sequence are not very accurate because of this modulation. At the same time, an order-of-magnitude calculation using the equation of Kittel and Abrahams gives a few microseconds for T_2. As the temperature is increased, diffusion presumably becomes more important, giving the observed temperature dependence of T_2.

ACKNOWLEDGMENTS

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Degenerate Germanium. II. Band Gap and Carrier Recombination

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The data bearing on the band structure of degenerate germanium have been abstracted from the literature and intercompared. A variety of effects are described in terms of a voltage characteristic of each. It is found that all the voltages have essentially the same value and show a striking independence of the carrier concentrations. The conclusion is drawn that this voltage closely represents the band gap of degenerate germanium. It is shown that the thermal current at low temperature must be carried by recombination in the junction, which gives the proper barrier if the recombination centers lie near the band edge. This model of recombination explains the thermal current, the minority carrier lifetime, the excess current, and the emission spectrum. The reflectivity peak at 2.2 ev is also consistent if the bands at the [111] edge are roughly parallel to each other. The barrier found from the transition capacitance is not understood. The recombination centers lie close to the band edge. Assuming they are donors and acceptors, their capture cross section at room temperature is about 10^{-15} cm^2 per neutral atom. On the basis of this model, the thermal gap of highly degenerate germanium is about 30 mv less than for the unperturbed lattice. The shrinkage is independent of temperature.

I. INTRODUCTION

THIS paper studies the change of the band gap of germanium doped to degeneracy and the change in carrier recombination processes for diodes of degenerate germanium by a comparison of information contained in several recent publications. It offers an interpretation of the effects found and in particular of the studies of the forward admittance of germanium tunnel diodes by Meyerhofer *et al*,[1] to which it is a sequel.

Evidence is accumulating that the onset of degeneracy produces important modifications of the energy bands of germanium and the recombination processes. Reflection measurements by Cardona and Sommers[2] and emission[3] and absorption[4] measurements by Pankove show that doping to degeneracy has a significant effect on the band edges of *n*-type germanium. In forward-biased tunnel diodes, there occurs a carrier transport process which is associated with neither the normal Zener effect nor with the thermal current.[5] Meyerhofer *et al.*[1] found that the potential barrier controlling the flow of the thermal current in forward-biased tunnel diodes does not change with doping in the way predicted by the theory of Shockley[6] which has been so successful in explaining the forward current for germanium diodes of non-degenerate material. Finally, the injection efficiency of the emitter junctions of germanium transistors no longer changes with doping and with temperature as expected from the treatment of Shockley[6] when the emitter is degenerate.[7]

The large number of phenomena whose changes with doping in the region of degeneracy seem to be at variance with each other and with experience at lower dopings has pointed to the need of an analysis of the more striking discrepancies. In this paper we compare the findings of researches of two types; optical measurements on tunnel diodes[3] or homogeneous materials,[2] and studies of classical conduction[1,8] or tunneling[1,9] in junction diodes.

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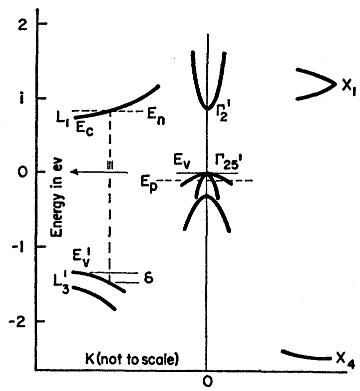

FIG. 1. Energy—K diagram for degenerate germanium. Energy band extrema at the center, [100], and [111] edges of the Brillouin zone in Ge. (E_n and E_p are the Fermi levels for heavily doped n- and p-type materials, respectively.) After Cardona and Sommers.[2]

We designate the principal role of the crystal in controlling the phenomena by a characteristic potential. Intercomparison of the data reveals that to good approximation this voltage has the same value for a variety of experiments on degenerate germanium, and that it is essentially independent of the penetration of the Fermi levels into the allowed bands. This result further emphasizes that the onset of degeneracy has introduced important modifications into the energy bands and the behavior of junction diodes.

Following this we present an energy diagram of the band gap of an abrupt junction diode of degenerate germanium, including the impurity states involved in recombination, and discuss the optical emission and carrier transport processes in terms of it. Only a single impurity level close to the band edge is needed to explain the emission spectrum, the forward conduction of tunnel diodes in both the excess and thermal current regions, and the insensitivity of the characteristic potential to the position of the Fermi level. The analysis also indicates why the injection efficiency of the emitter junction has a new behavior with temperature and doping when the junction becomes degenerate.

Based on these interpretations, we deduce a value for the thermal energy gap and discuss the nature of the impurity centers. The forbidden band seems to be somewhat less than for pure germanium, but the shrinkage is appreciably less than has been suggested.[3,4] The recombination centers are probably the neutral donors and acceptors.

II. DATA

In the experiments we are considering, the principal role of the crystal can be expressed by a voltage parameter V_m. For optical studies, this is the energy of the optical transition; for the diode current at large forward bias it is the potential barrier opposing the thermal current; for transition capacitance it is the built-in potential of the space charge in the junction.

Only four items from the experimental studies give an empirical value for V_m which comes directly from the instrument readings independently of our assumptions as to the details of the process. In these cases we believe the accuracy of V_m is limited by the measurement techniques rather than by the interpretation. Item 1 is the peak of the emission spectrum measured by Pankove[3] on a forward-biased tunnel diode at 80°K. From his description of the method of fabrication of the diode, we deduce that both sides were doped to about 10^{19} carriers/cm^3. His emission peak at 710 mv defines the characteristic potential for optical emission.

