THE ELECTRICAL CONDUCTIVITY OF GERMANIUM IN HIGH ELECTRIC FIELDS AT LOW TEMPERATURES

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The electrical properties of single-crystal germanium doped with Sb, Bi, and Zn were studied in the temperature range 2 — 10° K. In high electric fields the electrical conductivity of germanium displays three regions, in the last of which (the so-called "breakdown" region) a sharp conductivity increase is observed. The phenomenon of breakdown is associated with the development of an avalanche in the conduction band, independent of the conduction mechanism in the germanium at low temperatures. The product of E_b and the mobility μ is a function of I/kT, where I is the ionization energy of the impurity in the germanium. The effect of various factors (temperature, magnetic field) on E_b is mainly due to their influence on the carrier mobility. The dependences of E_b and resistance on magnetic field are found to be similar in character.

THE aim of the present work was to study the phenomenon of the sharp conductivity increase in germanium at low temperatures in fields of the order of several volts per centimeter.

Originally this phenomenon was discovered at hydrogen temperatures,[1] but it was interpreted incorrectly. In 1953, Sclar, Burstein et al.[2] discovered the phenomenon at helium temperatures, so sharply displayed that they defined it as "breakdown" and attributed it to the effect of the impact ionization of neutral impurity atoms by electrons. In 1955 Darnell and Friedberg established the dependence of E_b on magnetic field.[3]

It was of interest to study more carefully the mechanism of this phenomenon, which is analogous to breakdown in dielectrics, but which differs in that it takes place reversibly. This interest is strengthened by the fact that the conductivity behavior in high electric fields can apparently throw light on the conduction mechanism in germanium at low temperatures in a region where an anomaly exists in the dependence on the resistance on temperature.[4]

After the present work had begun, the work of Sclar and Burstein[5] and Koenig and Gunther-Mohr[6] became known to us; the problems posed and their method of solution closely resembled those of our investigations.

EXPERIMENTAL PART

Several series of germanium specimens (of different origin) doped with antimony and bismuth were studied, as well as two specimens cut from one section of a bar doped with zinc (for details of the specimens, see Tables I and II).

A series consisted of crystals cut from one bar in a plane perpendicular to the direction of crystal growth [111]. The specimens were ground, etched in boiling hydrogen peroxide and repeatedly washed in triply-distilled boiling water. The specimen length usually exceeded the width by a factor of not less than four. Contacts were made using spectrographic-purity gold and were soldered to the faces of the specimen by a technique of prolonged heating (an hour at 300° C) in a high vacuum. The massive current contacts completely covered the ends of the specimen, but the potential contacts for Hall effect measurements consisted of gold beads with areas of contact 0.2 — 0.05 mm^2 at a distance of 2 — 3 mm. from one another. After soldering the contacts to the specimen, it was etched and washed again.

The specimen prepared for the experiment was mounted in an apparatus in which it was possible to make prolonged measurements at constant temperatures in the range 1.5 — 77° K. The glass bulb 1 (Fig. 1) was immersed in liquid helium or hydrogen and was evacuated before the experiment to a pressure of ~ 0.01 mm. Hg. Thermal contact between the specimen and the helium bath was made with the help of the copper "cold" conductor 2. To increase the specimen temperature relative to the external bath, a wire heater 3 was used, wound on the small cylinder of fused quartz 4 which served

