Journal of Low Temperature Physics, Vol. 8, Nos. 3/4, 1972

Investigation of the Excitonic Insulator Phase in Bismuth–Antimony Alloys

N. B. Brandt and S. M. Chudinov

Low Temperature Physics Section, Physics Department, Moscow State University Moscow, USSR

(Received January 5, 1972)

Pressure-induced metal–semiconductor transitions in bismuth–antimony alloys in a strong magnetic field (up to 70 kOe) at helium temperatures have been investigated. It is found that for values of the "overlap-gap" $|G| \lesssim 1$ *meV the alloy forms an excitonic insulator (EI) in magnetic fields above a certain "threshold" (30–40 kOe). It is inferred that the EI energy gap* Δ *increases with the magnetic field. The maximum gap observed in fields of* ~ 70 *kOe turns out to be* $\Delta_{00} \sim 7.5$ *K. An analysis of the results shows that transitions to the EI phase are observed from both the semimetal and the semiconducting states. The critical transition temperature* T_c *is related to the EI gap* Δ *by the expression* $T_c \simeq 0.7\Delta$. *Arguments are advanced in support of the fact that the formation of the EI phase involves the pairing of electrons at the* L *point with holes at the* T *point.*

1. ZERO-FIELD EXCITONIC INSULATOR

The possibility of the formation of an excitonic insulator (EI) in transition from the semiconducting to the metal state (or conversely) was first indicated by Mott in 1949.[1] The EI phase in the absence of a magnetic field H has been studied theoretically in a large number of papers.[2–12] It has been shown that a semiconductor having a narrow forbidden band G or a metal having an equal number of electrons and holes becomes unstable under certain conditions with respect to the pairing of electrons of one band with holes of the other. This type of pairing is possible when the Coulomb attraction of the electrons and holes prevails over the electron–phonon interaction normally responsible for the effective repulsion of these particles. Pairing produces a system with a spectrum similar to that of a superconductor, which is characterized by an energy gap Δ that is determined at $T = 0$ K by the binding energy E_B of the pairs. At a certain temperature T_c, called the critical temperature, the gap narrows to zero as $\sim(1 - T/T_c)^{1/2}$, and

the EI is transformed by a second-order phase transition to the original metal or semiconductor. The gap Δ_0 of the EI at $T = 0$ K is related to the band overlap energy $-G$ in the original metal or to the energy gap $+G$ in the original semiconductor and depends strongly on the spectral anisotropy of the unrearranged system. The relation between Δ_0 and G is called the gap function (EI phase diagram[7]) and determines the domain of existence of the EI phase at $T = 0$ K.

It is well known that the exciton levels in a semiconductor form in the forbidden energy region a zone whose edge at $T = 0$ K is situated below the bottom of the conduction band by an amount of the order of the exciton binding energy E_B. In the effective mass approximation the individual Mott exciton in a semiconductor is treated as a hydrogenlike electron–hole formation situated in a medium with a dielectric constant $\varkappa$.[1,4,7] The binding energy of this formation and its effective radius r^* can be estimated from the familiar Bohr equations:

$$E_B = m^* e^4 / 2\varkappa^2 \hbar^2 \tag{1}$$

and

$$r^* = \varkappa \hbar^2 / m^* e^2 \tag{2}$$

where m^* is the reduced exciton mass, which is related to the effective electron mass m_e^* and hole mass m_h^* as follows:

$$(m^*)^{-1} = (m_e^*)^{-1} + (m_h^*)^{-1}$$

The quantity E_B (1) is usually called the effective Rydberg constant Ry^*. In known semiconductors the exciton binding energy is two or three orders of magnitude smaller than the characteristic atomic energies, and the exciton radii are much greater than the interatomic distances in the crystal. A large value of r^* implies that the exciton is essentially a macroscopic formation in the crystal and the description of the specific atomic structure is significant only insofar as it affects the parameters m^* and $\varkappa$. The exciton may be regarded in the first approximation as a quasiatom moving in a vacuum. The distortion of the crystal structure due to the presence of an exciton or even a large number of excitons is negligible in this case.

