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EXPERIMENTAL INVESTIGATIONS OF SUPERCONDUCTIVITY IN DEGENERATE SEMICONDUCTORS

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I. INTRODUCTION

INTEREST has recently increased in the experimental and theoretical investigations of superconductivity in nonmetallic substances, particularly in degenerate semiconductors. Although the superconductivity of metals was discovered 50 years ago, the possibility of a transition of a semiconductor to the superconducting state has, for a long time, remained experimentally unconfirmed. The reports from various investigators published in the thirties and forties were contradictory:[1-3] usually, the reported superconductivity was found to be due to microscopic inclusions of a metal phase in a semiconductor.[1]

Only very recently some reliable results have been reported on the superconductivity of some semiconducting compounds.

It seemed useful to review briefly the results of such experiments and of investigations of the special features of the potential applications of superconducting semiconductors which are due to the combination of semiconducting and superconducting properties.

Investigations of the phenomenon of the superconductivity of semiconductors are interesting for several reasons.

First, it is desirable to know whether superconductivity is a property of metallic systems only or whether it can be observed also in heavily doped semiconductors in which an impurity band merges with the conduction or valence band (depending on the type of conduction).

Moreover, much is known now about the properties of semiconductors and the mechanisms of the various physical phenomena exhibited by these materials. In particular, in some cases the constants of interaction between various elementary excitations are known. It is obvious that this should give a better qualitative and quantitative understanding of the phenomenon of superconductivity in these materials.

In contrast to metals, the electrical properties (the energy band structure, the local level positions, the carrier density, etc.) of semiconductors can be varied relatively easily and within fairly wide limits by means of external agents (deformation, doping, irradiation, illumination, etc.). This makes it possible to determine the dependence of the superconducting properties on the parameters of a semiconductor.

From the practical point of view, it is an attractive prospect to be able to use the combination of semiconducting and superconducting properties in the same material to produce a new class of devices.

In view of the national policy of a planned search for semiconducting materials which can go over to the superconducting state, theoretical investigations have been carried out in which the Bardeen–Cooper–Schrieffer theory has been used to determine the conditions which such semiconductors must satisfy.[4-7]

The results of these investigations have established the following requirements:

1) a large electron–phonon interaction constant;
2) a high electron (hole) density in the conduction (valence) band;
3) many-valley band structure;
4) high permittivity;
5) large effective carrier mass.

On the basis of these requirements, it has been concluded[5,6] that sufficiently promising materials are semiconductors of the $SrTiO_3$ type, $KTaO_3$, GaAs–GaP, Bi_2Te_3, SiC.

II. EXPERIMENTAL INVESTIGATIONS OF THE PROPERTIES OF SUPERCONDUCTING SEMICONDUCTORS

So far, the transition to the superconducting state has been observed experimentally in the following semiconductors: GeTe, SnTe, $SrTiO_3$, $(Ba_xSr_{1-x})TiO_3$, $(Ca_ySr_{1-y})TiO_3$. The existence of superconductivity in PbS, PbSe, and PbTe, reported in [8,9], cannot yet be regarded as finally established.

1. GeTe

The compound GeTe is a semiconductor with a many-valley structure of the energy bands, which has a cubic lattice at temperatures above 400°C but at low temperatures its lattice is rhombohedral;[10] investigations of this compound have been reported in [11-17]. The room-temperature hole mobility in p-type GeTe samples, investigated in [11-14], is $\mu_p = 100\ cm^2 \cdot V^{-1} \cdot sec^{-1}$ and the effective mass is $m^* = m_0$. Measurements of the resistivity near 50°C have given an approximate value of the forbidden band width: $E_g = 0.5$–1 eV.

