charge carrier concentration the dependence on the impurity density is different for different ionization energies of the impurities. For all commonly used donor elements, the ionization energies differ only slightly. Therefore, the solid curve for donors in Fig. 1 is essentially correct for all group V donors. For p-type silicon, the ionization energies of boron and aluminum are only slightly smaller than that of gallium, while indium has a considerably higher ionization energy. Therefore, the solid curve for acceptors in Fig. 1, which has been drawn for gallium, is also approximately correct for boron and aluminum.[19] A different curve applies for indium. From this curve the extension of the gallium curve to lower densities can be calculated by considering the different ionization energies.

The dashed curves in Fig. 1 show the resistivity as a function of ionized impurity density. These curves were calculated by the method indicated above. From these curves, the mobility μ was obtained as a function of the ionized impurity density, which equals the charge carrier density (solid curves in Figs. 4 and 5).

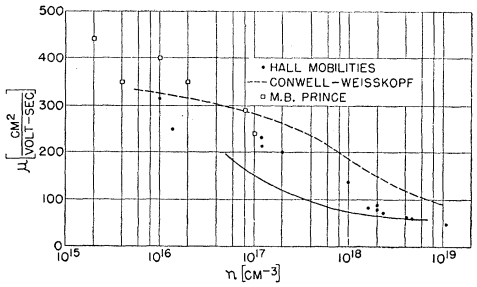

FIG. 5. Conductivity mobility μ in p-type silicon as a function of ionized impurity density.

The conductivity mobilities can be compared with Hall mobilities[6–8] which have also been plotted in Figs. 4 and 5. At an impurity concentration of 10^{17} (cm^{-3}) the ratio of Hall mobility μ_H to the conductivity mobility μ_c is about 1.5 and 1.6 for electrons and holes respectively. The ratio decreases and approaches unity with increasing impurity concentration.

Blatt's[5] theoretically computed ratio, μ_H/μ_d for the nondegenerate range for an impurity density of 10^{17} gives a value of 1.64 and 1.66 for electrons and holes, respectively. This is in good agreement with the present results. As pointed out previously the decrease to unity is expected theoretically as degeneracy is approached.

The theoretical calculated mobilities are also included in Figs. 4 and 5. These curves are calculated using the

[19] The differences in ionization energies would result in a boron curve shifted to smaller densities by 15% at 10^{18} (cm^{-3}) and by 3% at 10^{17} (cm^{-3}). The aluminum curve would be located between the gallium and the boron plot but would lie closer to the gallium line.

Conwell-Weisskopf formula[1] or the Brooks-Herring formula,[2] combined with lattice scattering.[20] The effective masses mentioned above have been used for electrons and holes. For n-type silicon the agreement is quite good between the measured and the theoretical mobilities above an ionized impurity density of 10^{18} (cm^{-3}). The agreement at lower impurity densities is not as good. Neutral impurity scattering is not taken into account in the theoretical curve. However, it can be neglected at lower concentrations and would decrease the mobilities by only about 10% at an impurity density of 10^{18} (cm^{-3}).[21] The measured curve shows the same shape as the Brooks-Herring curve but the experimental values are considerably smaller.

In p-type silicon the lattice scattering contributes more to the mobility than in equally doped n-type silicon. Therefore, the difference between the Conwell-Weisskopf formula and the Brooks-Herring formula is almost negligible for the combined mobility. The measured mobilities are almost a factor of two smaller than the theoretically calculated ones. However, the measured Hall mobilities are also considerably smaller than the theoretically computed conductivity mobilities which disagrees with the theoretical μ_H/μ_d ratio. This fact may be due to the assumptions made in the theory of impurity scattering, whereas the ratio μ_H/μ_d is less sensitive to details of the band structure.

[20] E. M. Conwell, Proc. Inst. Radio Engrs. **40**, 1327 (1952). Lattice mobilities of 1300 cm^2/v-sec and 360 cm^2/v-sec were used for electrons and holes, respectively.

[21] N. Sclar, Phys. Rev. **105**, 1559 (1956).

ACKNOWLEDGMENT

The author wishes to thank G. C. Dacey and F. M. Smits for encouraging this work. The author is obliged to J. D. Struthers and F. J. Morin for communication of their measurements and to I. M. Ross and J. M. Goldey for useful suggestions. A helpful discussion with C. Herring was appreciated very much.