The formation of an exciton in an intrinsic semiconductor requires the expenditure of an energy equal to $G - E_B$. The formation of excitons at $T = 0$ K becomes energetically favorable when the edge of the exciton band enters the valence band. This situation is equivalent to the condition

$$E_B > G \tag{3}$$

When inequality (3) is satisfied, the spontaneous production of excitons results, whereupon the semiconductor goes over to the EI phase. Consequently, in the case of an unrearranged semiconductor system ($G > 0$) the

gap function Δ_0 as a function of G is "cut off" at a value of $G \simeq E_B$, which limits the domain of existence of the EI on the semiconductor side. At $G = 0$ the function Δ_0 attains the maximum value Δ_{00}.[4] Zittars[8] has shown that for $G > 0$ the spectral anisotropy of the original semiconductor has practically no effect on the gap function.

In a metal with a basically isotropic spectrum the pairing of electrons and holes at $T = 0$ K takes place for any value of the overlap energy $-G$. In this case the gap Δ_0 decreases monotonically with increasing $|G|$ from the maximum value Δ_{00} at $|G| = 0$. In the interval $|G| \gtrsim E_B$ the decrease of Δ_0 becomes exponential.[2,4,6,7] The strong dependence of the EI gap Δ_0 on the anisotropy of the spectrum of the original metal was first indicated by Kopaev.[5] The allowance for anisotropy has the effect of limiting the domain of existence of the EI on the metal side ($G < 0$) to a certain value $|G|_{cr}$. The value of $|G|_{cr}$ does not exceed E_B. It has been shown[8] that $|G|_{cr}$ is determined by the following relation for a metal with an isotropic valence band and an anisotropic conduction band:

$$\pi/\ln[(1-\zeta)^{-1}] = (E_B/|G|_{cr})^{1/2} \ln[1 + (4\pi m^*/M)(|G|_{cr}/E_B)^{1/2}] \qquad (4)$$

where the anisotropy coefficient ζ is equal to the ratio of the light ($m^*_{e\perp}$) to the heavy ($m^*_{e\parallel}$) effective electron masses:

$$\zeta = m^*_{e\perp}/m^*_{e\parallel} \qquad (m^*)^{-1} = (m^*_{e\perp})^{-1} + (m^*_{e\parallel})^{-1}$$

and

$$M = m^*_{e\perp} + m^*_h$$

[Equation (4) is valid for small anisotropy: $1 - \zeta \ll 1$.] The form of the gap function Δ_0 as a function of G for isotropic and anisotropic spectra of the unrearranged system is illustrated in Figs. 1a and 1b, respectively.

The EI critical temperature T_c is related to the value of Δ_0 by the linear relation

$$T_c = \alpha\Delta_0 \qquad (5)$$

in which the coefficient α is determined by the form of the spectrum of the unrearranged system.[2–4,7,8] In the case of an isotropic initial spectrum, in particular, $\alpha \simeq 1.44$ for $m^*_e = m^*_h$, and $\alpha \simeq 0.72$ for $m^*_e \ll m^*_h$. In the strong anisotropy limit $\zeta \to 0$, and $\alpha \simeq 0.45$ for $m^*_{e\perp} \ll m^*_h$.[8]

The formation of an EI imposes a rather stringent condition on the purity of the original crystal. Scattering by impurities tends to diminish the gap Δ_0. As shown by Zittars,[8] with impurities present the gap Δ'_0 is related to the gap Δ_0 in the impurity-free system by the relation