TABLE I. Details of specimens

Series	Specimen	Doping impurity	Impurity concentration	ρ^*, ohm/cm	E_b^*, v/cm
Bi-I	Bi-1	Bi	$7.6 \cdot 10^{14}$	$\sim 10^8$	5
	Bi-2	Bi	$1 \cdot 10^{15}$	10^8	5
	Bi-3	Bi	$2.0 \cdot 10^{15}$	$1.1 \cdot 10^9$	10.2
	Bi-4	Bi	$5.0 \cdot 10^{15}$	$1 \cdot 10^7$	20
Sb-I	Sb-1	Sb	$7.6 \cdot 10^{14}$	$1.2 \cdot 10^8$	6.4
	Sb-2	Sb	$1 \cdot 10^{15}$	$1.3 \cdot 10^8$	7.5
Sb-II	Sb-B	Sb	$7.5 \cdot 10^{13}$	$5 \cdot 10^9$	14—16
	Sb-C	Sb	$1.6 \cdot 10^{15}$	$1 \cdot 10^{11}$	38—41
	Sb-H	Sb	$2.75 \cdot 10^{15}$	$9 \cdot 10^8$	56—70
	Ge-B	Not doped	$\sim 10^{13}$	$1.2 \cdot 10^9$	13
	U-20	" "	$\sim 10^{15}$	$8 \cdot 10^8$	9

*At 4.2°K.

TABLE II

Specimen	T° K	ρ ohm/cm	R, coulomb/cm³	$R/\rho \sim A\mu$	E_p, v/cm	μ (theoretical)
Bi-1	4.8	$1.6 \cdot 10^7$	$8 \cdot 10^{12}$	$5 \cdot 10^5$	5	$2 \cdot 10^5$
	5.25	$3.2 \cdot 10^6$	$1.6 \cdot 10^{12}$	$5 \cdot 10^5$	5	$2 \cdot 10^5$
Sb-B	4.2	$5 \cdot 10^9$	$1 \cdot 10^{15}$	$2 \cdot 10^5$	14—16	$2 \cdot 10^5$
	5.75	$1.67 \cdot 10^6$	$2.7 \cdot 10^{11}$	$1.6 \cdot 10^5$	14.5	$2 \cdot 10^5$
Sb-H	6.5	$5.1 \cdot 10^6$	$9 \cdot 10^{10}$	$1.76 \cdot 10^4$	35.5	$5 \cdot 10^4$
	7	$1.38 \cdot 10^6$	$3 \cdot 10^{10}$	$2.17 \cdot 10^4$	34	$5 \cdot 10^4$
	7.7	$3.66 \cdot 10^5$	$1 \cdot 10^{10}$	$2.73 \cdot 10^4$	—	$5 \cdot 10^4$
	8.7	$1.14 \cdot 10^5$	$2.4 \cdot 10^{10}$	$2.1 \cdot 10^4$	—	$5 \cdot 10^4$
Zn-1*	11.6	$8.3 \cdot 10^8$	$4.5 \cdot 10^{12}$	$5.5 \cdot 10^4$	31.5	$5 \cdot 10^4$
Zn-2*	13.96	$1.6 \cdot 10^6$	$1.35 \cdot 10^{11}$	$8.5 \cdot 10^4$	22.5	$5 \cdot 10^4$

*The impurity concentration in the zinc-doped specimens was $\sim 3 \cdot 10^{15}$.

as a thermal resistance (equilibrium between the specimen and the heater was established in a fraction of a second).

The specimen was soldered at one end to the cylinder 4 and at the other end through a plate of single-crystal quartz 5 to the calibrated carbon thermomenter 6. The soldered joints to the quartz were made using a silver paste which was deposited on the quartz and baked at a temperature of 500 — 700° K. The use of crystalline quartz ensured good electrical insulation of the specimen from the body of the apparatus, and, simultaneously, good thermal contact at helium temperatures with the thermometer.

Manganin wires (suspended in the vacuum "Staybrite" tube 12 through the polystyrene washers 10) were used for the electrical leads (potential and current) to the specimen.* To reduce thermal conduction along the leads, the lowest insulating washer, consisting of a quartz plate with tungsten seal-ins, was in thermal contact with the external bath. The leads to the heater and thermometer consisted of insulated copper wires immersed in the external bath 13.

For work in the temperature range obtained by pumping the vapors of liquid helium or hydrogen, the apparatus was not sealed off and the specimen was directly in contact with the bath.

Because germanium is very sensitive at low temperatures to infra-red radiation even of long wavelength, the entire apparatus was shielded by a metallic screen 14 maintained at the temperature of the external bath.