The critical temperature T_c of four samples ranging in composition from $Ge_{0.937}Te$ to $Ge_{0.976}Te$[11] has been found to vary from 0.31 to 0.06°K, respectively (Fig. 1). Figure 2 shows the dependence of T_c on the hole density (p) for samples with values of p ranging from 8.5×10^{20} to $15.5 \times 10^{20}\ cm^{-3}$; the superconductivity has not been observed at hole densities $p \leq 7.5 \times 10^{20}\ cm^{-3}$. To eliminate the influence of foreign superconducting impurities, samples of Ge and Te have been cooled, together with GeTe, to temperatures below 0.04°K. The superconductivity has been observed only in the compound.

The superconducting transition has been found also in powdered samples of GeTe.

Out of 19 samples of germanium telluride of various

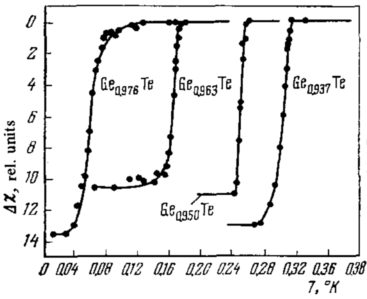

FIG. 1. Temperature dependence of the differential magnetic susceptibility of GeTe samples.

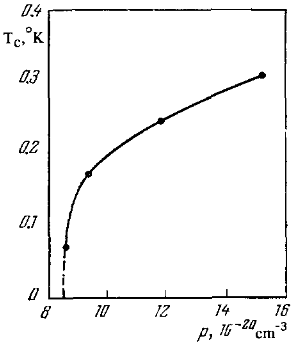

FIG. 2. Dependence of the critical temperature of GeTe on the hole density.

compositions, prepared by the powder metallurgy method (some of which have been compacted and then fired), 17 samples have exhibited a transition to the superconducting state.[12] The superconductivity has been deduced from the dependence of the magnetic susceptibility of these samples on the temperature and magnetic field. In the absence of a magnetic field, the critical temperatures of the samples have been found to lie in the temperature range 0.08–0.420°K. The behavior of the differential magnetic susceptibility as a function of the magnetic field at an approximately constant temperature has revealed the following two features:

a) The magnetic field begins to penetrate the sample at relatively low values of its intensity (1.5 Oe) but complete destruction of the superconducting state requires a field of ~115 Oe.

b) The lack of constancy of the dependence of the differential magnetic susceptibility on the field suggests sudden changes in the flux.

Measurements of the dependence of the magnetic moment on the applied field have confirmed this suggestion and this has made it possible to classify GeTe as a type II superconductor.

A calculation of the Ginzburg–Landau parameter κ, carried out on the basis of the determined temperature dependences of the first and second critical fields, has given values of 6.1 and 9.1, for samples of $Ge_{0.963}Te$ and $Ge_{0.950}Te$, respectively. These values are in good agreement with Gor'kov's theoretical value of 9.[13]

Hein and his colleagues[12] have confirmed that, in agreement with Cohen's theory, the superconductivity of GeTe is observed only when the carrier density is higher than 8×10^{20} cm^{-3}. The fact that $Ge_{1-x}Te_x$ becomes superconducting only when x is positive and greater than ~0.02 is in good agreement with a model of the complex structure of the valence band, consisting of two mutually displaced sub-bands with different densities of states, put forward by Kolomoets et al.[14] According to the theory of Kolomoets et al.,[14] when the concentration of Te in an alloy is higher than 50.2%, the position of the Fermi level is such that, in addition to the light holes, the effect is felt of the heavy holes from the sub-band with a higher density of states. It is at this concentration of Te in the alloy that germanium telluride becomes superconducting.

An investigation of the specific heat of a germanium telluride sample of the $Ge_{0.950}Te$ composition, in the temperature range 0.1–1.1°K,[15,16] has indicated the presence of a specific heat maximum below 0.3°K with a high-temperature wing (0.17–0.27°K) corresponding to the temperature of a change in the magnetic susceptibility reported in [11]. Some broadening of the specific heat maximum is evidently due to the inhomogeneity of the sample. A magnetic induction of 500 G destroys this specific heat maximum.