$$\Delta'_0 = \Delta_0 = (\pi\hbar/4\tau) \qquad (6)$$

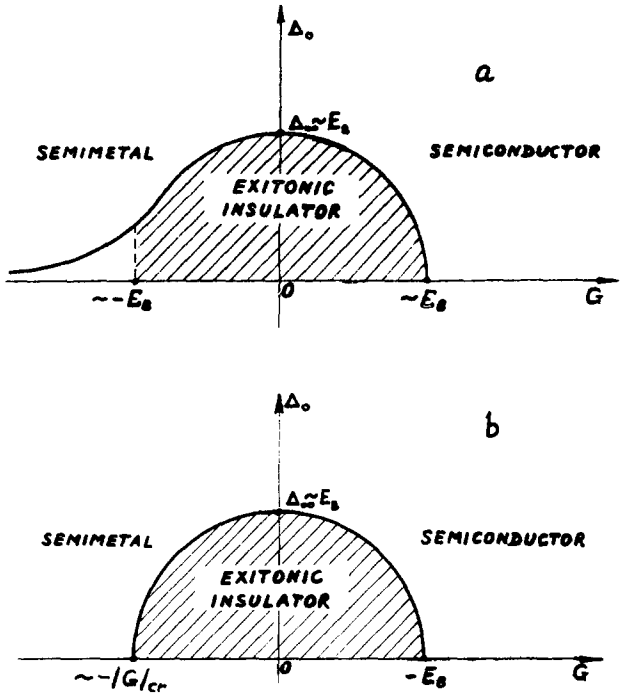

Fig. 1. Gap function (phase diagram) of an exitonic insulator for an isotropic (a) and anisotropic (b) energy spectrum of the unrearranged system.

where τ is the relaxation time for impurity scattering. Consequently, for the formation of the EI the carrier relaxation time has the lower bound:

$$\tau > \tau_{\min} \sim \pi\hbar/4E_B \tag{7}$$

from which it follows that E_B must satisfy the inequality

$$E_B > \pi\hbar/4\tau = \Delta_{st} \tag{8}$$

The concepts developed for the hydrogenlike exciton model are reasonably applicable to individual excitons in a semiconductor. This problem is covered in an extensive literature. Hydrogenlike series with the excitation of excitons have been observed experimentally. A detailed survey of excitons in semiconductors may be found in Ref. 13, and the numerous papers on diamagnetic excitons in a strong magnetic field are reviewed in Ref. 14.

Attempts have been made to apply similar notions to a nonequilibrium system of excitons in a semiconductor with a large concentration (up to $\sim 10^{18}$ cm^{-3}) of excitons. Under these conditions it is possible experimentally to observe the Bose–Einstein condensation of excitons, the formation of

exciton drops, the metallization of excitons in drops, the Mott transition in an exciton system, the formation of excitonic molecules (biexcitons), etc. The problems associated with a large-density system of excitons are treated in the collective work.[15]

The applicability of the notions valid for the individual exciton in a semiconductor to an excitonic insulator remains a moot question at the present time. To the best of our knowledge, no one to date has observed the EI phase in the absence of a magnetic field. Inequality (3) does not hold for any known natural narrow-gap semiconductor.

Semimetals with a small band overlap (As, Sb, Bi) have an acutely anisotropic energy spectrum, their overlap energy $|G|$ greatly exceeding the value of Ry^*. Consequently, the formation of an EI in the indicated semimetals for $H = 0$ is also impossible down to the very lowest temperatures. Condition (3) is satisfied automatically for the continuous transition from the semiconducting to the metal state, in the course of which the point $G = 0$ is passed. In metal–semiconductor (or the converse) transitions the formation of an EI can be expected at low enough temperatures, $T < Ry^*$. Inequalities (7) and (8), however, require that such transitions be observed in high-purity crystals. Numerical estimates associated with a choice of material in which the EI phase can be observed for $H = 0$ are given in Ref. 7. Estimates given for bivalent metals (Ca, Sr, Yb) show that the formation of an EI is possible in these substances, in principle, by transition to the semiconducting state under pressure. However, the postulated values of the pressure needed to accomplish this preclude the possibility of suitable investigations with single-crystal specimens.

In the interval of hydrostatic pressures $p \lesssim 25$ kbar metal–semiconductor transitions are observed in semimetal alloys $Bi_{1-x}Sb_x$ with $x < 0.065$.[23,25] In these substances, however, $Ry^* \lesssim 1{\cdot}3 \times 10^{-5}$ eV, and the pressure interval corresponding to $|G| \lesssim Ry^*$ is $\sim 10^{-3}$ kbar,[7] which falls outside the realm of possibility for monitoring of the pressure in an experiment.

Thus, our analysis of the available literature in which the observation of metal–semiconductor (or the converse) transitions is reported indicates that the detection of the EI phase for $H = 0$ is clearly impracticable down to ultralow temperatures, $T \sim 0.01$ K.