The circuit for measuring electrical resistance is shown in Fig. 2. From the potentiometers P_1 and P_2 for coarse and fine adjustment, the voltage from the battery B is applied to the germanium specimen and the calibrated resistance R_N, the value of which could be changed from 10^{11} to 10^2 ohm. The potential drops across R_N and the potential contacts of the specimen were measured using an SG-1M electrometer with sensitivity 2×10^{-2} v. The entire electrometer circuit was mounted on amber and polystyrene insulators and was carefully screened electrostatically.

To measure the Hall voltages and the resistances in a transverse magnetic field, the apparatus

*A similar method of soldering contacts and assembling the apparatus has been used simultaneously in this laboratory by I. A. Kurovaya.

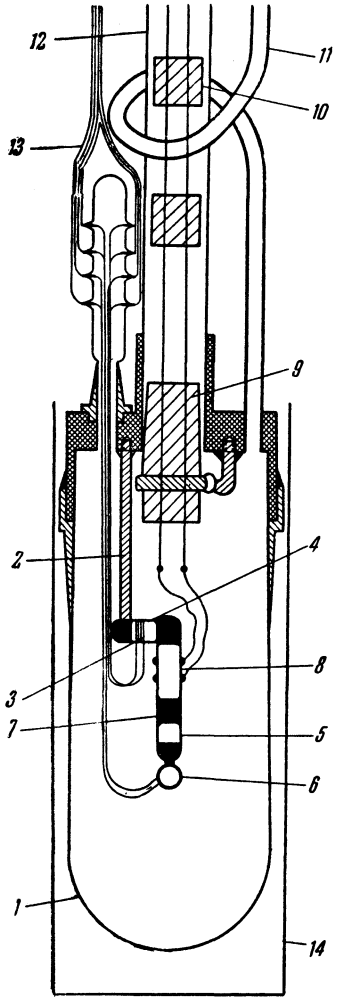

FIG. 1. General view of the apparatus: 1 – glass bulb, 2 – heat conductor, 3 – heater, 4 – fused quartz, 5 – single-crystal quartz, 6 – thermometer, 7 – contacts, 8 – specimen, 9 – quartz washer, 10 – polystyrene washer, 11 – pumping tube, 12 – tube, 13 – leads for thermometer and heater, 14 – metallic screen.

was placed between the poles of an electromagnet which allowed fields up to 10,000 oe to be obtained. The measurements were made using the circuit shown in Fig. 2, the electrometer being usually fed with the voltage from the contacts 1 and 3 (Fig. 2).

To study the dependence of the electrical conductivity on illumination, a miniature incandescent lamp was placed inside the apparatus, the light from which passed through Schott filters (Nos. 2, 4, 6, 7) and illuminated the central portion of the specimen with a sharp beam.

RESULTS

At low temperatures the electrical conductivity of germanium in strong electric fields is characterized by three regions:

A) A region in which Ohm's Law is obeyed;

B) A region of monotonic conductivity increase;

C) A region of sharp conductivity increase or "breakdown."

We took as the "breakdown" field (E_b) the value corresponding to the boundary between

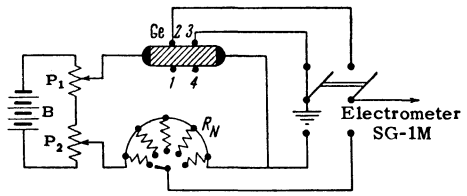

FIG. 2. Electrical measuring circuit: B – battery, P_1, P_2 – potentiometers, R_N – calibrated resistance.

regions B and C (see below, Figs. 3 and 5).

The extent of region A (σ = const.) depends on the specimen purity. For high-resistivity specimens it is significantly smaller than for low-resistivity specimens. Thus, for example, for specimen Sb-B (see Table I) the region A extends to 10% of the breakdown field, for Sb-C to 25% and for Sb-H to 80%.

