

if monocrystalline films can be made. Note that we have verified the energy dependence of the renormalized  $v_F$ . It is noteworthy that the thick film need not be a superconductor; a normal metal coated with relatively thin superconducting films on the back and (possibly) the front can be used.<sup>6</sup> Especially in that case, the effect presents a striking demonstration of the nature of superconductivity as an electron pair condensation which mixes hole and electron quasiparticles, since it is precisely an interference effect between hole and electron propagation, which appears meaningless in a normal metal.

It would also be interesting to study this effect as a function of  $\delta\Delta$  by using various coating materials, as well as to study the effects

of various surface preparations on  $\delta\Delta$ .

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<sup>1</sup>W. J. Tomasch, Phys. Rev. Letters **15**, 672 (1965).

<sup>2</sup>W. J. Tomasch, Phys. Rev. Letters **16**, 16 (1966).

<sup>3</sup>J. M. Rowell and W. L. McMillan, to be published. The full Green's-function calculation of the tunneling current carried out in this reference contains the terms leading to the Tomasch effect.

<sup>4</sup>J. R. Schrieffer, Theory of Superconductivity (W. A. Benjamin, Inc., New York, 1964).

<sup>5</sup>W. L. McMillan and J. M. Rowell, Phys. Rev. Letters **14**, 108 (1965).

<sup>6</sup>J. M. Rowell and W. L. McMillan, to be published.

### POLARIZATION DEPENDENCE OF THE INDIRECT PIEZOABSORPTION COEFFICIENT IN Ge AND Si†

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It has recently been shown<sup>1,2</sup> that measurements of the polarization dependence of the piezoreflectance in Ge and Si can give detailed information on the nature of the transitions involved. These measurements were in the energy region corresponding to direct transitions. We wish to report on the polarization dependence of piezoabsorption measurements in the indirect absorption region from which one can directly obtain information on the sign of the deformation-potential constants which are only indirectly obtainable otherwise. In addition, we obtain information about the symmetry of the intermediate state of the indirect transition. Furthermore, it may be possible that these techniques can be used to obtain the same information for materials with degenerate valence bands similar to those in germanium and silicon. We have verified that the valence-band deformation potentials in germanium are both negative.

The valence band in germanium and silicon is a fourfold degenerate  $J = \frac{3}{2}$  state at the zone center when spin-orbit splitting is taken into account.<sup>3</sup> Under uniaxial stress along  $\langle 111 \rangle$  or  $\langle 100 \rangle$ , the degeneracy is partly removed and two doubly degenerate levels  $m = \pm \frac{3}{2}$ ,  $m = \pm \frac{1}{2}$

result, which are quantized along the stress axis. The deformation potentials which determine the splitting have been determined for silicon by Hensel and Feher<sup>4</sup> and for germanium by Hall and Koenig<sup>5</sup> and Glass.<sup>6</sup> All these experiments establish directly the sign of the product of the deformation potentials and a valence-band effective-mass parameter  $B$  or  $N$ .<sup>3</sup> The signs of the latter in germanium are well known theoretically from the ordering of the energy levels at the zone center. In silicon Hasegawa<sup>7</sup> has shown that the effective mass of the  $|m| = \frac{1}{2}$  band should change with strain due to admixture of these states with the nearby spin-orbit split-off band. From the presence of a substantial change in the effective mass, Hensel and Feher<sup>4</sup> have determined that the  $|m| = \frac{1}{2}$  band moves upward under compressive stress relative to the  $|m| = \frac{3}{2}$  band for both  $\langle 100 \rangle$  and  $\langle 111 \rangle$  stress, establishing the sign of the deformation potentials. This resolved the previously existing theoretical uncertainty about the sign of  $B$ .<sup>3,4</sup>

In our direct method we measure the polarization dependence of the absorption coefficient of uniaxially stressed germanium and silicon in the region of the indirect absorption edge.

The experimental results determine directly which band moves up, as follows.

The rate of transition between one of the valence-band states and the intermediate conduction-band state near  $\vec{k}=0$  is proportional to the square of the matrix element of  $\vec{e}\cdot\vec{p}$ , where  $\vec{e}$  is the polarization direction of the incident light and  $\vec{p}$  is the electron momentum operator.<sup>8</sup> The various initially degenerate valence-band states contribute matrix elements which differ in their dependence on polarization. Since the crystal is cubic, as long as the valence-band states remain degenerate, there can be no overall polarization dependence when we take all the states into account. Also, all the matrix elements of the components of  $\vec{p}$  between valence- and conduction-band states can be calculated in terms of one independent parameter. Under uniaxial stress, which removes the valence-band degeneracy, the absorption constant will no longer be isotropic, since each of the split bands contributes its own polarization dependence to the absorption at a different wavelength.