2. EXCITON INSULATOR IN A MAGNETIC FIELD

The theory of the Mott exciton in a magnetic field H was formulated by Elliott and Loudon[16] and by Hasegawa and Howard.[17] It is based on Yafet, Keyes, and Adams'[18] analysis of a hydrogenlike atom in a strong magnetic field. The authors of Refs. 16 and 17 calculated the dependence of the binding energy E_B and effective dimensions r^* of the exciton on H. They

showed that the influence of the magnetic field on E_B and r^* is determined by the ratio γ of the cyclotron energy $\hbar\omega$ ($\omega = eH/m^*c$) to the ground-state energy $E_B = Ry^*$ for $H = 0$:

$$\gamma = \hbar\omega/Ry^* = H/H_k \tag{9}$$

The quantity H_k, which is equal to $(m^*c/e\hbar) \cdot Ry^*$, limits the strong-field interval. For $H \ll H_k$ a weak Zeeman splitting of levels is observed in the hydrogenlike atom. A pronounced rearrangement of the energy levels occurs for $H \geq H_k$. The critical field H_k for the hydrogen atom is $\sim 2 \times 10^9$ Oe. For the Mott exciton H_k depends on the dielectric constant $\varkappa$ of the medium and the ratio of m^* to the free-electron mass m_0:

$$H_k \cong 2 \times 10^9[(m^*/m_0)(1/\varkappa)]^2 \text{ Oe} \tag{10}$$

and has a considerably smaller value.

In the field interval $H \gg H_k$ ($\gamma \gg 1$) the exciton binding energy increases in the first approximation as

$$E_B \sim Ry^*[\ln (H/H_k)]^2 \tag{11}$$

and the effective Bohr radius decreases[18] as $r^*/[\ln (H/H_k)]^2$.

The behavior of the individual exciton in a strong magnetic field indicates that the conditions for the formation of an EI in this case are probably less stringent than for $H = 0$.

In an intrinsic semiconductor immersed in a strong field H the edge of the exciton band can attain the top of the valence band. However, the problem of the phase transition that must take place in this case is conjectural. So far no one, to the best of our knowledge, has made a rigorous theoretical study of the pairing of electrons and holes in a semiconductor in the ultrahigh magnetic field region. Fenton, in his paper[19] on excitonic insulators in a magnetic field, essentially relies on the results of Refs. 16–18, which are valid only for individual excitons, and he ignores the pairing problem.

A rigorous theory of EI's in a magnetic field for the case of an initial semimetal system has been formulated by Abrikosov. He considers[20] the electron–hole pairing problem in a semimetal with an isotropic spectrum for $m_e^* \neq m_h^*$. The problem of the formation of an EI in a magnetic field for the real spectrum of a semimetal of the Bi type is solved in the preceding paper in this journal. Here the possibility of the dielectric pairing of carriers within a single band due to electron–phonon interaction is stated for the first time. For $T = 0$ K this situation does not actually lead to an insulator, but to a state in which one band contains paired carriers and the other contains unpaired carriers. The condition for the formation of pairs within

a single band (second-order pairing) is given by the following double inequality:

$$\hbar\omega \gg \varepsilon_F \gg Ry^* \tag{12}$$

in which ε_F is the Fermi energy. For the pairing of electrons and holes from different bands in a magnetic field (first-order pairing) inequality (12) must be satisfied for both types of carriers. Consequently, in a magnetic field pairing takes place in the ultraquantum limit, when carriers are precipitated to the last Landau level. Inasmuch as only a small neighborhood of the particle Fermi momentum has any part in the pairing process, the anisotropy of the spectrum is no longer felt in this case.

We know of only one paper[21] in which the experimental observation of the EI phase in a magnetic field is announced. Its authors, Fenton, Jan, and Karlsson, have investigated semiconductor–metal transitions (observed by Brandt and Svistova[26]) in $Bi_{1-x}Sb_x$ alloys with $x = 0.082, 0.101$, and 0.116 in a magnetic field up to 100 kOe. They attribute the anomalous behavior of the temperature dependence of the magnetoresistance of the alloy with $x = 0.101$ in a field $H \simeq 53$ kOe to the possible formation of an EI phase.

The laws that they obtained, however, do not seem to us to afford conclusive evidence in support of the inception of the EI phase in a magnetic field. The strong dependence of the spectral parameters of the unrearranged system on H in the experiment described, it appears to us, does not provide a reliable determination of the EI phase or its quantitative characteristics (e.g., Δ_0). Fenton *et al.*[21] admit the possibility of an alternative explanation for the observed anomaly.