In region B the field dependence of conductivity is well described for most specimens by the exponential relationship $\sigma \approx \sigma_0 e^{\alpha E}$, where α = 0.1 – 0.3, α being larger in high-resistivity than in low-resistivity specimens.* In region C also, the field dependence of electrical conductivity can be represented by an exponential, the slope of which (at low temperatures) is tens of times greater than the slope in region B. On increasing the temperature (Fig. 3) this slope diminishes

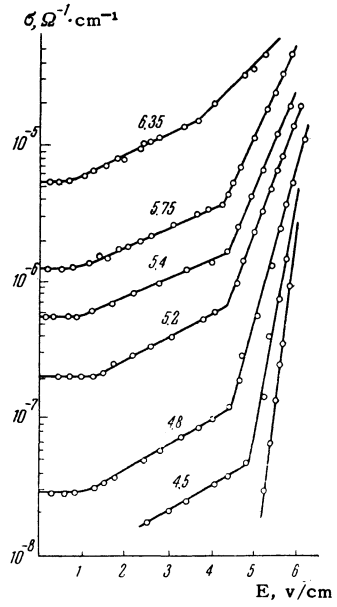

FIG. 3. The electrical conductivity of specimen Bi-1 in high electric fields at various temperatures (°K).

and the change-over between regions B and C is found to become less sharp. (For germanium doped with antimony and bismuth, the breakdown fields E_b already became difficult to determine at temperatures near 7°K). On increasing the

*Departures from the relationship $\sigma \approx e^{\alpha E}$, were found only in the zinc-doped specimens, the conductivity of which was approximately proportional to E^2 in region B.

temperature, whilst the transitions between regions A and B remain almost unchanged, the breakdown fields decrease very slightly. On further increasing the field, the specimen resistance falls so rapidly that the power dissipated causes significant self-heating — the start of "thermal" breakdown.

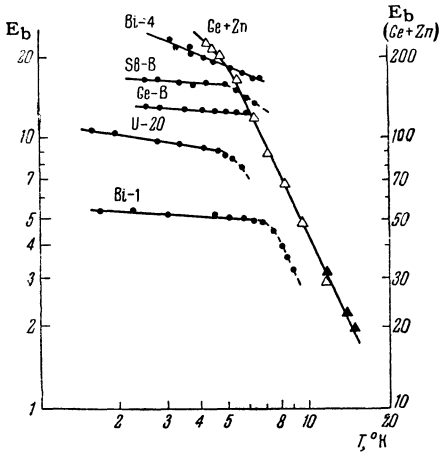

FIG. 4. Dependence of E_b on temperature. The left-hand ordinate scale refers to Sb- and Bi-doped specimens, and the right-hand scale to Zn-doped specimens. ▲ – Results for Zn-1, Zn-2 obtained using circuit in Fig. 2. Δ – Results for Zn-1, Zn-2 obtained not using the potentiometric method of measurement; the broken lines show regions where the specimens might possibly be overheated.

A different type of dependence of E_b on temperature was found for zinc-doped specimens (Fig. 4 — right-hand ordinate axis). The critical fields (E_b) get smaller with increase of temperature and are approximately inversely proportional to the square of the temperature; at hydrogen temperatures they become as small as those found at helium temperatures in specimens doped with Group III and Group V elements. The rapidity of the temperature dependence $E_b(T)$ for zinc-doped specimens is impossible to attribute to a thermal breakdown phenomenon, because the specimens retained a high resistance in the whole temperature range studied.

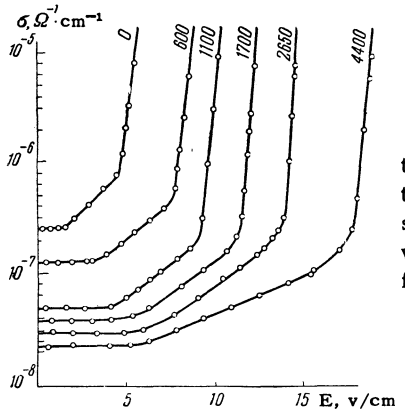

FIG. 5. The electrical conductivity of the high-resistivity specimen Bi-1 in various magnetic fields (Oe); T = 5.25°K.

