

Effect of Temperature and Doping on the Reflectivity of Germanium in the Fundamental Absorption Region

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The 2.1- and 4.4-ev peaks in the reflectivity spectrum of germanium have been studied as a function of temperature and doping. The temperature coefficient of the 2.1-ev peak is -4.2×10^{-4} ev/°K, that of the 4.4-ev peak -1.8×10^{-4} ev/°K. Large donor concentrations give a decrease in the energy gap at the zone boundary in the [111] direction which is nearly the same as the shrinkage of the thermal gap. No shift with doping of the 4.4-ev peak was detected. The spin-orbit splitting of the valence band at the L_3' point in the zone boundary was found to be 0.18 ev.

I. INTRODUCTION

THIS paper is concerned with some studies of optical transitions involving deep-lying energy bands in germanium, as a means of investigating the effect of doping and of temperature on the band structure. Interest in the problem of the effect of high concentrations of impurities has increased recently, mainly as a result of the extensive use of degenerate materials in tunnel diodes.¹

There is evidence accumulating that heavy doping does perturb the energy bands of germanium. Cardona *et al.*² showed that their measured free-carrier polarizabilities gave an effective mass of the electrons which increased more rapidly with energy than expected from the known nonparabolic shape of the conduction band. They concluded that this was due to a perturbation of the shape of the [111] minimum in the conduction band by the donor atoms, the effect became noticeable for donor concentrations above $10^{19}/\text{cm}^3$.

Pankove has made emission³ and absorption⁴ measurements on heavily doped *n*-type germanium which showed that interesting effects were occurring. Unfortunately, interpretation of these is difficult because of the large free-carrier contribution to the absorption spectrum and the unknown role of tunneling in the emission study. Some shrinkage of the effective thermal gap with doping seems indicated, but its nature and size is masked by uncertainties in the analysis of the data.

Studies of tunneling in forward-biased tunnel diodes have shown that unexpected effects occur in germanium doped to degeneracy. Yajima and Esaki⁵ found an excess current in the forward direction which does not seem to be associated with normal tunneling. Longo⁶ and Chynoweth⁷ have reported a similar effect associated with the presence of impurity states introduced by

bombardment damage, and they have shown quantitatively that this excess current is associated with tunneling via impurity states in the forbidden region.

In some studies on minority carrier injection in tunnel diodes, Brown⁸ found that the barrier height for minority carrier injection is less than one would predict for an unperturbed germanium lattice with the known free-carrier concentrations. This can mean either that injection occurs to impurity levels in the energy gap, perhaps the same ones producing the excess current, or that the thermal gap has shrunk drastically with doping.

The usual studies which, with pure materials, have been so successful in tracing the bands in the vicinity of the thermal gap are not as productive on degenerate germanium. As found by Pankove,⁴ the optical absorption spectra, which for pure material have been decomposed into direct and indirect transitions at the thermal gap,⁹ are seriously perturbed by free carrier absorption in degenerate germanium. Oscillatory magnetoabsorption measurements on high-purity samples¹⁰ and the exciton spectra,¹¹ have given very accurate values for the direct gap, but are no longer useful with degenerate materials because of the broadening of the Landau and exciton levels by the impurities. Impurity scattering also prevents observation of cyclotron resonance, while the large density of free carriers makes it difficult to reach the intrinsic range where Hall-effect measurements give information about the band gap.

One experiment whose utility is not expected to be seriously impaired by high doping is the optical reflectivity. The reflection spectrum of intrinsic germanium has been studied by Philipp and Taft.¹² They found that the reflectivity had a maximum at 2.1 ev and an even more pronounced peak at 4.4 ev. From the measured reflectivity and the Kramers-Kronig relationship between the real and the imaginary part of the dielectric constant, they calculated the refractive index and

¹ L. Esaki, Phys. Rev. **109**, 603(L) (1958).

² M. Cardona, W. Paul, and H. Brooks, Helv. Phys. Acta **33**, 329 (1960).

³ J. I. Pankove, Phys. Rev. Letters **4**, 20 (1960).

⁴ J. I. Pankove, Phys. Rev. Letters **4**, 454 (1960).

⁵ T. Yajima and L. Esaki, J. Phys. Soc. Japan **13**, 1281 (1958).

⁶ T. A. Longo, Bull. Am. Phys. Soc. **5**, 160 (1960).

⁷ A. G. Chynoweth, W. L. Feldmann, and R. A. Logan, private communication (to be published).