3. SELECTION OF THE MATERIAL

The present study represents an attempt to observe and investigate the EI phase in semimetal alloys $Bi_{1-x}Sb_{1-x}$ with $x < 0.065$ in metal–semiconductor transitions under pressure in the presence of a strong magnetic field. The $Bi_{1-x}Sb_x$ alloys were selected as the research object on the basis of the following considerations:

(1) In Bi and $Bi_{1-x}Sb_x$ alloys small effective masses are observed on the part of the current carriers (e.g., $m_e^*/m_0 \lesssim 0.01$ for certain directions in the crystal),[22,23] along with a very high value[24] of $\varkappa \geq 100$. This makes it possible to create an ultrahigh field regime $\gamma \gg 1$ for excitons in feasible static magnetic fields $H \sim 50$–70 kOe. Since the value of the effective Rydberg constant is $Ry^* \lesssim 1.4 \times 10^{-2}$ meV, in such fields the parameter γ attains a value of $\sim 10^4$, and the binding energy E_B of the individual exciton increases to ~ 1 meV. For a band overlap $|G| \sim 1$ or 2 meV inequality (12) is satisfied in fields of ~ 50–70 kOe for electrons at the L points as well as holes at the

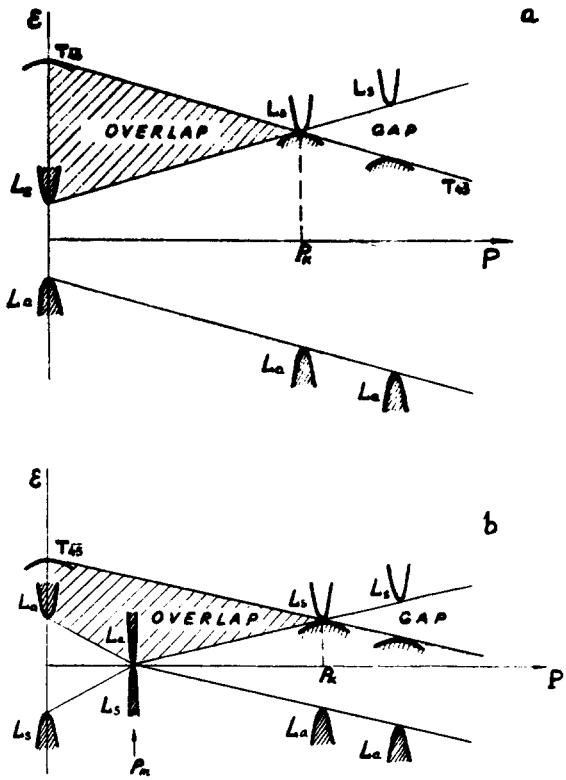

Fig. 2. Qualitative energy diagram of the levels L_s, L_a and $T_{\overline{45}}$ as a function of the pressure p for semimetal alloys $Bi_{1-x}Sb_x$. (a) $x < 0.04$; (b) $0.04 < x < 0.065$.[23]

T point in the Brillouin zone. These estimates give reason to expect EI formation in a magnetic field in the metal–semiconductor transition region for $Bi_{1-x}Sb_x$ alloys with $|G| \lesssim 1$ or 2 meV on both the semimetal and semiconductor sides for $T \lesssim 10$ K.

(2) The energy spectrum of Bi and $Bi_{1-x}Sb_x$ alloys near the Fermi level and its rearrangement due to various factors have been fairly thoroughly investigated (see the article in this journal concerning the gapless state). It is known that the band overlap G at L and T decreases monotonically as the Sb concentration x is increased, vanishing at $x \simeq 0.065$. In the spectrum of alloys with $x > 0.065$ there appears an energy gap G between the bands at L and T, which attains a maximum of ~ 24 meV at $x \simeq 0.15$.

In semimetal alloys $Bi_{1-x}Sb_x$ with $x < 0.065$ under a hydrostatic pressure p transitions to the semiconducting state are observed.[23,25] The motion of the energy levels under pressure in alloys with $x < 0.04$ and

$0.065 > x > 0.04$ is shown in Figs. 2a and 2b, which are borrowed from Ref. 23. In the metal–semiconductor transition region, at $p = p_k$ the quantity $\partial G/\partial p \simeq 1.35$ meV/kbar and is independent, in the first approximation, of the Sb concentration in the alloy. The hydrostatic pressure is a useful continuous parameter for varying the "overlap-gap" G in the alloy. The interval of values of $|G| \lesssim 1$ meV is in the interval $p_k - 0.7$ kbar $\lesssim p \lesssim p_k + 0.7$ kbar, which considerably exceeds the uncertainty error in the pressure values used in present-day low-temperature chambers.