To obtain a further confirmation of the bulk nature of the superconducting transition and to investigate the behavior of GeTe in a static magnetic field, Goodman and Marcucci[17] carried out measurements of the specific heat and isothermal magnetization on three samples of p-type GeTe. Samples whose compositions were $GeTe_{1.01}$, $GeTe_{1.02}$, $GeTe_{1.03}$ and whose hole densities were 1.05×10^{21}, 1.16×10^{21}, and 1.52×10^{21} cm^{-3}, respectively, were annealed for a week at 500°C before measurements. The specific heat was measured by the adiabatic demagnetization method. Comparison of the shape of the temperature dependences of the electronic specific heat, recorded in H = 0 and H = 200 Oe, as well as comparison of these dependences with the curve obtained in [15], confirmed the presence of a very wide superconducting transition. The high-temperature sides of the maxima coincide with the values of the critical temperatures of samples with comparable carrier densities, investigated in [11].

It also follows from the measurements of the magnetization of a sample of $GeTe_{1.03}$ composition that germanium telluride behaves as a typical type II superconductor with $H_{c2}(0) = 95$ Oe.

The superconducting energy gap of GeTe was measured for the first time in an investigation of $Al-Al_2O_3-GeTe$ tunnel junctions[18] prepared by the deposition, from the vapor phase, of a 4000 Å thick polycrystalline film of GeTe on an oxidized film of Al. The dependence of the differential conductance dI/dV on the applied bias V (Fig. 3), recorded in the temperature range 2.50–0.085°K, shows an additional structure, at temperatures below 0.5°K, due to the presence of an energy gap in GeTe. Measurements of the size of the gap in films with a hole density of 1.2×10^{21} cm^{-3} give a value of 150 μeV and the ratio of the gap to the value of kT_C is 4.3 (according to the Bardeen–Cooper–Schrieffer theory, this ratio should be 3.5). The application of a magnetic field of 20 Oe at right-angles to the plane of the junction has been found to destroy the superconductivity of GeTe.

To extend the range of the data on the carrier-density dependence of the critical temperature, the influence of a silver impurity on the superconducting properties of GeTe was investigated in [19]. Doping with silver makes it possible to increase the hole by a factor of five, compared with the maximum density in samples

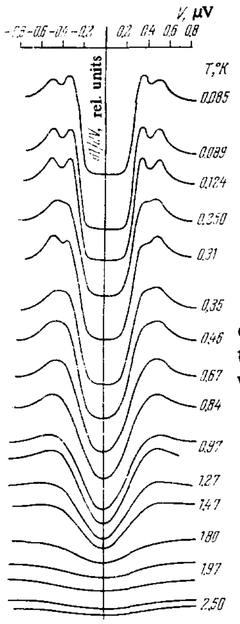

FIG. 3. Dependence of the differential conductance dI/dV of an Al–Al_2O_3–GeTe tunnel junction on the applied voltage at various temperatures.

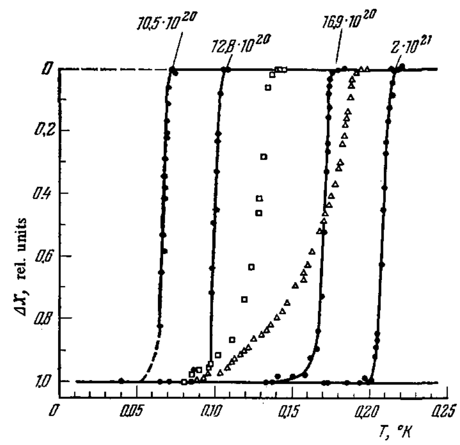

FIG. 4. Temperature dependence of the differential magnetic susceptibility of SnTe samples: ●) samples grown by zone melting or by the Czochralski method; □), Δ) fired samples of $Sn_{0.976}Te$ and $Sn_{0.966}Te$, respectively.

investigated before. The critical temperature is then determined by a dc induction method. The critical temperatures for samples with hole densities of 6.4×10^{21} and 2.7×10^{21} cm^{-3} are 0.41 and 0.21°K, respectively, in the absence of a magnetic field.