Item 2 is abstracted from the work of Meyerhofer *et al.*[1] on tunnel diodes. At extreme forward bias, they found an increase of current with voltage following the relation $\exp(qV/kT)$, where V is the forward bias and kT/q the temperature in volts. This demonstrated that the current was carried by thermal excitation over a barrier. At 4°K, the slope of the exponential is so great that no thermal current is detectable until the forward bias is within a very few millivolts of the value of the barrier; hence at 4°K the characteristic potential is directly deducible from the measurements.

Another set which we consider to be fundamental is derived from the experiments of Cardona and Sommers,[2] who measured the reflectivity spectrum of a group of wafers of single-crystal germanium with various dopings and at a number of temperatures. These authors discuss the origin of the spectrum and the assignment of the reflectivity peak at 2.2 ev to the excitation of an electron from L_3' to L_1 (see Fig. 1). Furthermore they point out that the shift in the energy of this peak with doping in p-type germanium is the decrease in the direct gap at the [111] zone boundary, (E_c-E_v'). We see no reason to expect a difference in the sign of the change in energy of (E_v-E_v') from the sign of the change of (E_c-E_v); accordingly we regard the measured shift of the reflectivity peak as an upper limit to the shift of the energy of the thermal gap (E_c-E_v). These considerations yield a lower limit to the thermal gap. There is a small but definite decrease of the gap of p-type germanium with doping.

The fourth item comes from the transition capacitance of abrupt junction diodes, which varies with voltage as $(V_m-V)^{-\frac{1}{2}}$, where V is the forward bias. Measurement of the capacitance as a function of bias thus yields an empirical value of the characteristic potential V_m. Item 4 is based on the published values for abrupt junction diodes of degenerate germanium, which are a single diode studied by Chynoweth, Feldman, Lee, Logan, Pearson, and Aigrain[8] and a series studied by Meyerhofer *et al.*[1] All values are for 300°K.

There is one other piece of primary information on diodes of degenerate germanium, which refers to the recombination processes rather than the potential. Item 5 is the minority carrier lifetime deduced from the storage capacitance of junction diodes. In the region of thermal injection where the conductance increases as $\exp(qV/kT)$, a ratio of conductance to capacitance which is independent of forward bias determines the

storage lifetime of the current carriers. Meyerhofer *et al.*[1] list values for a number of diodes of degenerate germanium, both n and p type. All their lifetimes are around a nanosecond.

In spite of the scatter of the data and the variety of conditions of the experiments, one conclusion can be drawn from a quick inspection of the data; the usual theory of minority carrier injection which describes the forward characteristic of diodes of low doping is no longer valid. According to Shockley,[6] the potential controlling the minority carrier injection increases with the position of the Fermi level; when this side becomes degenerate, the characteristic potential should exceed the band gap by the Fermi-level penetration into the allowed band. The characteristic potential from light emission is actually slightly less than the band gap instead of greater by 30 mv as predicted. The same discrepancy exists with the data of Meyerhofer *et al.*[1] for the barrier to thermal current at 4°K.

Our discussions will frequently include measurements besides these primary data. The reader is referred to the original publications for descriptions of them.

III. ENERGY BAND DIAGRAM, CONDUCTION EQUATIONS, AND RADIATIVE TRANSITIONS

For clarity, we at once introduce our ideas of the band model and the recombination processes in an *ad hoc* fashion. Their logical necessity and internal consistency will be explored in the rest of the paper.

A. Energy Band Diagram

Figure 2 is the diagram of energy vs position for the thermal gap and forbidden region near the junction of a diode of degenerate germanium under forward bias V. It is the simplest model we have found which explains the bulk of the observations, in particular all the conductance and emission data.

The thermal gap, which has the same value E_{vc} on both sides of the junction, is slightly less than for pure germanium. The donor states n_D are broadened and extend from a position overlapping the conduction band to a position $q\phi_D$ inside the gap. The acceptor states n_A are distributed in a roughly corresponding position at the edge of the valence band, penetrating into the gap a distance $q\phi_A \cong q\phi_D$. The two Fermi levels lie inside the allowed bands by the energies ζ_n and ζ_p, respectively. All energies are positive by definition.

For generality the diode is shown as doped unsymmetrically, with $n_D \gg n_A$. Under these conditions the chemical junction is on the n side of the center of the depletion layer and the base of the diode is p type. Recombination will involve mainly the acceptor states. If donor states are concerned, parallel processes occur. No other recombination centers are postulated with the possible exception of states near the band edge introduced by particle radiation or other damage.

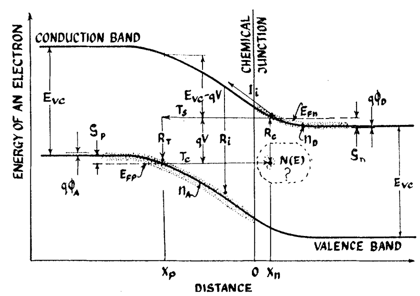

FIG. 2. Energy—position diagram of a diode of degenerate Ge.

B. Band-to-Band Tunneling

Under forward bias, current can be carried by a number of different processes, each of which occurs under appropriate conditions. At lower forward bias than shown in Fig. 2 [bias such that $V<(\zeta_n+\zeta_p)/q$, where q is the fundamental charge] the allowed regions overlap in energy, and tunneling from band to band occurs along a horizontal path. This band-to-band tunneling is approximately described by[10,11]:

$$J_0 = A_0 \exp[-\alpha E_{vc}/(n^+)^{\frac{1}{2}}], \tag{1}$$

J_0 is the current density due to band to band tunneling, A_0 is a function of the applied voltage describing the Esaki effect,[12,13] α is a constant depending on the dielectric constant and effective masses, and n^+ is the reduced doping on the two sides of the junction. The band-to-band tunneling is not the subject of this paper; it is mentioned because of its relationship to the excess current.