PHYSICAL REVIEW VOLUME 108, NUMBER 6 DECEMBER 15, 1957

Indirect Transitions at the Center of the Brillouin Zone with Application to InSb, and a Possible New Effect*†

WILLIAM P. DUMKE
Chicago Midway Laboratories, University of Chicago, Chicago, Illinois
(Received August 5, 1957)

The theory of indirect optical transitions is extended to the case where both the valence and the conduction band extrema occur at the center of the Brillouin zone. For this band structure, the dominant electron transition involves a virtual optical transition to a conduction band state, accompanied by scattering to a real state in the conduction band by absorption of a long-wavelength optical mode phonon. An analogous transition may also occur for holes. It is likely that the hole transition will be dominant over the electron transition when the curvature of the conduction band is greater than that of the valence band. It is shown that the absorption edge data on InSb are in agreement with this theory. The experimental evidence on InSb is reviewed and found to be consistent with degenerate valence bands at the center of the Brillouin zone. The absence of any evidence of indirect transitions involving acoustic modes tends to indicate that the shift of the valence maximum away from $\mathbf{k}=0$ due to spin-orbit energy terms is small. A new effect is predicted involving the modulation of the indirect absorption constant by the selective excitation of the long-wavelength optical modes. A simplified theory of this effect is presented and the experimental possibilities of observing it in InSb are discussed. Its existence would verify the proposed indirect transition process as well as indicating the position of the band extrema.

INTRODUCTION

ONE of the more recent methods for discovering information about the band structure of semiconductors is the detailed analysis of the absorption constant at the interband transition edge on the basis of indirect optical transitions.[1] By an indirect transition we mean a second-order transition through a virtual intermediate state which involves scattering in $\mathbf{k}$ space by the absorption or emission of a phonon in addition to the usual absorption of an optical photon. By fitting the experimental absorption data with the characteristic curves for indirect transitions one can find the temperature of the photons involved, and with a knowledge of the lattice vibrational spectrum it is then possible to estimate the separation in $\mathbf{k}$ space between the valence and conduction band extrema. Using such a procedure, Macfarlane and Roberts estimated the distance from the center of the Brillouin zone of the conduction minima in Ge [2] and Si.[3] Although

* A preliminary report of this work has been published: Bull. Am. Phys. Soc. Ser. II, **2**, 185 (1957).

† This research was supported by the U. S. Air Force, through the Office of Scientific Research of the Air Research and Development Command.

[1] Bardeen, Blatt, and Hall, *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954* (John Wiley and Sons, Inc., New York, 1956).

[2] G. G. Macfarlane and V. Roberts, Phys. Rev. **97**, 1714 (1955).

[3] G. G. Macfarlane and V. Roberts, Phys. Rev. **98**, 1865 (1955).

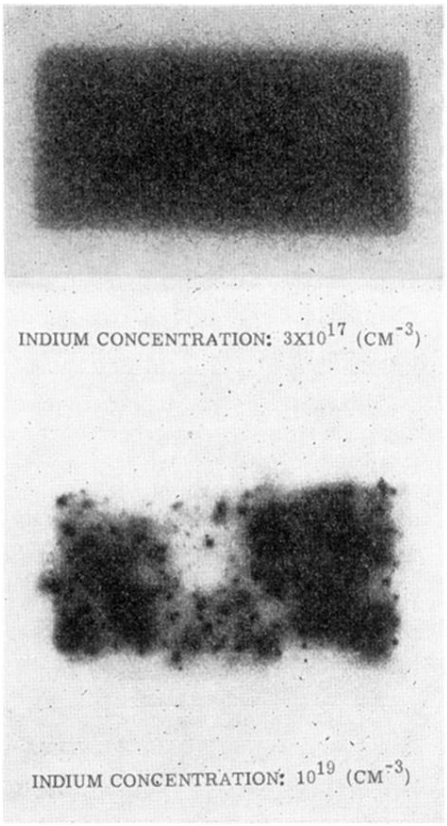

FIG. 3. Radiograms of indium-doped silicon wafers.