2. SnTe

The convincing demonstration of the existence of superconductivity in compounds of the GeTe system has stimulated a search for other compounds with properties and crystal structure similar to GeTe and capable of becoming superconductors at high carrier densities. One result of this search has been the discovery of the superconductivity of the compound SnTe.[20]

The p-type SnTe samples, used in [20], were prepared by two methods: annealing of crystals (grown by zone melting or by the Czochralski method) in the presence of Te vapor for 100 h, or pressing followed by firing. Polycrystalline samples of various compositions, prepared by the first method, exhibited a narrow transition (0.01 deg K), whereas two fired samples exhibited wider transitions within the range 0.05–0.22 deg K (Fig. 4).

The dependence of the critical temperature on the hole density p of these materials is in qualitative agreement with theoretical predictions[4,6] and the superconductivity is not observed at $p < 8 \times 10^{20}$ cm^{-3}, as in GeTe samples.

A further investigation of SnTe[21] demonstrated that, like GeTe, it is a type II superconductor. Hein[21] studied samples with different carrier densities p (10.5×10^{20}, 12.5×10^{20}, 16.5×10^{20}, and 20×10^{20} cm^{-3}) and found that the Ginzburg–Landau parameter $\kappa(T)$, corresponding to the critical temperature in the absence of a magnetic field, depends on p: it decreases with increasing p.

Hein reports also that the superconductivity of SnTe appears first at a carrier density at which the second valence band begins to take part in the transport phenomena, i.e., the second band must be populated for the appearance of superconductivity.

3. $SrTiO_3$

Strontium titanate is the most thoroughly investigated superconducting semiconductor. $SrTiO_3$ has the perovskite-type structure. According to theoretical calculations[22] and experimental results, obtained by measuring the magnetoresistance of reduced and doped $SrTiO_3$ at 4.2°K[23] and in the range 1.4–2.1°K,[24] $SrTiO_3$ has a many-valley structure of the energy bands. However, this has been questioned in [25].

The best agreement between the values of the longitudinal and transverse effective masses, found for various orientations of a magnetic field relative to the [100], [110], and [111] crystallographic directions, is obtained if it is assumed that the constant-energy surfaces of electrons are three ellipsoids of revolution oriented along the [100] directions.

In the normal state, $SrTiO_3$ has the following parameters:[23,24,26–28] $E_g = 3.15$ eV; longitudinal and transverse effective masses $m_l = 6.0\,m_0 \pm 30\%$, $m_t = 1.5\,m_0 \pm 15\%$, respectively; an electron mobility of 6 $cm^2 \cdot V^{-1} \cdot sec^{-1}$ at room temperature, ranging from 75 (for samples annealed in 10^{-2} mm Hg vacuum at 1000°C for 28h) to 3300 $cm^2 \cdot V^{-1} \cdot sec^{-1}$ (Ti-doped samples, annealed for three days at 900°C in 10^{-5} mm Hg vacuum) at 4°K.

The temperature dependence of the permittivity ϵ has a maximum at low temperatures: $\epsilon = 250$ at 300°K and rises to a value of 10^4 [22] (2×10^4 according to [29]) below 20°K. In spite of such a high value of the permittivity, a ferroelectric transition has not been observed in $SrTiO_3$ at low temperatures.

The superconducting transition is reported in [30] for three single crystals of $SrTiO_3$, exhibiting n-type conduction in the normal state. Samples I and II were subjected to chemical reduction during prolonged heating in 10^{-5}–10^{-7} mm Hg vacuum. In the case of sample I, this was done in the presence of metallic titanium. Sample III was reduced in a stream of hydrogen at 950°C. All three samples were found to be degenerate at liquid helium temperature.