C. Excess Current

When the bands are uncrossed by an increased forward bias (the condition shown in Fig. 2), band to band tunneling is pinched off; now another current component due to tunneling becomes important, one which does not conserve carrier energy. It is called excess current. A carrier at the Fermi level passes through the diode by tunneling along the path T_s and making a vertical transition R_T to an empty impurity state. In a good quality diode, this state seems to be a neutral doping atom, a neutral acceptor in this case.[14] The model has the basic difference from those proposed by Chynoweth *et al.*,[9] which are illustrated for comparison by the process $[T_c-N(E)-R_c]$, that our impurity states are a terminus for the complete process while their states $N(E)$ are an intermediate between the

[10] H. S. Sommers, Jr., Proc. Inst. Radio Engrs. **47**, 1201 (1959).
[11] E. Spenke, *Electronic Semiconductors* (McGraw-Hill Book Company, Inc., New York, 1958).
[12] L. Esaki, Phys. Rev. **109**, 603 (1958).
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[14] An equivalent process which may occur simultaneously, an electron at the Fermi level on the n side dropping from a neutral donor to an empty tunneling state from which it is field-emitted to the valence band, is omitted from Fig. 2 for simplicity.

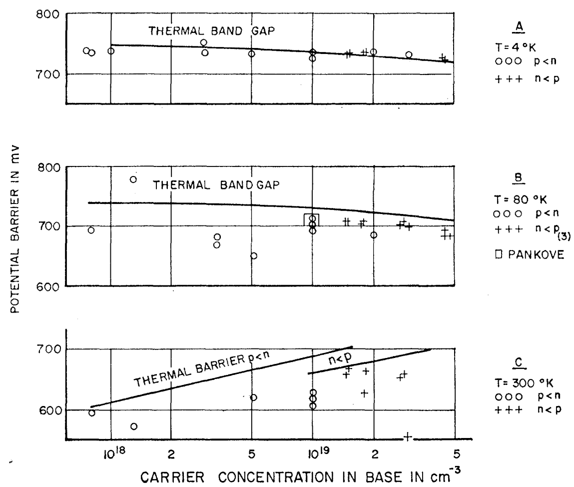

FIG. 3. Potential barrier from forward current.

tunneling and the vertical transitions. That this difference is important will be brought out in Sec. IV.

The excess density J_x follows the law[9]

$$J_x = A_x \exp[-\alpha(E_{vc} - qV)/(n^+)^{\frac{1}{2}}]. \tag{2}$$

A_x is a constant proportional to the density of impurity (acceptor) states which terminate R_T but essentially independent of applied voltage.

D. Thermal Current from Minority Carrier Injection

There are also two modes of thermal current flow which we will consider. Minority carrier injection and diffusion, which gives the total forward current in an ideal diode of nondegenerate germanium, follows the equation given by Shockley,[6]

$$J_i = A_i \exp[-(E_{vc} + \zeta_p - qV)/kT],$$
$$A_i = qN_c(L/\tau). \tag{3}$$

J_i is the current density of injected minority carriers, kT the temperature in electron volts, N_c the effective density of states in the conduction band, and L and τ the minority carrier diffusion length and lifetime in the base. For a degenerate material, ζ_p is positive. This current (not shown in the diagram) is via minority carrier injection into the conduction band of the p side of the junction, diffusion away from the junction, and recombination with the electrons via the states n_A (capture by a neutral acceptor).

E. Thermal Current from Junction Recombination

The second mode of thermal current, recombination in the junction, has been described by Sah *et al.*[15] For our diode, this follows an array of paths $(I_i - R_i)$ and involves the capture in the junction of a thermally excited electron by a recombination center n_A (usually a neutral acceptor for the path shown or a neutral donor for its inverse). As shown in the Appendix, this follows the expression

$$J_j = A_j \exp[-(E_{vc} - q\phi_A - qV)/kT],$$
$$A_j \cong qN_c(X/\tau). \tag{4}$$

J_j is the density of thermal current due to recombination in the junction and X is the length of junction in which recombination is occurring; it is the distance from the chemical junction to the appropriate Fermi level, or X_p in Fig. 2. τ is the same lifetime occurring in Eq. (3). One of the contributions of this paper is the realization of the growing importance of this process as the material becomes degenerate, even for ideal diodes.

F. Optical Emission

The recombination processes involved in Eqs. (2)–(4) may be partially or wholly radiative. Accompanying the excess current, we expect emission from the transition R_T whose upper limit will be the applied voltage. The spectrum from minority carrier injection will peak at the energy $(E_{vc} + \zeta_p)$, while radiation from junction recombination will peak at $(E_{vc} - q\phi_A)$ corresponding to the transition R_i.

IV. COMPARISON OF MODEL WITH EXPERIMENT AND EVALUATION OF PARAMETERS

In this section we study the implications and the internal consistency of our model of the band gap and recombination processes of degenerate germanium.

A. Band Gap of Degenerate Germanium, *n* and *p* Type

As already stressed in Sec. II, except for the possibility that a fortuitous cancellation of large terms has masked the shrinkage of the band gap with doping, the studies of Cardona and Sommers[2] determine an upper limit to the shrinkage with doping of the thermal gap of p-type germanium. This upper limit is 30 mv for gallium doping of up to 10^{20} holes/cm^3.