⁸ G. Brown, private communication (to be published).

⁹ G. G. MacFarlane and V. Roberts, Phys. Rev. **97**, 1714 (1955).

¹⁰ S. Zwerdling, B. Lax, and L. M. Roth, Phys. Rev. **108**, 1402 (1957).

¹¹ G. G. MacFarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Proc. Phys. Soc. (London) **B71**, 863 (1958).

¹² H. R. Philipp and E. A. Taft, Phys. Rev. **113**, 1002 (1959).

the absorption coefficient as a function of photon energy between 0 and 10 eV. The calculated absorption coefficient showed a sharp edge at 2.1 eV and a maximum at 4.4 eV. Phillips¹³ attributed the 2.1-eV absorption edge to vertical transitions between the L_3' valence band maxima and the L_1 conduction band minima because of the energy and the intensity of the peak. The absorption maximum at 4.4 eV has been tentatively attributed by Phillips to transitions between the X_4 valence band and the X_1 conduction band.

We have measured the temperature and impurity dependence of the 2.1- and 4.4-eV peaks in the reflectivity of germanium. At this high photon energy, the free carrier polarizability and absorption are very small compared to the interband effects and do not alter the position of the reflectivity maxima. Thus, direct observation of the effect of high doping on the band structure and a comparison of the effect of donors and of acceptors can be made. At the same time, we have studied the temperature coefficients of these transitions and measured the spin-orbit splitting at the zone boundary for intrinsic germanium.

II. METHOD OF MEASUREMENTS

A. Equipment

The details of the method and apparatus used for the reflectivity measurements have already been described by one of the authors.¹⁴ The sample was placed inside a quartz-window cryostat and evacuated to 10^{-6} mm Hg. The sample temperature was monitored with a copper-constantan thermocouple in direct contact. The light source was a Leiss single monochromator with two different sets of optics. Around the 2.1-eV peak we used a tungsten lamp, and a flint prism with a resolution of 0.005 eV for the 100- μ setting of the slits. For the 4.4-eV region we changed to a hydrogen arc and quartz prism, using a resolution of 0.04 eV with 500- μ slits.

In spite of the good vacuum, at liquid air temperature the sample slowly accumulated a thin film of ice and the reflectivity gradually decreased with time. Warmed to room temperature, the sample soon returned to its original reflectivity. Careful study showed that the reduction of the reflectivity by the film did not depend on the wavelength over either peak, and its presence did not shift the positions of the peaks.

Since we were not interested in the absolute reflectivity, we were able to make a first-order correction for the film by monitoring the change in reflectivity with time for a single reference point which for convenience we took near the peak. Over an entire run, a typical change in the reflectivity at the monitor wavelength might be 3%.

¹³ J. C. Phillips, *J. Phys. Chem. Solids* **12**, 208 (1960).

¹⁴ M. Cardona, *Z. Physik* **161**, 99 (1961).

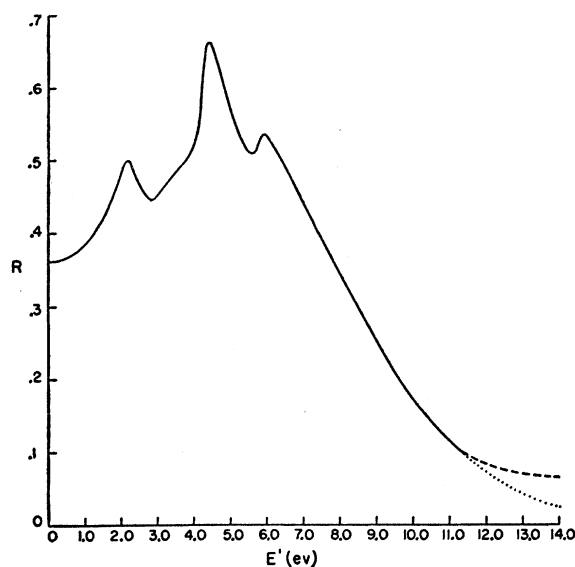


FIG. 1. Measured reflectivity of Ge surfaces (see reference 16).

B. Sample Preparation

Slices along the (111) plane were ground and then polished on one surface with Linde A-5175 polishing compound. The damaged surface layer left by the polishing was removed by etching in CP4. Unetched samples have broadened reflectivity peaks although their positions are not changed.¹⁵ Proper etching gives a higher reflectivity and a narrow reproducible peak.