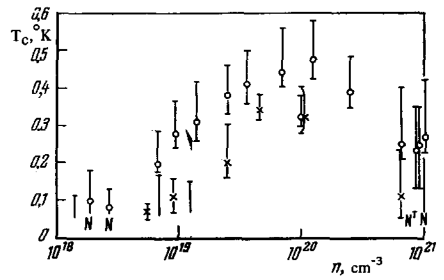

FIG. 5. Dependence of the critical temperature of $SrTiO_3$ on the electron density.

The transition, not wider than 0.1 deg K, was observed at 0.25 and 0.28°K for samples I and II, respectively, using measurements of the dc resistance. An investigation of the dependence of the magnetic susceptibility χ of sample III on the magnetic field confirmed the "bulk" nature of the semiconducting transition.

The transitions found from the electrical measurements are much narrower compared with those found from variation of χ, which is due to the presence of inhomogeneities in the samples.

The dependence $T_c(n)$ has been investigated in detail[31,32] for electron densities n in the range 10^{18}–10^{21} cm^{-3}, determined from the Hall effect at temperatures of 300, 77, and 4°K. It was found that the critical temperature T_c varies from 0.1°K, passes through a maximum (0.5°K) at $n \approx 10^{20}$ cm^{-3}, and decreases to 0.1°K at higher values of n (Fig. 5). The observed dependence $T_c(n)$ has been interpreted using Cohen's theory of the superconductivity of many-valley degenerate semiconductors.[6] A many-valley model of the conduction band, with minima lying along the [100] direction near the Brillouin zone boundary, was used for $SrTiO_3$ in [22]. In order to determine the dependence $T_c(n)$, the equation of the Bardeen-Cooper-Schrieffer theory was solved for several values of n. It was assumed that the attractive interaction between electrons is mainly due to virtual intervalley phonons. The screening of this interaction by free carriers plays an important role: it gives rise to a maximum in the dependence $T_c(n)$. Since the scattering by intervalley phonons involves large changes in the momentum, it is screened at much higher carrier densities than the attraction due to the scattering by intravalley phonons. The increase of T_c with increasing n, observed at low values of n, is due to an increase in the density of states; the decrease of T_c at high values of n is due to the screening. A reduction in the average transferred momentum with increasing n is also important because the Fermi surface consists of ellipsoids strongly elongated along the [100] direction. This calculation agrees semiquantitatively with the experimental data.

An investigation of the magnetic susceptibility, using dc and ac, of spherical and flat $SrTiO_3$ samples[32] made it possible to compare the theoretically calculated and experimental values of the depth of penetration of the magnetic field into samples with different electron densities. The measured values are somewhat larger than the calculated ones and they depend strongly on the state of the surface of the sample, which is probably due to a change in the carrier density near the surface because of oxidation.[7]

Using a precision magnetometer, the dependence of the magnetization of superconducting $SrTiO_3$ on the magnetic field has been measured in fields right up to the second critical value and at temperatures from 0.1°K to the critical point.[33] The investigated samples had electron densities n corresponding to the maximum in the $T_c(n)$ curve (cf. Fig. 5). Such samples were prepared either by doping with niobium during growth or by partial reduction at elevated temperatures after growth.

The temperature dependence of the lower and upper critical fields, representing several and several hundred oersteds, respectively, indicate, like other results,[30] that $SrTiO_3$ behaves as a type II superconductor with the Ginzburg-Landau parameter depending on the electron mobility in the normal state, i.e., the parameter increases with decreasing mobility.

To obtain more accurate values of the critical temperature, as determined by the magnetic method, measurements have been made of the temperature dependence of the specific heat of Nb-doped polycrystalline $SrTiO_3$ with an electron density of 1.4×10^{20} cm^{-3}. The inflection point in the linear dependence of the specific heat corresponds to a critical temperature $T_c = 0.38$°K, i.e., it lies within the range of temperatures found from the magnetic measurements ($0.36 < T_c < 0.41$°K).

