These results suggest that the conductive process are influenced by quenching from a temperature somewhere above 600°C. All of our "moderately" heat-treated samples have been quenched at this and lower temperatures. If both Hall effect and the conductivity of samples quenched from temperatures between 600°C and 1100°C can be measured, then we should be able to determine at which temperatures these "anomalous" conduction mechanisms appear and perhaps gain some insight into the temperature of formation or dispersion of some of the impurity centers mentioned in Sec. IV.

An infrared photoconductivity experiment at liquid helium temperatures could decide between the first model and the last two, while a photoconductivity experiment at shorter wavelength to establish the existence of traps could eliminate the second or third. Thermoluminescent curves of samples heated from liquid helium temperatures after irradiation with ultraviolet light should also add some information on the shallow impurity levels of the physical models suggested in Sec. III for each of these energy schemes.

High-temperature Hall effect and conductivity measurements should certainly shed some light on the mechanism of the D-center formation. At temperatures at which the D centers might start to dissociate into positive and negative ion vacancies, the Hall coefficient should rise due to the capture of two electrons by each oxygen ion vacancy. The effect on conductivity may or may not be masked due to the possible exponential change of mobility with temperature. Further, on heating to temperatures that are high enough to dissociate the D center and quenching to temperatures that are low enough to prevent diffusion, we should be able to vary the concentration of D centers. This would affect both Hall and conductivity measurements at low temperatures. The destruction of D centers with the increase of oxygen ion vacancies should diminish the intensity of the green luminescence while enhancing the output of the ultraviolet peak.

The existence of two, lattice vacancies of opposite sign side by side could be detected by a peak in the variation of the dielectric loss constant as a function of frequency similar to that reported by Breckenridge[41] for the alkali halides. This frequency would correspond to the jump frequency of the pairs of vacancies.

Experiments just mentioned may help decide whether the D-center model is applicable. Alternatively, they may suggest that we need a more complex impurity system to explain all of the effects of ZnO or that the bulk effects that we have measured are not associated with centers that produce the other effects discussed.

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Lattice-Scattering Mobility in Germanium

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The temperature dependence of lattice-scattering mobility in germanium is determined from conductivity. It is found to be $T^{-1.66}$ for electrons and $T^{-2.33}$ for holes. The result for holes suggests that the valence band is not at the center of the Brillouin zone. The ratio Hall mobility/conductivity mobility is also determined. It is found to be constant with temperature at $\sim$1.05 for electrons. The ratio for holes shows significant temperature dependence. This suggests that the valence band is composed of multiple surfaces of minimum energy.

THE temperature dependence of lattice-scattering mobility in germanium has been reported[1–5] as being different from the theoretically predicted $T^{-1.5}$: in general, it is found to be $T^{-1.6}$ for electrons and $T^{-2.3}$ for holes. These results have theoretical significance since the prediction $T^{-1.5}$ assumes the band edge to be located at the center of the Brillouin zone. In the references cited above, the temperature dependence of lattice-scattering mobility was determined from conductivity and drift or Hall mobility. In this note, it is determined from conductivity. This method has some advantage over the others since drift measurements are more difficult and perhaps less precise, and Hall results will be misleading if the ratio of Hall mobility to conductivity mobility is a function of temperature.

The ratio Hall mobility/conductivity mobility, μ_H/μ, as a function of temperature has also been determined. The magnitude and temperature dependence of this ratio has theoretical significance with regard to the shape and number of the surfaces of minimum energy

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in the Brillouin zone. For spherical energy surfaces, theory predicts $\mu_H/\mu=1.18$ and constant with temperature. Early measurement of μ_H/μ for electrons gave a value <1 and led Shockley[6] to suggest the possibility of re-entrant energy surfaces. However, recent results of Debye and Conwell[4,7] show $\mu_H/\mu\sim1.1$ in agreement with theory.

The temperature dependence of lattice scattering mobility μ_L can be determined from the conductivity of high-purity samples measured in the range where carrier concentration is constant (all impurities ionized). In such samples, the difference between donor and acceptor concentration may be 10^{14} cm^{-3} or less with the majority impurity level lying at about 0.01 ev from the valence band or the conduction band. Carrier concentration is predicted to be constant over the approximate temperature range 60 to 250°K. In such high purity samples, theory also predicts impurity scattering to be negligible above 100°K. Thus, from 100 to 250°K the conductivity $\sigma=n$ (or p) $e\mu_L$ and the temperature dependence of σ gives the temperature dependence of μ_L, n and e being constant.