We annealed one sample to see if strains might affect the spectrum. No significant change in the shape of the reflection peaks was observed on a sample doped with 10^{18} Ga/cm³ following 2 hr of baking at 750°C.

The free carrier concentration N was deduced from the room temperature Hall coefficient R_H and the formula $R_H = 1/eN$, where e is the elementary charge. The Hall constant was measured on bars cut from each optical sample after the other measurements were finished.

III. RESULTS

For reference we show Fig. 1, the reflectivity spectrum of germanium as measured by Philipp and Taft^{12,16} who covered a sufficiently large energy range to permit application of the Kramers-Kronig relations. Our spectrometer was too limited in wavelength for this, and we confined our studies to the neighborhood of the two reflectivity peaks to determine the effect on them of temperature and doping.

We made an extensive series of measurements on the 2.1-eV maximum and a lesser set on the 4.4 eV, since the lower resolution of our instrument at 4.4 eV reduced

¹⁵ V. S. Vavilov, A. A. Gippius, and U. N. Gorschka, *Soviet Phys.—Tech. Phys.* **2**, 230 (1958).

¹⁶ M. P. Rimmer and D. L. Dexter, *J. Appl. Phys.* **31**, 775 (1960).

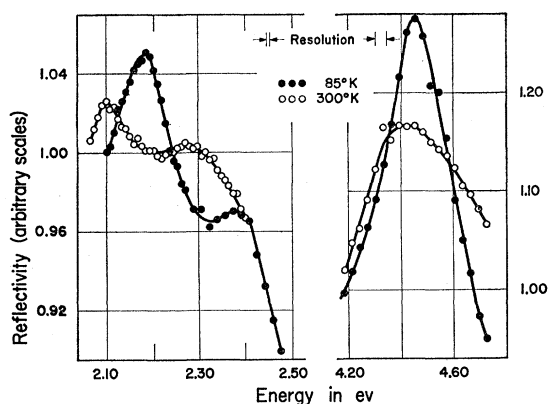


FIG. 2. Reflectivity peaks in a 5-ohm cm Ge sample at 85° and 300°K.

the utility of these studies. Our work covered temperatures at selected points from liquid air to 460°K, using single crystals of germanium doped with As, P, Sb, or Ga up to the maximum solubility at which we could grow single crystals.

Figure 2 shows typical peaks as measured on a very pure 5-ohm cm sample of germanium at 85° and 300°K. Both curves are normalized arbitrarily, for we made no attempt to measure the absolute reflectivity. There is no disagreement between these curves and Fig. 1, the results of Philipp and Taft, the apparent difference arising from the fact that we have greatly magnified the scales to permit study of the peaks. Notice that the doublet structure of the 2.1-ev peak is clearly resolved. From a number of measurements on two different high resistivity samples, we found the value of this splitting for pure germanium to be $0.18 \text{ eV} \pm 10\%$, in agreement with the somewhat less accurate value reported by Tauc.¹⁷

As the temperature is increased, the peaks shift toward lower energy, as one expects from the behavior of the thermal gap, and become broader. A similar broadening results from heavy doping of the germanium, as shown in Fig. 3. With pure germanium, the doublet structure is clearly resolved at 80°K; at 200°K a slight broadening can be observed, and by 300°K the doublet

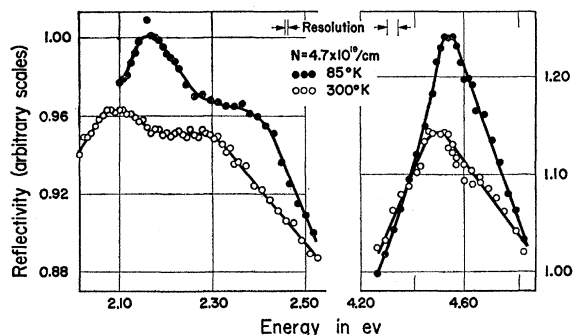


FIG. 3. Reflectivity peaks in an *n*-type Ge sample with 4.7×10^{19} carriers/cm³ at 85° and 300°K.

¹⁷ J. Tauc and E. Antoncik, Phys. Rev. Letters 5, 253 (1960).

is just resolvable. With doping of $10^{18}/\text{cm}^3$, there is also a slight broadening noticeable at 80°K. It is hardly observable at room temperature because of the larger size of the thermal broadening. With doping of $4 \times 10^{19}/\text{cm}^3$, the doublet is seldom resolvable even at liquid air temperature.