The calculation of the relative strengths of the transitions through the intermediate states proceeds as follows: In the notation of Koster et al.,<sup>9</sup> at the zone center the valence-band wave functions of Ge transform under rotations as the  $\Gamma_8^+$  representation of the  $O_h$  group (these are  $J=3/2$  states), the intermediate states as  $\Gamma_7^-$ , and the components of the momentum as  $\Gamma_4^-$ . Under uniaxial stress along a  $\langle 100 \rangle$  direction, the  $|m|=1/2$  sublevels of  $\Gamma_8^+$  separate from the  $|m|=3/2$  sublevels quantized along  $\langle 100 \rangle$ . The relative values of the matrix elements can be found directly from the table of coupling coefficients,<sup>10</sup> which are given in a  $\langle 100 \rangle$  coordinate system.

For uniaxial stress along  $\langle 111 \rangle$ , the valence band also splits into two twofold sublevels  $|m|=1/2$ ,  $|m|=3/2$  now quantized along the  $\langle 111 \rangle$

direction. The wave functions for  $|m|=1/2$  quantized along  $\langle 111 \rangle$  expressed in terms of the  $\langle 111 \rangle$  coordinate system have a different form than have the wave functions for  $|m|=1/2$  quantized along  $\langle 100 \rangle$  in terms of the  $\langle 100 \rangle$  coordinate system. This is easily seen by realizing that the state quantized along  $\langle 100 \rangle$  must be invariant under a fourfold rotation about  $z$  whereas the state quantized along  $\langle 111 \rangle$  must be invariant under a three-fold rotation about  $z'$ . We must therefore calculate the matrix elements by rotating all our representation to the  $\langle 111 \rangle$  coordinate system, and we can thereby express the desired matrix elements in terms of the ones referred to a  $\langle 100 \rangle$  system.

The results show that, in germanium, the  $|m|=3/2$  valence-band states have zero matrix elements for absorption parallel to  $\langle 111 \rangle$  stress while the matrix element for absorption perpendicular to  $\langle 111 \rangle$  stress is three times larger for the  $|m|=3/2$  than for the  $|m|=1/2$  states. Therefore, in order to determine which band is nearest to the conduction band, one merely has to observe whether parallel or perpendicular polarization has a larger absorption coefficient at long wavelengths. Similar effects take place for  $\langle 100 \rangle$  stress and for silicon. Table I lists the relative size of the matrix elements from the various states for germanium and silicon. For germanium, the absorption for parallel polarization is seen to come entirely from  $|m|=1/2$  states if the stress is in  $\langle 111 \rangle$  and from  $|m|=3/2$  states for stress in  $\langle 100 \rangle$ .

In Fig. 1, we plot the absorption coefficient  $\alpha$  of a germanium sample under a stress of  $4.5 \times 10^3$  kg/cm<sup>2</sup> in the  $\langle 100 \rangle$  direction versus incident photon energy. We plot  $\alpha$  for both parallel and perpendicular polarization. We note that the onset of absorption occurs earlier for perpendicular polarization than for parallel polarization by an energy of about 0.02 eV. This indicates that the  $|m|=1/2$  state is upper-

Table I. Relative matrix elements (squared) for transitions from the valence band  $|m|$  to the conduction band at  $\Gamma$ . In unstressed germanium or silicon the various  $|m|$  states are degenerate, and the sum over  $|m|$ , which we normalized to one, is the same for polarization parallel and perpendicular to the stress.

| Stress direction | Polarization direction | $\langle 111 \rangle$ |               | $\langle 100 \rangle$ |               |
|------------------|------------------------|-----------------------|---------------|-----------------------|---------------|
|                  |                        | Parallel              | Perpendicular | Parallel              | Perpendicular |
| Germanium        | $ m =3/2$              | 0                     | $3/4$         | 1                     | $1/4$         |
|                  | $ m =1/2$              | 1                     | $1/4$         | 0                     | $3/4$         |
| Silicon          | $ m =3/2$              | 7/12                  | 11/24         | $1/4$                 | $5/8$         |
|                  | $ m =1/2$              | 5/12                  | 13/24         | $3/4$                 | $3/8$         |