Shapiro[34] investigated the current-voltage characteristics of the tunnel current at a contact between In and n-type strontium titanate with an electron density of 7×10^{19} cm^{-3} at 300°K, and measured the magnetic susceptibility at low temperatures and found a wide (0.1 deg K) superconducting transition at 0.25°K. However, tunnel measurements could not be used to detect the superconducting energy gap, due to the considerable inhomogeneity of the investigated samples.

Pfeiffer and Schooley[35] determined the effect of a hydrostatic pressure P up to 1.5 kbar and of a uniaxial compression, applied along the [100], [110], and [111] directions, on the critical temperature of $SrTiO_3$. They used samples with an electron density of 6.3×10^{19} cm^{-3}, whose critical temperature in the absence of a compressive stress was $T_c(0) = 0.27$°K. The transition to the superconducting state was deduced from measurements of the ac mutual induction of a set of coils surrounding the samples. To reduce the error in the measurement of the shift of T_c, an unstressed control sample was used in each experiment together with a sample subjected to compression. These experiments show that the effect of the hydrostatic pressure is nonlinear and the value of $\Delta(\ln T_c)/\Delta P$ is approximately an order of magnitude larger than in metallic superconductors. The shift of the critical temperature in the hydrostatic case is $\Delta T_c \approx 0.1$ deg K at a pressure of 1.48 kbar. In the uniaxial compression case, ΔT_c is somewhat smaller and the shift of the critical temperature for the [111] and [110] directions is larger than that for the [100] axis.

Superconducting properties of ceramic strontium titanate, in which some Sr atoms have been replaced with Ba and Ca, have also been investigated.[32,36–37] This approach is interesting because it represents a gradual transition to crystals with a well-defined ferroelectric phase transition.

Superconductivity has been found in samples of mixed titanates $(Ba_xSr_{1-x})TiO_3$ for $x \leq 0.1$ and $(Ca_ySr_{1-y})TiO_3$ for $y \leq 0.3$ with electron densities $n = (6 \pm 3) \times 10^{19}$ cm^{-3}. The transition to the superconducting state was deduced from the temperature dependence of the ac magnetic susceptibility measured in the temperature range 0.10–1.0°K. The critical temperature of some samples was determined from the magnetization curves recorded at various temperatures. The maximum value of T_c (0.55°K) of such mixed titanates is somewhat higher than that of pure reduced $SrTiO_3$. Samples of strontium-free titanates show no transition to the superconducting state throughout this temperature range at electron densities up to 10^{20} cm^{-3}. The difference between the transition temperatures of $SrTiO_3$ and mixed titanates is attributed by the investigators of the mixed materials to the difference between the permittivities.

The dependence of the critical temperature of the electron density[32] of mixed titanates is similar to the corresponding dependence of a single crystal of $SrTiO_3$. However, the value of T_c of mixed titanate samples remains above 0.2°K at $n < 10^{18}$ cm^{-3},

Measurements of the specific heat of ceramic $Sr_{0.925}Ba_{0.075}TiO_3$ with $n = 9.6 \times 10^{19}$ cm^{-3} [38] have confirmed the presence of the superconducting transition at 0.5°K.

Thus, the superconductivity is now firmly established for the degenerate semiconductors GeTe, SnTe, and $SrTiO_3$, and some relationships governing this phenomenon have been determined. New experimental investigations are being published continuously, indicating the interest in these materials.

III. "INDUCED" SUPERCONDUCTIVITY IN SEMICONDUCTORS AND ITS APPLICATIONS

Several investigators have pointed out the possibility of establishing "induced" superconductivity in semiconductors by the application of external fields, and have proposed devices in which semiconducting and superconducting properties are used in combination.