We have not been able to give a quantitative statement about the broadening because, lacking a theoretical knowledge of the shape of the lines, we cannot split the doublet into its two components. Besides, the condition of the surface has some effect on the shape though not on the position of the peaks. Poor etching gives a fictitious broadening, although a well-etched sample is reproducible from day to day and through successive etchings. On the most heavily doped sample (that doped with gallium to give 3.8×10^{20} holes/cm³), the surface never etched to a good mirror finish. This sample had a lower reflectivity than the others and perhaps an extra broadening from surface effects.

Figure 3 shows the spectra of an arsenic-doped sample with 4.7×10^{19} electrons/cm³ at 85° and 300°K. Phos-

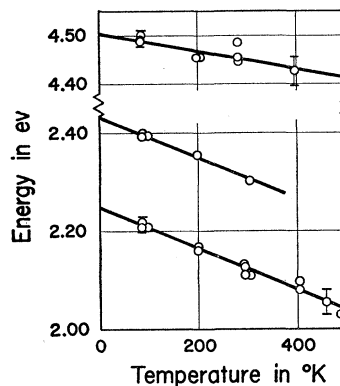


FIG. 4. Temperature dependence of the energy of the reflectivity peaks in high-purity Ge.

phorous- and gallium-doped samples with this same carrier concentration showed no systematic difference from the arsenic-doped samples. We also made comparisons between arsenic-, antimony-, and gallium-doped samples with 10^{18} carriers/cm³ and found that their spectra were indistinguishable. Thus at similar doping, our measurements failed to reveal any spectral properties associated with the chemical nature of the added impurity.

From these data we deduced the shift of the peaks with temperature and with doping. Figure 4 shows the position of the reflectivity maxima at temperatures from liquid air to 500°K. The most accurate results are for the low-energy component of the doublet, since the location of this peak remained reasonably well defined, even when the less intense higher-energy branch was not resolved. We have indicated our estimate of the uncertainty in the location of the peak by the vertical lines through the lowest and highest temperature points, which show how the uncertainty increases with temperature. The estimate includes the reproducibility

of the readings plus allowance for systematic error due to distortion of the line shape with temperature.

The lesser member of the doublet was harder to define, and the only points available are those cases where it was clearly resolved. The 4.4-ev peak retained a good shape, but because of the low spectrometer resolution we did fewer studies at this energy. Also, as discussed in the next section, the physical importance of this peak is less obvious than that of the doublet.

The temperature coefficient of the major component of the doublet we find to be -4.2×10^{-4} ev/°K $\pm 10\%$. The other member of the doublet has the same coefficient. It is interesting that the doublet has the same temperature coefficient as the thermal gap.

The 4.4-ev peak has a temperature coefficient of -1.8×10^{-4} ev/°K $\pm 25\%$, about half that of the thermal gap. This difference between the coefficients of the two reflectivity maxima seems to lie well outside the experimental error and is felt to be significant.

We have been especially interested in the shift of the peaks with doping, shown in Fig. 5, and in particular with the problem of whether any systematic difference exists between the effects of different impurities. Except for the general impurity broadening,

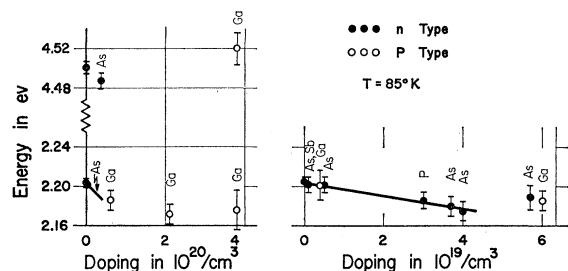


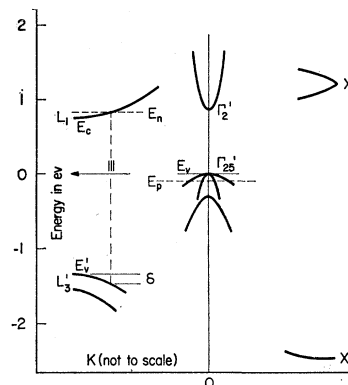
FIG. 5. Dependence on doping of the energy of the reflectivity peaks in Ge.

the effects of doping are small, but certain important results can be deduced from this figure.