The conductivity of high-purity n- and p-type germanium single crystals has been measured on bridge-shape samples.[4,8] Over the range where carrier concentration is constant, mobility has been determined using the relation

$$\mu_T=\mu_{300}\sigma_T/\sigma_{300}\ \text{cm}^2/\text{volt sec},$$

where μ_T is mobility at temperature T, μ_{300} is drift mobility at 300°K (3800 for electrons and 1820 for holes) obtained by M. Prince of these Laboratories, σ_T is conductivity at temperature T, and σ_{300} is conductivity at 300°K. Mobility determined in this way is plotted against log temperature in Fig. 1, for several n-type and p-type samples. Straight-line regions are found whose slopes show electron mobility $\propto T^{-1.66}$ and hole mobility $\propto T^{-2.33}$. Since carrier concentration is constant and impurity scattering negligible,[9] these slopes represent the temperature dependence of lattice-scattering mobility μ_L. Because of assumptions in the theory, $T^{-1.66}$ cannot be considered a significant departure from $T^{-1.5}$. $T^{-2.33}$ is significant and suggests that the valence band is not at the center of the Brillouin zone. Complete expressions for μ_L can now be given: $\mu_L=4.90\times10^7T^{-1.66}$ for electrons and $\mu_L=1.05\times10^9T^{-2.33}$ for holes.

The ratio μ_H/μ can be determined in the range where carrier concentration is constant from measured Hall mobility μ_H and μ determined above. Results from a number of samples are shown in Fig. 2. The ratio for electrons is nearly constant at ~1.05. The ratio for holes shows significant temperature dependence. These results suggest that the valence band is composed of multiple surfaces of minimum energy. In the region below 100° where μ_H/μ for holes approaches a constant with temperature, the temperature dependence of lattice-scattering mobility is expected to become $T^{-1.5}$. This behavior is obscured by impurity scattering in the results shown in Fig. 1.

The theoretical implications of these results were suggested by C. Herring.

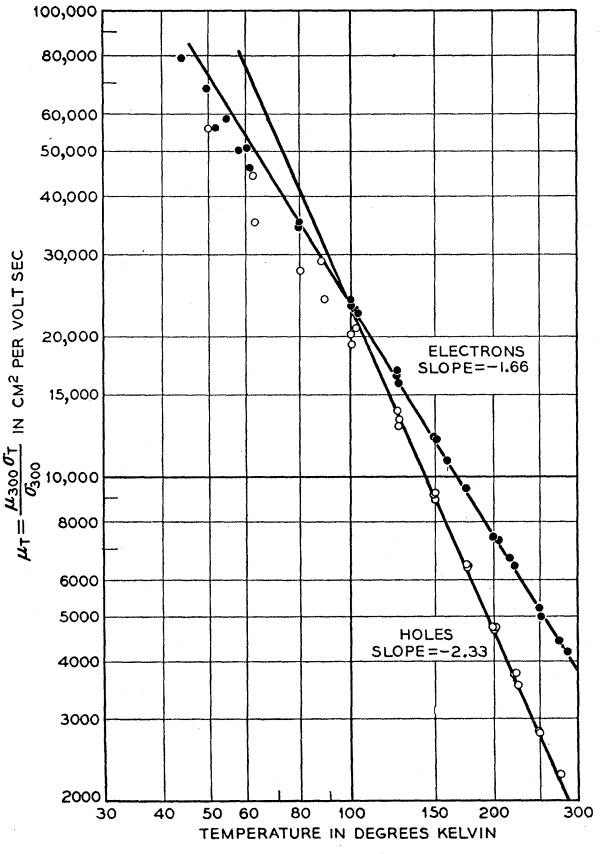

FIG. 1. Mobility as a function of temperature in the range where carrier concentration is constant.

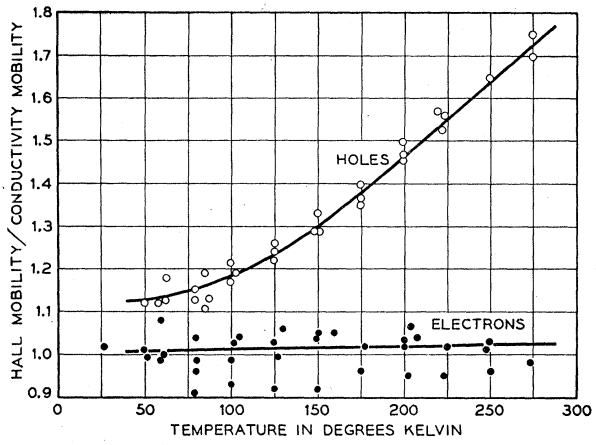

FIG. 2. Hall mobility/conductivity mobility as a function of temperature.

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[7] P. P. Debye, Phys. Rev. **91**, 208 (1953).
[8] Some of these data were taken by P. P. Debye.
[9] Impurity scattering becomes evident where measured mobility departs from the straight-line behavior below 80° for electrons and below 100° for holes.