## ELECTRONIC EFFECT IN THE ELASTIC CONSTANTS OF GERMANIUM

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We have measured the elastic constants of pure and heavily doped *n*-type germanium and discovered a difference which can be attributed to the electronic contribution to the strain energy function. The importance of electronic energy bands in the theory of the elastic constants of metals has been appreciated for a long time. Satisfactory quantitative verification of the electronic theories of elastic constants has not been possible in metals, however, because pertinent parameters of the band structures and their dependence on strain are not known. Such parameters are known for certain semiconductors, however, and, in particular, are far more accurately known for germanium than for any other solid. Therefore germanium provides a unique opportunity for a study of the role of electronic energy in the theory of elastic constants.

We have measured the elastic constants of two samples of germanium. One, "pure," contains less than 10<sup>14</sup> carriers per cm<sup>3</sup>. The other, "heavily doped, " contains  $3.5 \times 10^{19}$  arsenic donors per cm<sup>3</sup>. The heavily doped sample was a  $\frac{3}{4}$ -inch cube with exceptionally uniform resistivity, as measured by surface probes.<sup>1</sup> The measurements consisted of the determination of the velocities of 10-Mc/sec ultrasonic waves for an appropriate set of crystal directions by a conventional pulseecho technique. Measurements were made through the temperature range 4.2°K-240°K. The results at very low temperatures for the pure specimen and the specimen degenerately doped with arsenic are given in Table I. The values of  $C_{44}$  as a function of temperature are given in Fig. 1. Our values of  $C_{44}$  for the pure specimen differ from those of  $McSkimin^2$  by almost 1% and from those of Fine<sup>3</sup> by 0.5% in the temperature range covered by both sets of measurements.

Referring to Table I,  $\frac{1}{3}(C_{11} + 2C_{12})$  and  $\frac{1}{2}(C_{11} - C_{12})$ are not significantly different in the two specimens, while  $C_{44}$  is 5.5% smaller in the heavily doped specimen. Measurements on another specimen of similar doping level but not as homogeneous confirmed this difference in  $C_{44}$ . The fact that only  $C_{44}$  is affected by the addition of the arsenic characterizes the difference between the samples

Table I. The elastic constants of germanium at  $4.2^{\circ}$ K (in units of  $10^{11}$  dyne/cm<sup>2</sup>).

Specimen	C <sub>44</sub>	$(C_{11} - C_{12})/2$	$(C_{11} + 2C_{12})/3$
Pure	6.80	4.06	7.58
Heavily doped	6.42	4.04	7.66

as an electronic effect. The terms in the strain energy function of the crystal which are proportional to  $C_{44}$  involve just those components of strain which alter the conduction band of germanium by removing the degeneracy of the valleys. On the other hand, the terms in the strain energy



FIG. 1. The temperature dependence of  $C_{44}$  in pure and in heavily doped *n*-type germanium.

function which are proportional to  $C_{11}$  and  $C_{12}$  contain only components of strain which do not affect the structure of the conduction band of Ge. It can be concluded that the change of elastic constants results from the addition of electrons to the conduction band.

The effect on  $C_{44}$  is very large. The addition of 0.08% impurity changes  $C_{44}$  by 5.5%, or seventy times the impurity concentration. The large magnitude of the change is also in agreement with the predictions of the electronic interpretation. We have used the usual multivalley-deformation potential model to construct a theory of the electronic contribution to the strain energy function. The theory resembles that of Leigh,<sup>4</sup> who calculated the elastic constants of aluminum from a multivalleytype model, but is not restricted to the degenerate limit assumed by Leigh. According to this model the effect arises in the following way: When the crystal is strained by a pure shear, the energy of some valleys is increased and the energy of other is decreased. The mean energy of the valleys is constant, so that the electronic energy is not changed to first order in the strain. However, in the strained crystal the energy can be lowered by transferring electrons from the higher energy valleys to the lower energy valleys. This re-establishment of statistical equilibrium among the electrons lowers the energy in terms of second order in the strain. Therefore it amounts to a decrease in the shear elastic constant. The quantitative theory shows that in the low-temperature limit,

$$(\delta C_{44}/C_{44})_0 = -(4/3)^{5/3} \pi^{2/3} m^* \Xi_u^2 N^{1/3}/h^2 C_{44}.$$
(1)

Here  $m^*$  is the density-of-states mass for one valley and the remaining notation is standard. For our heavily doped sample  $(N=3.5\times10^{19} \text{ cm}^{-3})$ , Eq. (1) gives  $(\delta C_{44}/C_{44})_0 = -0.075$ . The observed effect is about three-fourths of this.

The highest temperature of our measurements

is about one-third of the electronic degeneracy temperature in the doped crystal. The theory predicts that  $(\delta C_{44}/C_{44})$  should increase slightly (about 10%) in this range. Figure 1 shows that in fact  $(\delta C_{44}/C_{44})$  decreases by about 20%.

Thus the change in elastic constants produced by the solution of arsenic in germanium agrees with an electronic interpretation in two respects: (1) Only  $C_{44}$  is changed; (2) the magnitude of the change is very large, and is given semiquantitatively by the theory. The discrepancies with the theory, namely, the difference between the calculated and observed magnitude of  $\delta C_{44}/C_{44}$  and the difference between its observed and predicted temperature dependence, probably indicate an inadequacy of the theoretical model. However, it is difficult to completely rule out any effects of inhomogeneities, which are so common in heavily doped germanium. Note that the period of our ultrasonic wave  $(10^{-7} \text{ sec})$  is very long compared to the scattering times of electrons in germanium so that failure of establishment of equilibrium in the electron populations of the valleys cannot be the source of the discrepancies. For example, the smallest intervalley scattering rate found in all of the samples studied by Weinreich et al.<sup>5</sup> was  $5 \times 10^8$  sec<sup>-1</sup> in a high-purity specimen.

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