The application of a magnetic field, whilst preserving the general character of the curves, increases the breakdown fields, extends the regions A and B, and in the majority of cases continuously diminishes the conductivity in these regions (Fig. 5). A different behavior is only found in highly doped specimens (with impurity concentrations of about 5×10^{15}) at temperatures below 4°K; for these specimens the conductivity in region A is independent of the magnetic field (Fig. 6). However, in this case also, a conductivity decrease is observed in region B, comparable with the decrease in region A at higher temperatures.

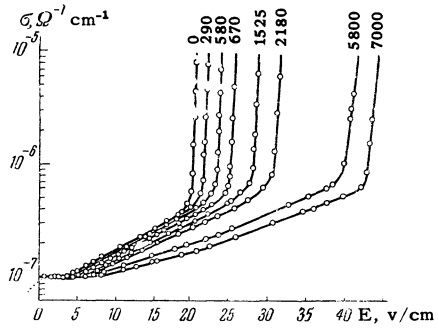

FIG. 6. The electrical conductivity of the low-resistivity specimen Bi-4 in various magnetic fields (Oe); T = 4.2°K.

The changes of resistance $[\rho(H)/\rho(0)]$ and of breakdown field $[E_b(H)/E_b(0)]$ are found to be similar in the manner of their dependence on magnetic field (Fig. 7), although in absolute measure the increase of $\rho(H)/\rho(0)$ can exceed the increase of $E_b(H)/E_b(0)$* by a large factor (especially in high-resistivity specimens).

The Hall voltage measurements in high electric fields (Fig. 8) show that the Hall constant R barely changes during the transition into region B. Change of Hall angle within the accuracy of the experiment only takes place in the immediate vicinity of E_b.

On illuminating the specimen, the j-E characteristics are displaced upwards along the ordinate axis and are distinct from the curves obtained without illumination. E_b remains approximately unchanged.

The curves described were reversible and reproducible in a series of experiments under identical conditions. Resoldering the contacts, re-etching the surface and re-assembling the apparatus produced discrepancies smaller than 10% (in absolute terms); these were apparently

*It should be noted that the dependence of $E_b(H)/E_b(0)$ on magnetic field H shown in Fig. 7 by circles is observed only using the four-electrode circuit. The use of the two-electrode method gives the dependence shown in Fig. 7 by crosses.

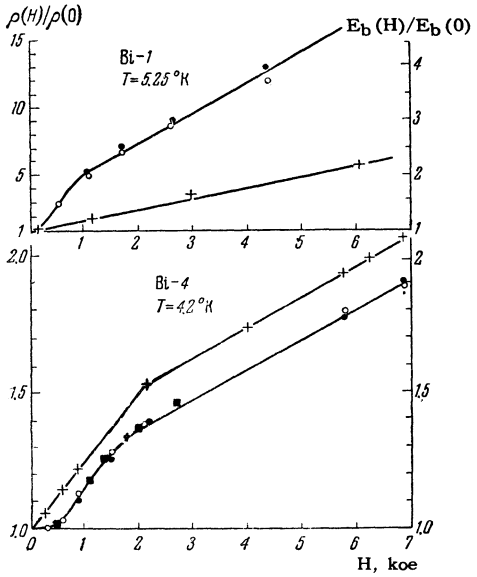

FIG. 7. The dependence of breakdown field and resistance on magnetic field H for specimens Bi-1 and Bi-4. ● – $E_b(H)/E_b(0)$ from measurements obtained using the circuit shown in Fig. 2; + – $E_b(H)/E_b(0)$ from measurements made when not using the potentiometric method; o – $\rho(H)/\rho(0)$ in region A for specimen Bi-1, in region B for specimen Bi-4; ■ – increase of resistance in magnetic field for specimen Bi-4 in region A at T = 7°K.

caused by errors in determining the dimensions.*

The bulk nature of breakdown was confirmed by studies on specimens of complex shapes with various ratios of surface to volume along their lengths.