We can reach nearly as firm a conclusion about the band gap of As-doped germanium from the characteristic potential for thermal current,[1] plotted in Fig. 3(A). This is a graph of the potential against the doping of the less degenerate side of the junction, an appropriate way to portray the measurements since the minority carriers are injected into the lower-doped side of the diode. The solid line is the thermal gap deduced from the reflectivity of p-type Ge. In the region of 10^{19} carriers/cm^3 or greater, we find no evidence of a systematic difference between the p-type base (circles) and the n-type base (crosses). The same complementarity is evident in all measurements yet reported. Hence we conclude that the change with doping of the

[15] C.-T. Sah, R. N. Noyce, and W. Shockley, Proc. Inst. Radio Engrs. 45, 1228 (1957).

thermal gap of arsenic-doped germanium is little different from that of the gallium doped. In particular, the gap of n-type germanium has not shrunk appreciably more than that of the p type.

Actually, Cardona and Sommers found the shift of the reflectivity peak with doping was independent of the doping atom. Because of the uncertain role of the Burstein shift[16] in n-type germanium, they could not give a unique interpretation of this fact. The further comparison shown in Fig. 3 reduces the ambiguity; this point will be discussed at the end of Sec. IV.

B. Thermal Current under Forward Bias and the Role of Junction Recombination

Sah *et al.*[15] have shown that the forward current due to recombination in the junction will increase as $\exp(qV/kT)$ providing the recombination center is more than 10 kT from the center of the band. In the Appendix we will present an approximate phenomenological derivation of the equation governing this type of flow, Eq. (4), to permit a simple comparison with the case of minority carrier injection and diffusion, Eq. (3).

At 4°K, the thermal current in degenerate diodes is carried by recombination in the junction rather than minority carrier injection, whatever the nature of the recombination center. Because of the similarity of Eqs. (3) and (4), it is easy to see that in any short lifetime diode the current will certainly proceed via recombination centers in the junction if the penetration of the Fermi level into the allowed band is large enough, 20 kT for example. At helium temperature, this will be the case for germanium with heavier doping than $10^{17}/\text{cm}^3$.

According to Fig. 3, the barrier height at 4°K (the circles and crosses) is approximately the thermal band gap, shown as the solid line. The theory of junction recombination [Eq. (4)] interprets this barrier as the vertical distance of the recombination centers (or the edge of their impurity band) from the farther band edge (distance $E_{vc}-q\phi_A$ in Fig. 2). This position is suggestively close to the doping centers; for low-doped germanium the gallium and arsenic states lie about 10 mv from the band edge.[17] Considering the scatter of the data and the possibility that the interaction of the doping atoms may have somewhat spread their energies, this agreement seems quite satisfactory.[18,19]

In the rest of the analysis, we will assume the recombination centers are neutral donors or acceptors so that we can evaluate some of their parameters. The edge of the doping band (which must overlap the allowed band to prevent freeze-out of carriers at low temperature) lies somewhere around 10 mv from the edge of the free carrier band.

There are of course possibilities for the states which carry the recombination other than the donors and acceptors. They could be localized levels such as the interstitials or vacancies found in bombardment studies.[17] There is a stringent requirement on such levels; they must lie near enough to one band edge to maintain thermal equilibrium with the corresponding carriers.[20] Otherwise the barrier height to injection would be quite different from the band gap, and the thermal current would no longer have the voltage dependence $\exp(qV/kT)$ found experimentally.[15] The relationship between diffusion and junction recombination currents[1] indicates that the recombination states are distributed throughout the base and transition region.

We now resort to the model of recombination in the junction to analyze the conductance data of Meyerhofer *et al.*[1] at 80°K. Inserting reasonable numbers in Eqs. (3) and (4) shows that conduction via recombination in the junction should be favored for a barrier-height difference of 4 kT or even less; this requires a doping of only slightly over $10^{18}/\text{cm}^3$. So again we find the forward current at extreme bias is carried by junction recombination.

The characteristic potential for junction recombination, $(E_{vc}/q-\phi_A)$ of Eq. (4), is deduced from the data of Meyerhofer *et al.*[1] for $T=80$°K. To derive the barrier from the data we have assumed values for the material parameters. For X, which is approximately the barrier thickness under bias, we take 30 A; τ, which is the minority carrier lifetime, we take as 10^{-10} sec, ten percent of the value at room temperature.[1] An error of an order of magnitude in any of these parameters will change the barrier height by 2.3 kT, or 16 mv.

Figure 3(B) is the plot of the barrier to thermal current flow against the carrier concentration of the base for 80°K. The solid line is the band gap from the reflectivity studies. We find a result similar to that at 4°K [Fig. 3(A)]; the barrier is about the band gap, possibly lower by 10 mv. Also any difference between diodes with base p type (circles) and base n type (crosses) is masked by the scatter of the data.

At room temperature normal minority carrier injection into the base seems to be the favored process even for the most heavily doped diodes. Experimentally this is demonstrated for the lower-doped diodes by the observation of a minority carrier storage time.[1] Figure 3(C) is the barrier to minority carrier injection at room temperature, as deduced by Meyerhofer *et al.*[1] through Eq. (3). Even though there is some direct information on all the parameters, the accuracy is low because now

[16] E. Burstein, Phys. Rev. **93**, 632 (1954).

[17] *Semiconductors*, edited by N. B. Hannay (Reinhold Publishing Corporation, New York, 1959).

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

[19] L. V. Keldys, L. S. Vavilov, and K. I. Bricin, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Publishing House, Czechoslovakian Academy of Science, Prague, 1960), p. 824.