1. There is a small but measurable shift of the 2.1-ev peak toward lower energy with increasing doping. This is best illustrated by the curve on the right, whose expanded scale is drawn to include all our donor concentrations. Up to 4×10^{19} electrons/cm³, all the data agree with a linear shift with doping. The value of the shift in the 2.1-ev peak at 4.0×10^{19} /cm³ is -0.03 ev $\pm 25\%$.

2. There is some indication that the shift saturates at higher doping. The two points at 6×10^{19} carriers/cm³ seem to lie above the extrapolation of the curve through the lower concentration points. One of these two points at 6×10^{19} is for arsenic doping, the other for gallium. We do not know the arsenic content of this sample, for above 5×10^{19} electrons/cm³ we have found that an increasing fraction of the arsenic is un-ionized and that the carrier concentration is nearly independent of the doping. Hence, this sample may not be representative of high-quality germanium.

FIG. 6. Energy band extrema at the center, [100], and [111] edge of the Brillouin zone in Ge (E_n and E_p are the Fermi levels for heavily doped *n*- and *p*-type material, respectively).



The curve at the lower left, which extends to higher doping to cover the gallium crystals, has little further shift for higher concentration of holes. We cannot definitely state, however, whether there is a true saturation of the shift with doping or whether the gallium merely gives slightly less shift than the arsenic. Studies with gallium doping in the range just below 4×10^{19} holes/cm³ are needed to clarify this point.

3. We have not demonstrated a shift with doping of the 4.4-ev peak. The limited data suggest that the shift is no larger than for the 2.1-ev peak.

4. The result that the donors and acceptors produce essentially the same shift of the reflectivity peaks does not mean that the perturbation of the lattice is the same for both. As discussed in the next section, it may actually imply a considerable difference between the two types of impurities.

IV. INTERPRETATION AND CONCLUSIONS

A. Origin of the Reflectivity Peaks

Philipp and Taft¹² showed that the reflectivity peak at 2.1 ev indicated the existence of an absorption edge at this energy. Phillips¹³ attributed this edge to transitions between the L_3' valence band maximum and the L_1 conduction band minimum (Fig. 6), because of the correlation with the calculated value of the energy

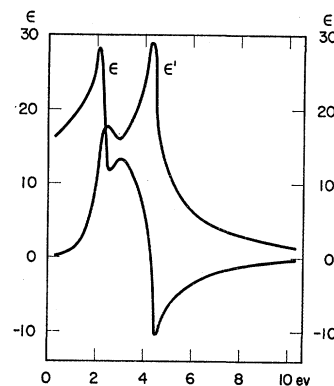


FIG. 7. Real and imaginary parts of the dielectric constant in Ge.

difference between those extrema¹⁸ and with the estimated absorption coefficient for the corresponding optical transitions. A 2-ev energy gap between the L_1 and L_3' extrema is also required by the experimental effective g factor for the electrons at the L_1 conduction band minimum, as shown by Roth and Lax.¹⁹

Figure 7 shows the real (ϵ) and the imaginary (ϵ') parts of the dielectric constant as a function of photon energy which we derived from Philipp and Taft's data. It is easy to observe that the 2.1-ev reflectivity peak corresponds to a maximum in the real part of the dielectric constant, while the 4.4-ev peak corresponds to a maximum in the imaginary part.

Korovin²⁰ calculated the spectral dependence of the dielectric constant produced by allowed and by forbidden transitions between parabolic bands. With his results, which should be valid near an absorption edge, it is easy to show that the real part of the dielectric constant has a maximum precisely at the band edge. This means that the energy of the reflectivity maximum gives directly the energy difference ($E_c - E_v'$) without the arbitrariness associated with the determinations of an energy gap from an absorption edge. This is true even for heavily doped material, since at the high photon energies involved in the measurements the free carrier absorption does not significantly contribute to the reflectivity. Furthermore, one sees from this result that the doublet structure of the 2.1-ev peak must originate in a splitting of one of the bands. This splitting, which we find to be $0.18 \pm 10\%$, agrees well with the value of 0.2 ev estimated for the spin-orbit splitting of L_3' .^{19,21,22} It seems, therefore, reasonable to attribute this doublet to transitions from each one of the bands into which the L_3' edge is split by spin-orbit interaction to the L_1 conduction band minimum. The doublet structure of the reflectivity peak has also been observed for GaAs, GaSb, InAs, InSb, and InP.^{14,17,23} In all these materials, a similar interpretation in terms of the spin-orbit splitting is possible.