DISCUSSION OF RESULTS

The impact ionization[2,5] of neutral impurity atoms by electrons which have acquired the necessary energy in fields of the order of several volts per centimeter is, apparently, the only possible mechanism of breakdown, because for germanium doped with Group III and Group V elements the Zener mechanism,[7] involving the extraction of electrons into the conduction bands (the tunnel effect), ought only to appear in fields greater than 500 v/cm.

There being no quantitative theory of avalanche development, the results are compared with conclusions obtained from a qualitative consideration of the equilibrium between the rate of energy accumulation by electrons in the field and the rate of

*It should be remarked that in specimens of series SbII a phenomenon of "delayed breakdown" was observed; this meant that for breakdown it was necessary to apply to the specimen a somewhat higher voltage than that for which "breakdown" started to develop. These phenomena could not be attributed to the effect of the contacts.

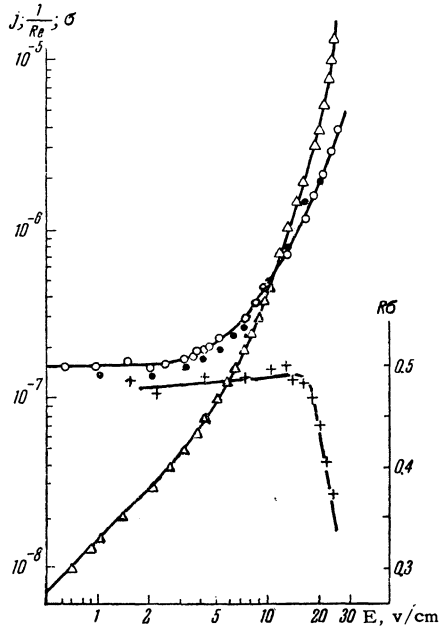

FIG. 8. The behavior of specimen Sb-B in high electric fields (T = 5.75°K). Δ – current density j(E), ● – electrical conductivity σ(E) (in reduced units, o – 1/RE, + – Rσ in relative units.

energy dissipation into thermal oscillations of the lattice;[5,8] this leads to the formula

$$E_b \approx \frac{u}{\mu}\sqrt{\frac{2I}{kT}} \qquad (1)$$

or

$$E_b\mu \approx \text{const}, \qquad (1a)$$

where u is the speed of sound, I the ionization energy of the impurity and μ the mobility. The relationship between E_b and μ obtained experimentally (Fig. 9) does not contradict Eq. (1a).

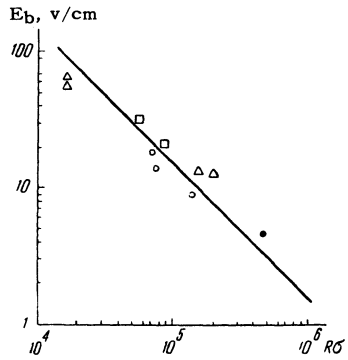

FIG. 9. Dependence of E_b on the mobility Rσ for Δ – the series Sb-II, ● – the specimen Bi-1, □ – the specimens doped with zinc, o – results of reference 6; the continuous line is the theoretical curve (from reference 5).

From Fig. 9 it is clear that the E_b values for specimens of germanium doped with antimony, bismuth and zinc — the ionization energies of which

differ by a factor of approximately three — lie satisfactorily on the single straight line given by Eq. (1) if the ratio $I/kT \approx$ const.*

It should be noted that the scatter of the points in Fig. 9, apart from errors in determining the geometrical dimensions of the specimens, is perhaps also due to the fact that E_b is compared not with the mobility μ, but with a quantity $R\sigma$, proportional to μ; depending upon the mechanism of scattering, $R\sigma$ can change from μ to 1.93μ. Also we have used mobilities obtained from measurements in region A, which refer to the specimens' behavior in low electric fields. According to (1), the mobility entering into it should be taken as that for $E \to E_b$. Such considerations, by diminishing the mobility in the pre-breakdown fields, should lead to better agreement of our results with the theoretical curve.