[20] A. Rose, Phys. Rev. **97**, 322 (1955).

the correction term involving A_i is half the total barrier. In particular the arbitrary extrapolation of the minority carrier lifetime over the range of carrier concentrations has introduced some systematic error not present in the preceding comparisons.

The expected value of the thermal barrier, $(E_{vc}+\zeta_p)$ of Fig. 2 for p-type base or $(E_{vc}+\zeta_n)$ for n type, is shown by the solid lines. The agreement between the ideal diode equation and the measurements is probably as good as one can expect because at these higher temperatures the details of the recombination mechanism become important.

To summarize our conclusions about the thermal current under forward bias: This current is carried via recombination through the doping states in high quality diodes. At room temperature the current consists of minority carrier injection and the recombination takes place in a diffusion length. The barrier for thermal injection of minority carriers, which exceeds the band gap by the penetration of the Fermi level into the allowed band, equals $(E_{vc}+\zeta_p)$ of Fig. 2.

At low temperature the mode is quite different, for carrier recombination in the junction carries the thermal current; the onset of degeneracy has introduced an extra height to the barrier the minority carriers must surmount which prevents injection at reduced temperature. The lower height of the effective barrier for junction recombination $(E_{vc}-q\phi_A)$ is decisive even though the same recombination process occurs in both the diffusion region and the junction. This fact explains why the barrier to current flow found at lower temperatures for degenerate diodes does not exceed the thermal gap as well as the anomalously low injection efficiencies found at reduced temperatures.[7]

C. Recombination Cross Section

Before proceeding further with the discussion, we want to verify the creditability of the suggestion that recombination proceeds via the doping centers. Specifically the question is whether the size of the cross section needed to give the minority carrier lifetime is plausible and whether it will support an appreciable rate of recombination in the junction.

TABLE I. Capture cross section per neutral atom, N_A = density of acceptor states, N_D = density of donor states.

Temp. (°K)	Doping N_A (cm^{-3})	N_D (cm^{-3})	Cross section (cm^2)
	A. From minority carrier lifetime[a] $(N_D \gg N_A)$		
300	8×10^{17}		2×10^{-15}
	10^{18}		$\frac{1}{2}\times10^{-15}$
	3×10^{18}		1×10^{-15}
	B. From thermal current density[a]		
195	5×10^{19}	4×10^{19}	6×10^{-15}
80	5×10^{19}	4×10^{19}	3×10^{-14}

[a] See reference 1.

Table I lists the values of recombination cross sections for five diodes where this can be estimated. In part A, the cross section is deduced from the room temperature minority carrier lifetimes measured by Meyerhofer *et al.*[1,21] These are all diodes with carrier concentrations in the base of around 10^{18}/cm^3. The minority carrier is an electron injected into the gallium-doped base. We can calculate the recombination cross section if we assume the electron is captured by a neutral gallium atom. The one other assumption we must make is the extent of the ionization of the acceptors; we assume 90% are ionized, leaving 10% active. This gives a room-temperature-capture cross section of around 10^{-15} cm^2 for an electron by a neutral gallium atom.[17]

The cross section may be large enough to affect the lifetime of germanium with more than 10^{16} Ga/cm^3. Alekseyeva *et al.*,[22] however, found no recombination associated with acceptor states for Ge with 10^{17} Ga/cm^3. Their measured lifetime at this doping was 20 μsec, which contrasts with the $\frac{1}{2}$ μsec estimated from the extrapolation of the data of Meyerhofer *et al.*[1] The latter authors are not certain whether or not the discrepancy is a real effect. One difference between the two experiments is that Meyerhofer *et al.* study lifetime in diodes where the p layer is saturated with Sn and Pb while Alekseyeva *et al.* study homogeneous crystals doped only with Ga.

For two other diodes of nearly symmetrical doping, we can deduce the cross section from the value of the thermal current at a given bias using Eq. (9). One diode was measured at 195°K, the other at 80°K. We must assume a value for N_A, the effective density of impurity states. At 80°K we take this as 10% of the total doping, as the broadening of the impurity band has reduced it appreciably below the doping density. It should scale with temperature roughly as does N_c, or as $(T)^{1.5}$.[17] Since the barrier for thermal injection was not measured at 195°K, we evaluated it by extrapolation of the low temperature barrier. We use 30 Å for X_p.

The data and cross sections are shown in Table I(B). The cross section at lower temperature may be somewhat higher than at room temperature. It should be emphasized these are all order-of-magnitude calculations. The significant fact is that the capture cross section per neutral atom measured by minority carrier lifetime and by junction recombination current are in approximate agreement with each other. This is not

[21] Our analysis has not included the lifetimes of Meyerhofer *et al.* for very degenerate diodes with arsenic-doped bases. They indicate the capture cross section per neutral arsenic is appreciably smaller than 10^{-15} cm^2; however because of the large errors associated with all the lifetime measurements and the difficulty of estimating the percentage of neutral centers in such degenerate materials, we do not feel certain there is a difference between arsenic and gallium. Proper analysis requires better data and a firmer understanding of the doping centers in degenerate materials.

[22] V. G. Alekseyeva, S. G. Kalashnikov, L. P. Kalnach, I. P. Karpova, and A. J. Morozov, Soviet Phys. (Tech. Phys.) 2, 1794 (1957).

complete proof that recombination is via the doping centers, but it certainly suggests the same recombination centers are involved whether recombination occurs in the transition region or in the diode base.

D. Excess Current

In forward biased diodes of degenerate material, there is a component called excess current which is carried by tunneling through the depletion layer but in which carrier energy is not conserved. This fact was reported by Yajima and Esaki,[5] who proposed the transition proceeded via impurity states in the junction.