The 4.4-ev reflectivity peak, which corresponds to a maximum in the imaginary part of the dielectric constant, is probably due to a maximum in the combined density of states for all the transitions. This maximum will occur for transitions between states near the middle of both the initial and the final bands. The maximum in the real part of the dielectric constant at 3 ev could be due to extrema of the bands which produce the 4.4-ev reflectivity peak if these are other than L_1 and L_3' . A closer identification of these bands has not been possible.

B. Effect of Temperature

The temperature coefficient found for the $L_3' - L_1$ gap, -4.2×10^{-4} ev/°K $\pm 10\%$, is the same as that of the thermal gap and of the direct absorption edge.¹¹ It is noteworthy that gaps of such different energies should have the same temperature coefficient. The thermal gap in silicon also has this temperature coefficient.²⁴ This behavior is in contrast to the pressure coefficients of the various gaps which differ widely.²⁵

We find that the spin-orbit splitting is temperature independent, in agreement with the observations that the spin-orbit splitting at Γ_{25}' is independent of temperature²⁶ and pressure.²⁷

The smaller temperature coefficient of the 4.4-ev peak is in qualitative agreement with our previous conclusion that this peak is due to transitions between states near the center of both bands. Here one would expect the perturbation of the energy due to the phonons to be very small, since in second-order perturbation theory the contribution from the higher intermediary states tends to compensate that due to the lower states. The remaining temperature coefficient would be that due to thermal expansion, which is always smaller than the total temperature effect at a band edge.

C. Effect of Doping

One of the most interesting results, and one subject to the most difficulty in interpretation, is that the 2.1-ev peak in reflectivity shifts to lower energy by 0.03 ev for material doped to give 4×10^{19} free carriers/cm³, either electrons or holes. This shift, though small, implies a considerable perturbation of the absorption edge and a large asymmetry between donors and acceptors.

The identification of this reflectivity peak with the transition $L_3' - L_1$ means that the transition is from an extremum of the valence band to the absolute minimum of the conduction band, Fig. 6. This gives an asymmetry between the reflection spectrum with added donors and that with added acceptors, which originates in the location of the free carriers rather than in the nature of the interaction of the impurities with the lattice, and adds some difficulties in the deduction of the changes in band separation.

As pointed out by Burstein²⁸ in connection with the absorption spectrum of degenerate InSb, absorption of a photon of energy corresponding to the absorption edge in n -type InSb will leave the electron at the Fermi level, which is well above the band edge. A similar Burstein shift should occur with the 2.1-ev reflectivity peak in n -type germanium, as can be seen from Fig. 6. Hence,

¹⁸ F. Herman, *Physica* **20**, 801 (1954).

¹⁹ L. M. Roth and B. Lax, *Phys. Rev. Letters* **3**, 217 (1959).

²⁰ L. I. Korovin, *Soviet Phys.—Solid State* **1**, 1202 (1969).

²¹ The spin-orbit splitting at L_3' should be roughly $\frac{2}{3}$ of the Γ_{25}' spin-orbit splitting because the L_3' state is doubly degenerate while the Γ_{25}' state is triply degenerate.

²² The doublet structure has been independently observed and similarly interpreted by Tauc and Antoncik (see reference 17).

²³ M. Cardona, *J. Appl. Phys.* **32**, 958 (1961).

²⁴ W. Dash and R. Newman, *Phys. Rev.* **99**, 1151, (1955).

²⁵ W. Paul, *J. Phys. Chem. Solids* **8**, 196 (1959).

²⁶ A. H. Kahn, *Phys. Rev.* **97**, 1647 (1955).

²⁷ D. M. Warschauer and W. Paul (private communication).

²⁸ E. Burstein, *Phys. Rev.* **93**, 632 (1954).

TABLE I. Energy changes due to doping. (Δ is the change from pure germanium. The other symbols are defined in Fig. 6.)

3×10^{18} As/cm ³	$\Delta(E_n - E_v) = -0.06$ ev	$\Delta(E_c - E_v) = -0.12$ ev
3×10^{19} As/cm ³	$\Delta(E_v - E_v') + \delta = 0.04$ ev	$\Delta(E_c - E_v') + \delta = -0.08$ ev
2×10^{20} Ga/cm ³	$\Delta(E_c - E_v') = -0.03$ ev	

for *n*-type germanium the energy of the peak exceeds the band gap energy by the Burstein shift.