The similar dependences on magnetic field of resistance and critical field (Fig. 7)

$$\rho(H)/\rho(0) \approx kE_b(H)/E_b(0), \qquad k = 1 \div 4, \qquad (2)$$

can also be explained qualitatively by the dependence of E_b on μ, if one takes into account that in region A the resistance increase in a magnetic field is caused only by a fall of mobility:

$$\rho(H)/\rho(0) \approx \mu(0)/\mu(H).$$

That the coefficient k differs from unity is due, it would appear, to the different carrier concentration increases in strong electric fields (in region B) with and without magnetic field. In so far as the carrier concentration increase depends on the energy gathered by the electron in the field E, then the concentration increase in a magnetic field can be slower and can cause $\rho(H)/\rho(0)$ to increase more rapidly than $E_b(H)/E_b(0)$ (Fig. 7, upper graphs).

The temperature dependence $E_b(T)$ is determined, it seems, by the temperature dependence of μ. The existing theory[9] can explain both a weak and a strong temperature dependence of $\mu(T)$ ($\mu \sim T^{1/2}$ and $\mu \sim T^{3/2}$). Comparison with the theory is made difficult by the absence for our specimens of accurate data on the concentration of donors N_D and acceptors N_A separately.

The dependence of E_b on $N_D - N_A$ (Fig. 10) is not a universal function, and is described by a series of curves similar to the curve obtained by Burstein and Sclar.[5] Their character cannot be ascribed to the dependence of the mobility on $N_D - N_A$ and is probably determined by the raw materials and the growth conditions of the germanium crystals, or, in other words, the different degree of compensation in the specimens. The possibility exists of using the dependence of E_b on $N_D - N_A$ for monitoring the properties of specimens during manufacture.

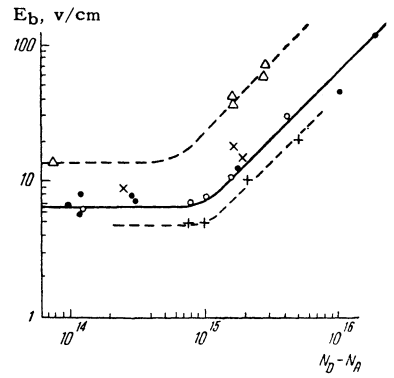

FIG. 10. The dependence of E_b on the concentration $N_D - N_A$ for various specimens: specimen series, o – Sb-1, Δ – Sb-II, + – Bi-1; continuous curve – according to Burstein and Sclar.[5] × – according to reference 6.

The exponential growth of the number of carriers with increase of field in region B, $\sigma \sim \sigma_0 e^{\alpha E}$, where $\alpha = 0.1 - 0.3$, is not explicable in terms of the specimen warming up, because its temperature is maintained constant with an accuracy of 0.01° K, even for the very large current densities. Possibly this increase in the number of carriers is due to their decreased recombination[6,10] in high electric fields.

Apart from breakdown phenomena, the study of high-field conductivity has an interest of its own. At very low temperatures (below 4° K) the conductivity of germanium is determined, as is known, not only by the straightforward effect of the conduction band, but also by certain other processes, in particular those connected in a complicated fashion with the impurity concentration.

The conductivity of specimens with large impurity concentrations (greater than 5×10^{15}) is due to conduction in the sharp impurity zone formed by the crossing of the impurity center wave functions.

The fact that the resistance is observed experimentally to be independent of magnetic field (in region A) for highly-doped specimens (Fig. 6), supports the idea of a sharp impurity zone with small carrier mobility. The resistance increase found in a magnetic field (in region B) (Fig. 6) can be attributed to the increased role of the conduction band in high electric fields shunting the impurity conduction mechanism. The latter circumstance enables one to deduce that, whatever the conduction mechanism of germanium in low electric fields, the phenomenon of breakdown is connected with avalanche development in the conduction band.

*The ionization energies of the impurities used were calculated from the temperature dependence of specimen resistance.

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