Quantitative studies of the excess current have been made by Chynoweth *et al.*[9] and by Meyerhofer *et al.*[1] The latter gives a review of the literature.

The excess current is observed at medium forward bias, in the region between the current minimum of the Esaki effect[12] and thermal injection. A striking fact is that the current is essentially independent of temperature but follows the law $\exp(\sigma V)$ over a range of biases which may be more than half the band gap.[1] The accepted explanation is that the excess current is due to tunneling via impurity states. Not only has σ the variation with temperature and junction thickness associated with tunneling,[1,9] but the current density increases linearly with bombardment damage for diodes subjected to high energy radiation.[9,23]

Chynoweth *et al.*[9] have developed a phenomenological theory of the excess current which describes it quantitatively. Their process involves tunneling through the junction to an impurity state in thermal equilibrium with the majority carriers, along paths (T_c-R_c) in Fig. 2. The model has been criticized by Meyerhofer *et al.*[1] on the basis that it can yield an exponential increase of current with voltage over only that range of voltages for which $N(E)$ is constant or changing exponentially with depth; such an energy distribution for localized states extending over half the gap seems most improbable, and contrary in particular to the present information from bombardment damage.[17]

The model of recombination in the junction which we have discussed leads directly to an explanation of the excess current which is free from this objection. The process is tunneling through the junction along the path T_s followed by capture by an impurity center in thermal equilibrium with the other band, the vertical transition R_T.

The important difference between the two models is the location of the impurity states (see Fig. 2 and Sec. III). Each bias voltage brings into play a new impurity level for the models of Chynoweth *et al.*, while but one set of impurity centers is involved in our process, irrespective of the voltage. Our revision leads to a proportionality between current density and the product tunneling probability times *total* impurity state density; in theirs the product involves the impurity state density per unit energy at the appropriate energy level. It is their dependence on density ***per unit energy*** which has been criticized.[1]

The new model removes a second difficulty inherent in the earlier one, the requirement that the impurity states be spatially localized. If the states overlapped, they would introduce a broad allowed band in the center of the forbidden gap. Aside from questions as to what this would do to normal transport properties and the optical spectrum, the tunneling alone would be quite different from that observed; the excess current would be a form of band-to-band tunneling, which displays the Esaki effect.[12] Yet it seems improbable that the heavy impurity concentrations inferred by Chynoweth *et al.* would not form an impurity band, at least at lower temperatures. This question does not arise on our model because the impurity state is not directly involved in the tunneling.

The objection may be raised that the vertical transition from a tunneling to an impurity state is far too improbable. Franz[24] has analyzed the transition probability for a related process, the shift with applied field of the optical absorption edge of a semiconductor due to light absorption by carriers which have tunneled a short distance into the forbidden region. For insulators he finds the effect is small. We believe that our case will be considerably more probable because of the ability of the impurity center to lift the selection rules for step R_T, Fig. 2. R_T may also include a large nonradiative component which cannot contribute to the optical absorption. The importance of this point is demonstrated by the large capture cross section for free carriers.

In summary, the success of Eq. (2), which has been formally developed and discussed by Chynoweth *et al.*[9] in connection with their model of excess current, is retained by our process. Our contribution has been to put in on a firmer basis and to suggest a relationship between the excess and the thermal currents, a relationship possibly detected in the measurements of Meyerhofer *et al.*[1] The basis of the connection is that the same recombination center is involved in both processes.

E. Emission Spectrum

We are now ready to explain the emission spectrum of Pankove.[3] His measurements were one of the first strong indications of the inadequacy of the customary treatment of processes in degenerate germanium.

Pankove decomposed the emission spectrum from a forward-biased tunnel diode at 80°K into two parts. There was a continuous spectrum whose intensity increased slowly with frequency toward an emission

[23] T. A. Longo, Bull. Am. Phys. Soc. **5**, 160 (1960).

[24] W. Franz, Z., Naturforsch. **13A**, 484 (1958).

edge with energy equal to the forward bias. At higher voltages, a strong peak developed at the high frequency edge; its position became voltage-independent and its intensity a steep function of bias.

As mentioned in Sec. III, we expect optical emission from excess current, from junction recombination, and from minority carrier injection, all three processes involving vertical transitions to the same recombination center. The long wavelength tail of the emission spectrum corresponds to excess current; for low bias it will cut off at an energy equal to the applied voltage because this is effectively the energy available for the transition R_T, Fig. 2. At higher voltage, junction recombination dominates, giving a peak at the energy of R_i; its intensity will be proportional to J_j, [Eq. (4)].

The measured position of the emission peak is shown by the square in Fig. 3(B). In agreement with our expectations, it has the same energy as the barrier to thermal current, the circles and crosses. Previous speculations on the energy of the peak,[3] based on a correspondence to recombination radiation following minority carrier injection, had led to the suggestion of a drastic shrinkage or modification of the thermal gap, an idea in conflict with the behavior of III–V compounds[25,26] and with later measurements on the reflectivity spectrum of p-type germanium.[2] The explanation of why this peak is less than the thermal gap is an important achievement of our approach.

F. Reflection Spectrum and the Band Gap at the [111] Edge

Cardona and Sommers[2] discussed their reflection spectrum in terms of the energy-k vector diagram of the bands of germanium, Fig. 1. The assignment of the reflection peak at 2.2 ev to the direct transition at the [111] edge seems to be firmly established.