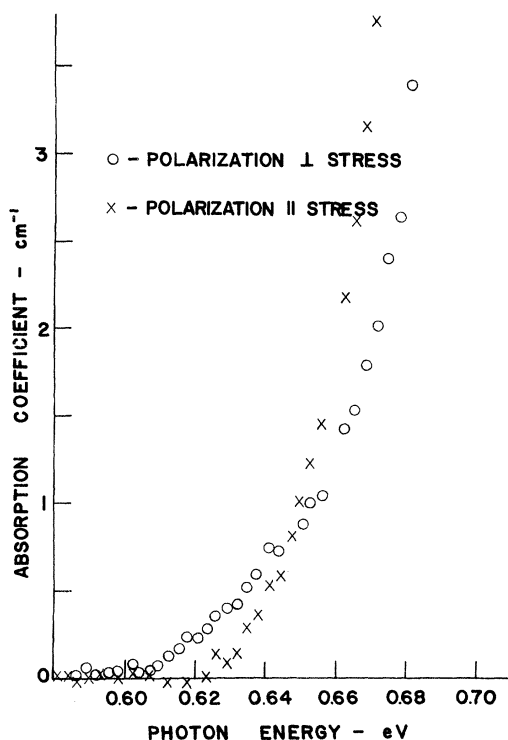


FIG. 1. Absorption coefficient versus incident photon energy for the case of a uniaxial stress of  $4.5 \times 10^3$  kg/cm<sup>2</sup> applied to a germanium crystal along [100]. The two sets of data are for polarization parallel and perpendicular to the stress axis.

most and permits a calculation of the deformation potential  $b$ . We find  $b = -1.8$  eV, in good agreement with the data of Hall.<sup>5</sup> This verifies the correctness of our interpretation. It also verifies that the intermediate state is at  $\Gamma$  since the valence-band splitting could determine the polarization dependence only for a transition at  $\Gamma$ . Incidentally, it also shows that the intermediate state could not be  $\Gamma_{15}$  as it is in silicon.

In Fig. 2, we plot the same data for a stress of  $7 \times 10^3$  kg/cm<sup>2</sup> in the  $\langle 111 \rangle$  direction. We note that absorption starts at the same energy for both polarizations, but is much stronger for parallel than for perpendicular polarizations. This shows that the  $|m| = \frac{1}{2}$  state is highest in this case too, since the  $|m| = \frac{3}{2}$  states do not contribute to the parallel polarization. Furthermore, the  $|m| = \frac{1}{2}$  states are expected to absorb the parallel polarization more strongly than the perpendicular polarization, which is indeed the case. We thus conclude that the deformation potential  $d$  is also negative. If

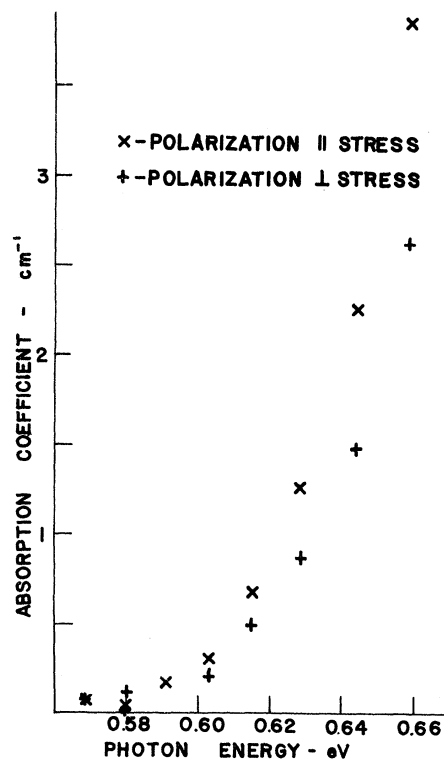


FIG. 2. Absorption coefficient versus incident photon energy for the case of a uniaxial stress of  $7 \times 10^3$  kg/cm<sup>2</sup> applied to a germanium crystal along [111]. The two sets of data are for polarization parallel and perpendicular to the stress axis.

the experiment were performed using tensile stress, one should see only perpendicular polarization initially and be able to measure the magnitude of the deformation potential.

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<sup>1</sup>U. Gerhardt, Phys. Rev. Letters **15**, 401 (1965).

<sup>2</sup>G. W. Gobeli and E. O. Kane, Phys. Rev. Letters **15**, 142 (1965).

<sup>3</sup>E. O. Kane, Phys. Chem. Solids **1**, 82 (1956).

<sup>4</sup>J. C. Hensel and G. Feher, Phys. Rev. **129**, 1041 (1963).

<sup>5</sup>J. J. Hall, Phys. Rev. **128**, 68 (1962).

<sup>6</sup>A. M. Glass, Can. J. Phys. **43**, 12 (1965).

<sup>7</sup>H. Hasegawa, Phys. Rev. **129**, 1029 (1963).

<sup>8</sup>T. P. McLean, in *Progress in Semiconductors*, edited by A. F. Gibson (John Wiley & Sons, Inc., New York, 1960), Vol. 5, p. 55.

<sup>9</sup>G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (MIT Press, Cambridge, Massachusetts, 1963), p. 88.

<sup>10</sup>Ref. 9, Table 83, p. 93.