For *p*-type germanium, however, the shift of the energy of the peak with doping is precisely the change in the energy difference $L_1 - L_3'$. Here no Burstein shift occurs because the Fermi level is between the two extrema involved in the transitions. Our data with gallium doping give immediately the change of bandgap due to large concentrations of acceptors. We find that the $L_3' - L_1$ bandgap decreases by 0.03 ev for germanium doped to 3.8×10^{20} holes/cm³.

The possibility of a reduction in the thermal gap with heavy doping has been investigated by a number of authors, Stern and Talley²⁹ and Aigrain and des Cloizeaux³⁰ have suggested that in *n*-type InSb the experimental value of the Burstein shift is too small, being reduced by a band narrowing due to the doping. However, if the Burstein shift is calculated using the average effective mass appropriate to the density of states, one finds there is no longer a need to postulate a shrinkage of the thermal gap.³¹ Stern and Talley also suggest that *n*-type InAs has too low a value of the Burstein shift, but again there is not solid evidence for this. The published data on the shift of the absorption edge of InAs with donor concentration²⁹ has considerable uncertainty because of the distortion of the edge and the presence of free carrier absorption. It is not certain whether the Burstein shift alone accounts for the displacement of the edge. The same difficulties were encountered by Pankove⁴ with degenerate *n*-type germanium.

Stern and Dixon³² have measured the absorption edge of compensated InAs with 5×10^{18} impurities/cm³ but only 9×10^{15} free electrons. They report that for this sample, which has no Burstein effect because of the good compensation, the thermal gap is decreased by 0.07 ev. Their theoretical calculation, based on a model describing the impurities as an interpenetrating lattice of metallic hydrogen, agrees well with this value. Since their gap shrinkage is independent of the effective mass, one can scale the value to *n*-type germanium by correcting for the dielectric constant; it predicts a lowering of the conduction band minimum by about 0.075 ev for 4×10^{19} donors/cm³. The results of Brown⁸ indicate that this estimate is somewhat small (see Table I). Their model gives no change for the reflectivity peak of *p*-type germanium since the effect of acceptors would be

to introduce additional states at the top of the valence band which is not involved in the transition causing the peak.

One can make a simple perturbation theory argument which shows that the effect of donors should be greater than that of acceptors. The first-order perturbation produced by the screened Coulomb potentials of the donor ions on the conduction- and valence-band edges will give a lowering of both edges. Because of the *s*-like nature of the conduction band wave functions, the perturbation of the conduction band should be larger than that of the valence band, and a net decrease in energy gap will result from the difference of both perturbations. The second-order perturbation on the conduction-band edge through the higher lying conduction-band states will lower the band edge, but the valence-band edge will be raised. Therefore, for donors the second-order perturbation will enhance the bandgap shrinkage of the first-order perturbation. The argument applied to acceptor centers gives a smaller net effect. Now the first-order perturbation increases the gap because of the reversal in the sign of the perturbing potential, while the second-order perturbation, which keeps its sign, subtracts from the effect of the first-order perturbation.

In the *n*-type germanium, we must correct for the Burstein shift before we can deduce the change in the bands. There is some uncertainty as to the effective mass to use in calculating the position of the Fermi level because of the difference between the density-of-states effective mass for the unperturbed band and the optical mass found by Cardona for degenerate germanium.² Besides this, we do not know how far below E_v' (Fig. 6) the carriers involved in the reflectivity originate. If crystal momentum is conserved, the carriers in the valence band must have the same momentum as the electrons at the Fermi level. This will make the Burstein shift exceed that due to the penetration of the Fermi level into the conduction band by an energy δ .

We can partially avoid these uncertainties by combining our results with those of Brown⁸ who measured the energy ($E_n - E_v$) from the forward characteristic of tunnel diodes. At liquid air temperatures he found this to be 0.689 ev for germanium with 3×10^{19} As/cm³, appreciably smaller than 0.747 ev for the thermal gap of intrinsic germanium.¹¹

Table I shows the energy shifts of the various gaps from their values for pure germanium obtained from the combined results of Brown and ourselves. The shifts shown in column 2 involve no assumption about the Burstein effect.

These results are consistent with our perturbation-theory argument about the behaviour of the bands under doping. The biggest effect is the displacement of the conduction-band minimum by the donors, which accounts for most of the decrease of the thermal gap reported by Brown.

²⁹ F. Stern and R. M. Talley, Phys. Rev. **100**, 1638 (1955).

³⁰ P. Aigrain and J. des Cloizeaux, Compt. rend. **241**, 849 (1955).

³¹ G. W. Gobeli and H. Y. Fan, Phys. Rev. **119**, 613 (1960).