For p-type germanium the carriers reside at (0,0,0); hence the reflection spectrum is not modified by a Burstein shift associated with the displacement of the Fermi level.[16] For n germanium, however, the carriers fill the lower levels of the [111] minimum of the conduction band, and one expects the spectrum to be shifted to shorter wavelengths by at least the penetration of the Fermi level into the conduction band. They could offer no reason for the failure to observe this shift other than a fortuitous cancellation of several effects.

We now propose the lack of an appreciable Burstein shift is direct evidence that the valence band a L_3' is essentially parallel to the conduction band at L_1. The question of the sign of the curvature at L_3' has not yet been settled. The calculation of Herman[27] indicated the bands should have the same sign of the curvature as at [111], but this has not yet been generally accepted. Our suggestion is that the reflection measurements, with the support sited in the present work, is easily understandable if there is a parallelism of the bands at [111], or at least there is a saddle point at L_3'.

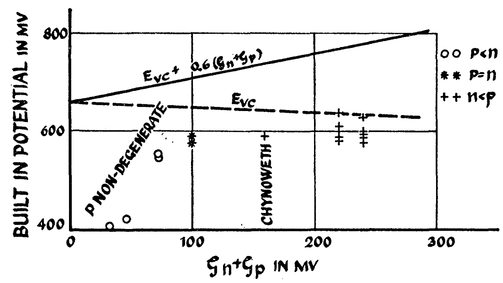

FIG. 4. Barrier from transition capacitance; built-in potential—Fermi level penetration.

V. TRANSITION CAPACITANCE

The one group of data which we cannot interpret satisfactorily is the values of the built-in potential determining the transition capacitance.[1,8] We have graphed this data in Fig. 4, which shows the built-in potential V_m against the sum of the penetrations of the Fermi levels into the allowed bands. According to the recent theory of Sah[28] for abrupt junction diodes of degenerate material at low temperature, the built-in potential should have the value

$$V_m = E_{vc}/q + 0.6(\zeta_n + \zeta_p). \tag{5}$$

This value is given by the solid line of Fig. 4; the dashed line is the band gap alone.

At all dopings, the measured values of the built-in potential are far below the predictions. This holds when only one side of the junction is degenerate as well as when both are. Chynoweth *et al.*[8] observed this difficulty, which they found at both reverse and forward bias. In fact, the data on germanium indicate the built-in potential equals the band gap at dopings where both sides are degenerate.

We expect, without formal proof, that at very heavy doping the factor of 0.6 in the expression of Sah[28] will yield to a smaller factor of the form 0.6β, where β is the ratio of free carriers in the flat band to the total impurity density. This type of correction should be important for high degeneracy. For diodes of low degeneracy we can offer no explanation of the small observed value of the built-in potential. As shown by Sah,[29] including the effects of free carriers cannot affect the result except for bias far greater than used here.

This anomalous behavior is very pronounced in

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[25] F. Stern and J. R. Dixon, J. Appl. Phys. **30**, 268 (1959).
[26] R. Talley and F. Stern, J. Electronics **1**, 186 (1955–1956).
[27] F. Herman, Proc. Inst. Radio Engrs. **43**, 1703 (1955).
[28] C.-T. Sah (private communication).
[29] C.-T. Sah, Proc. Inst. Radio Engrs. **49**, 603 (1961).

silicon diodes.[8] The question requires further study, both experimentally and theoretically.

VI. SUMMARY

From an analysis of published data which bear on the band structure of degenerate germanium, data on optical emission and reflectivity and on the forward admittance of diodes for a variety of samples and temperatures, we have shown that the effects are controlled primarily by the band gap. The positions of the Fermi levels in the allowed bands have little effect.

Analysis of the forward current indicates it will be independent of the Fermi level if recombination is through appropriate impurity states in the depletion region. Comparison of several processes shows these states are probably the same ones which determine the minority carrier lifetime, and the suggestion is made that they are the doping atoms. Extension of the analysis of recombination in the junction gives an improved understanding of the excess current in tunnel diodes.

The position of the 2.2-ev maximum in the reflectivity of p-type germanium should be independent of the position of the Fermi level, as found. For n-type germanium the similar observed independence can be understood if the bands at the [111] edge are parallel to each other.

Our best evidence of the effect of doping on the band gap is that the thermal gap has shrunk by about 0.03 ev for material doped to 4×10^{19} carriers/cm^3. We find no evidence for a difference between doping with gallium and doping with arsenic, either in connection with the bands or recombination processes.

The anomolously small value of the built-in potential deduced from the transition capacitance is not understood.

ACKNOWLEDGMENTS

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APPENDIX

Comparison of Diffusion and Junction Recombination Currents

Shockley[6] has shown that the forward current of electrons injected into the base of a diode in which no recombination occurs in the junction is

$$J_i=A_i\exp[-(E_{vc}+\zeta_p-qV)/kT],\quad A_i=qN_c(L/\tau). \tag{3}$$

J_i is the diffusion current from minority carrier injection into the base, q is the fundamental charge, and N_c the effective density of states in the conduction band. L and τ are the minority carrier diffusion length and lifetime in the base, E_{vc} the band gap, and ζ_p the distance of the Fermi level of the base from the band edge. It is taken as positive for degenerate material. V is the forward bias.

We present a simple phenomenological derivation of the current flow via recombination in the junction,[15] based on the specific model proposed in Fig. 2, to permit ready comparison with the diffusion current.

Recombination in the junction consists of holes recombining with neutral donors on the right of the chemical junction, which lies at $x=0$, and electrons with neutral acceptors on the left. Let J_e equal the electron recombination current density. Formally

$$J_e=-\int_{-\infty}^{0} qn(x)n_A{}^0(x)S_n\sigma_A dx, \tag{6}$$

$n(x)$ and $n_A{}^0(x)$ are the densities of free electrons and of neutral acceptors, S_n is the thermal velocity of electrons, and σ_A the capture cross section of a neutral acceptor for an electron.