Selivanenko[39] suggested that superconductivity may be observed in pure undoped semiconductors with a suitable energy band structure by establishing a high carrier density (up to 10^{20}–10^{21} cm^{-3}) using the radiation from a powerful laser. Using $SrTiO_3$ as an example, he showed that the power output of a ruby laser is sufficient to produce a carrier density at which the superconducting transition would take place in $SrTiO_3$ at a suitable temperature.

However, estimates of the heat balance given by Selivanenko are not convincing. Therefore, it is not certain whether lasers can be used to establish a high carrier density and whether a very low temperature is required.

Vul and Selivanenko[40] suggested tunnel p-n junctions made of semiconductors with n- and p-type superconductivity. Figure 6 shows the energy diagram of such a junction given by these authors. Unfortunately, they have not derived the current–voltage characteristic of such a p–n junction. It is likely to have the shape shown in Fig. 7.

Sandomirskiĭ[41] suggests that superconductivity may be induced and controlled in suitable semiconductors by the field effect or similar means, such as injection by electric current, contact phenomena, and chemisorption. Estimates carried out for $SrTiO_3$ show that the field effect can be used to produce a surface carrier density of up to 10^{21} cm^{-3}, i.e., an uncharged semiconductor in the normal state may become superconducting due to charging.

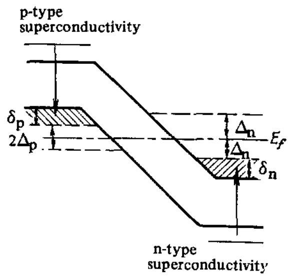

FIG. 6. Energy scheme of a superconducting tunnel p–n junction. E_f is the Fermi level; $2\Delta_p$, $2\Delta_n$ are the energy gaps in the superconductors; δ_p, δ_n are the energies between the forbidden band edges and the superconducting gap in the p- and n-type regions, respectively.

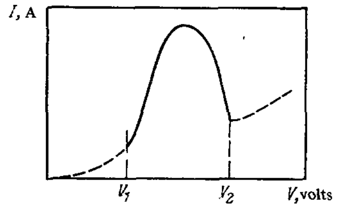

FIG. 7. Qualitative shape of the current–voltage characteristic of a superconducting tunnel p–n junction. $V_1 = \Delta_n + \Delta_p$, $V_2 = \Delta_n + \Delta_p + \delta_n + \delta_p$.

Esaki and Stiles[42] reported a new phenomenon in semimetals and semiconductors, which they have attributed to the appearance of superconductivity due to the injection of carriers. They investigated a very small (~10^{-10} cm^2) ohmic contact between a normal metal (Al, In, or Ag) with single-crystal samples of Bi and Sb semimetals and a BiSb semiconducting alloy.

Esaki and Stiles investigated the current–voltage characteristics in the temperature range 2–4.2°K and found a step in the current (a region where the current is independent of the voltage) at some critical value of the current I_c in an otherwise linear I–V characteristic (Fig. 8). An increase of the temperature and a decrease of the magnetic field H perpendicular to the contact plane reduce the value of I_c and of the length of the step; at certain values of T and H, the step disappears. The nature of the dependence $H_c(T_c)$ resembles the dependence in the case of superconductivity.

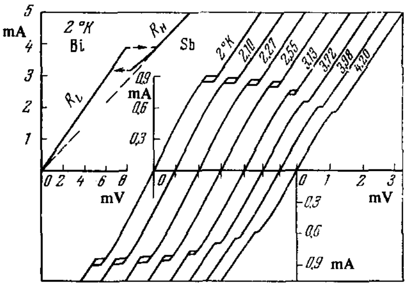

FIG. 8. Current–voltage characteristics of an Al–Sb contact, recorded at various temperatures. A corresponding characteristic of an Al–Bi contact at 2°K is given in the top left-hand corner.

On this basis, the observed phenomenon has been attributed to the appearance of superconductivity in Bi, Sb, and BiSb in the contact region due to injection from the metal.

It is evident that any method of producing induced superconductivity can be used to develop a controlled active element and is therefore very interesting from the point of view of practical applications.

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