³² F. Stern and J. R. Dixon, J. Appl. Phys. **30**, 268 (1959).

Any additional change due to shift of E_v relative to E_v' should be small, as already discussed. We also expect δ to be small because the effective mass at E_v' should be no smaller than that at E_c . Thus we can account for the smallness of the shift of $(E_v - E_v' + \delta)$ with doping.

In the last column we have included an estimate of the Burstein shift to give a better comparison of the effects of donors and acceptors. Based on the effective mass of pure germanium, we expect the Fermi level to be 0.06 eV above the conduction-band edge for 3×10^{19} As/cm³. This gives a thermal gap shrinkage of 0.12 eV for the arsenic-doped sample which greatly exceeds the total change $\Delta(E_c - E_v')$ for *p*-type germanium

with 2×10^{20} Ga/cm³ in agreement with the perturbation theory argument.

Note added in proof. A slight error has been found in the origin of the energy scales for the 4.4-eV peak in Figs. 2 and 3. The scales should be shifted by the amount required to bring the maxima to the energy values given in Fig. 5.

ACKNOWLEDGMENTS

We wish to acknowledge the help of Heinrich Meier in assembling the equipment and processing the data. The samples were prepared by the Materials and Device Technology section of the Radio Corporation of America Laboratories in Princeton, New Jersey.

Electron Microscope Observation of Precipitates on Grown-In Dislocations in MgO†

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The defect structure of undeformed, single-crystal, Norton MgO has been examined by transmission in the electron microscope. It is observed that precipitate particles in the form of 0.2- μ diam spheres and short rods are present in large numbers on as-grown dislocations. By using special etching and optical techniques which are described, the concentration of the precipitate spheres is shown to average 10^9 "balls"/cc (but range from 10^7 to 10^{10} "balls"/cc) for a large number of samples examined. Qualitative evidence is presented which indicates that these precipitates are the origin of Tyndall scattering frequently observed in MgO.

MAY and Kronberg,¹ on the basis of experiments concerned with the temperature dependence of the yield stress of Norton Company MgO, have concluded that the material contains precipitate particles which give rise to prominent macroscopic effects on the mechanical properties of the crystals. The purpose of this paper is to present direct microscopic evidence of the existence of many such particles.

The defect structure of undeformed MgO has been examined by transmission in the electron microscope. Samples obtained from the Norton Company have been shaped in the form of 0.010-in. thick slabs by rapid cleaving (to introduce a minimum of fresh dislocations) and then chemically thinned by a method similar to that of Washburn *et al.*² with a jet stream of hot phosphoric acid. Examination in the electron microscope of a large number of samples prepared in this manner has shown that grown-in dislocations invariably take the form shown in Fig. 1. The dislocation does not appear as a smooth line, but rather is seen to be bogged down with precipitate particles in the form of rods and spheres

arranged in a "ball and chain" configuration. The "balls," which range in size from 0.1 to 0.3 μ in diameter occur rather evenly spaced along the dislocation at intervals of $\sim 1 \mu$. The "balls" may, in some instances, be joined with an otherwise undecorated dislocation; however, it is also found that rodlike precipitates, which have the dislocation as their axis, occur on the dislocation between the "balls." They are usually < 500 Å in diameter and between 0.2 and 0.8 μ long. In addition to isolated dislocations, several very low-angle boundaries have been examined and reveal the same structure, i.e., the dislocations which make up the boundary are weighted down with "ball and chain" precipitates.

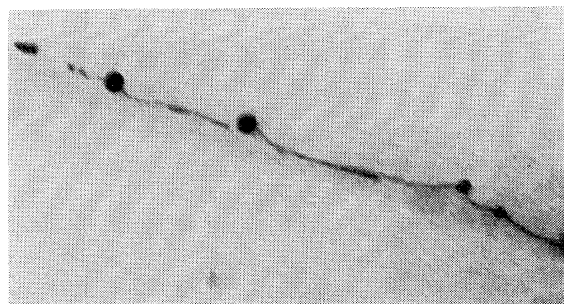


FIG. 1. Electron micrograph of grown-in dislocation in MgO showing precipitates distributed along its length ($\times 10,000$).

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¹ J. E. May and M. L. Kronberg, J. Am. Ceram. Soc. **43**, 525 (1960).

² J. Washburn, G. W. Groves, A. Kelly, and G. K. Williamson, Phil Mag. **5**, 991 (1960).