Since electrons in the conduction band to the left of the chemical junction are nondegenerate, we have

$$n=N_c\exp[-(E_c-E_{Fn})/kT],$$

where N_c is the effective density of states in the conduction band and E_{Fn} the quasi-Fermi level for electrons. Holes in the valence band may be degenerate, so in general

$$\begin{aligned} n_A{}^0&=N_A/\{1+\exp[(E_{Fp}-(E_v+q\phi_A))/kT]\}\\ &=N_A/\{1+\exp[(E_{Fn}-qV-E_v-q\phi_A)/kT]\}.\end{aligned}$$

This follows because the quasi-Fermi levels are displaced by qV. N_A is the effective density of states of acceptor atoms, and $(E_v+q\phi_A)\geqslant E_v$ is their band edge.

Examine the variation with position of the product

$$n(x)n_A{}^0(x)=\frac{N_cN_A\exp\{-[E_c(x)-E_{Fn}]/kT\}}{1+\exp\{[E_{Fn}-(qV+q\phi_A+E_v(x))]/kT\}}. \tag{7}$$

In the region where all the acceptors lie below the hole Fermi level, this product becomes

$$n(x)n_A{}^0(x)=N_cN_A\exp[-(E_{vc}-q\phi_A)/kT]\times\exp(qV/kT), \tag{8}$$

which is independent of position. Moreover, as we pass farther to the left where the top of the acceptor states lies above E_{Fp}, the product $n(x)n_A{}^0(x)$ decreases from Eq. (8) because now the denominator of Eq. (7) is essentially constant while the numerator still drops exponentially with distance. Since the point at which $n(x)n_A{}^0(x)$ begins to decrease is very close to X_p, the position where the hole Fermi level cuts the edge of the valence band, we need only integrate Eq. (6) from X_p

to 0. This gives the result

$$J_e = X_p q N_c N_A S_n \sigma_A \exp[-(E_{vc} - q\phi_A)/kT] \times [\exp(qV/kT)],$$
$$J_p = X_n q N_v N_D S_p \sigma_D \exp[-(E_{vc} - q\phi_D)/kT] \times [\exp(qV/kT)]. \quad (9)$$

In the last equation the roles of electrons and holes and of acceptors and donors have been permuted.

The similarity between Eq. (9) and Eq. (3) is apparent. The drift length has been replaced by the portion of the transition region where recombination occurs, and the minority carrier lifetime by a formally identical term in which the density of active recombination centers in the bulk has been replaced by their effective density in the transition region. Without a more rigorous analysis of the quantity N_D, we replace Eq. (9) by the approximate expression for electron flow into a p-type base.

$$J_j = A_j \exp[-(E_{vc} - q\phi_A - qV)/kT], \quad (4)$$
$$A_j \doteq qN_c(X/\tau),$$

with the identification that J_j is the thermal current recombining in the junction, X the distance in the junction (from the chemical junction to the Fermi level) in which recombination is occurring, and τ is the ordinary minority carrier lifetime, which determines the drift length in the field-free region. This form permits comparison of the relative importance of minority carrier injection and junction recombination, under the condition that the recombination centers lie close to the band edge. We see that for degenerate materials, junction recombination is always favored at sufficiently low temperature.

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Relaxation Equations for Two-Magnon and Magnon-Phonon Processes in Ferrimagnetic Resonance

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Equations which give the relaxation behavior of the magnetization in the case of ferrimagnetic resonance are derived from quantum mechanical rate equations for spin-wave magnons. It is shown that the concept of a unique relaxation time for a particular component of magnetization is not in general valid.

INTRODUCTION

In a previous paper[1] the relationship of linewidths to fundamental transition parameters for two-magnon and magnon-phonon processes in ferrimagnetic resonance was calculated by a method using quantum mechanical rate equations for spin-wave magnons, without recourse to a phenomenological equation of motion. This method allows one to take the fundamental two-quantum transitions into account directly instead of lumping all loss processes into an extra term in the equation of motion without regard to the processes involved. In addition, the validity of deriving relaxation times in analogy with paramagnetic resonance was discussed and it was pointed out that the paramagnetic resonance analogy is not good and care must be exercised in its use. The advent of experimental apparatus allowing the measurement of times in the mμsec range makes it feasible to do direct relaxation experiments on ferrites. It is therefore desirable to investigate more fully the relaxation behavior of the magnetization for the ferrimagnetic resonance case in order to learn what additional information may be obtained from relaxation experiments.

In a typical experiment designed to directly measure relaxation times, one may conveniently measure the behavior of the component of magnetization parallel to the dc magnetic field and the component of magnetization perpendicular to the field. We will calculate expressions for these components of the magnetization from the quantum mechanical rate equations previously derived.[1,2]

GENERAL RELAXATION EQUATIONS

The number of spin-waves present in an ellipsoid of revolution about the dc magnetic field is given by

$$M = M_0 - \sum_k \gamma\hbar n_k, \quad (1)$$

$$M_z = M - \gamma\hbar n_0, \quad (2)$$

where M_0 is the saturation magnetization, n_0 is the number of uniform precession magnons ($k=0$), and n_k is the number of spin-waves of wave number k where $k \neq 0$. From these two equations we may write

$$M_z - M_0 = -\gamma\hbar[n_0 + \sum_k n_k], \quad (3)$$

which gives the behavior of the longitudinal component

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[2] H. B. Callen, J. Phys. Chem. Solids **4**, 256 (1958).