(3) The motion of the band boundaries and concomitant electron transitions in a magnetic field have been studied in $Bi_{1-x}Sb_x$ alloys in the Sb concentration interval $x \lesssim 0.15$ with H in all the principal crystallographic orientations.[26] The ratio of the spin and orbital splitting and velocities of the bands are known in order-of-magnitude terms for H in practically any direction.

(4) Tremendous progress is being made at the present time in the preparation of pure and perfect single crystals of $Bi_{1-x}Sb_x$ alloys. The concentration N_i of residual impurities of the donor and acceptor type in the better crystals at our disposal is about 3×10^{13} to 1×10^{14} cm^{-3}. The carrier relaxation time τ in these alloys in the metal–semiconductor transition region ($G \simeq 0$) is $\sim 3 \times 10^{-12}$ sec for electrons at L and $\sim 1.5 \times 10^{-11}$ sec for holes at T.[23,25] For $\Delta_{st} = \pi\hbar/4\tau$ this gives values of ~ 0.2 and ~ 0.03 meV for electrons and holes, respectively. Consequently, if Δ_0 is of the order of 1 or 2 meV for the EI (in the absence of scattering), the inequality $\Delta_0 > \Delta_{st}$ holds, implying that one should expect the inception of positive values of the gap $\Delta_0' = \Delta_0 - \Delta_{st}$ under actual experimental conditions.

4. REGISTRATION OF THE EXCITONIC INSULATOR PHASE

We now examine in more detail the problem of reliably detecting the excitonic insulator phase when it occurs.

It has been shown in Refs. 7–9 that in the absence of impurities the conductivity σ of an EI for $T < T_c$ is determined by the concentration of unpaired electrons and holes, which is proportional to $\exp(-E_A/T)$, where E_A is the EI activation energy. The value of E_A depends on the value of Δ for the EI and, hence, on G in the spectrum of the unrearranged system. In the presence of impurities the nature of the temperature dependence of σ for $T < T_c$ is related to the ratio $\delta = \Delta_{st}/\Delta_0$.[8] For $\delta < 1$ the system behaves qualitatively as in the absence of impurities. In the case $\delta > 1$, despite pairing, the "insulator" properties do not occur. This situation cannot be accounted for in terms of the spectral energy gap, because in this case the quasiparticle description[8] is inapplicable.

The longitudinal conductivity σ_{zz} for the EI phase formed in a semimetal in a magnetic field has been investigated by Abrikosov. He showed that in both first- and second-order pairing there is a residual conductivity σ_0 at $T = 0$ K. The difference $\sigma_{zz} - \sigma_0$ in this case is proportional to $\exp(-E_A/T)$ (an exception is the case of an ideal semimetal with an isotropic spectrum comprising one electron and one hole ellipsoid for $m_e^* = m_h^*$; in such a system only first-order pairing is possible, and $\sigma_0 = 0$). The dependence of E_A on H is realized both through Δ and through G.

If we reject the motion of the band boundaries in a magnetic field suitable for changing G, we should expect Δ to be an increasing function of H for an *EI* phase formed in the unrearranged spectrum of a semiconductor. This hypothesis is based on the fact that the binding energy of the individual exciton in a semiconductor increases in a magnetic field (we stress once again the fact that the lack of a rigorous theory of the EI in this case prevents us from estimating the limits of applicability of the stated hypothesis). Abrikosov's analysis of the EI formed in a semimetal[20] shows that Δ at first increases together with H, passes through a maximum, and then decreases.

Consequently, in measurements of the longitudinal conductivity σ_{zz} in moderate magnetic fields H the EI should behave in every case in a way similar to a semiconductor, whose energy gap increases in a magnetic field. This characteristic of the EI in a magnetic field can be utilized for its detection. We note that it is essential in any investigation of the conductivity σ of an EI to take account of the fact that the gap Δ is temperature dependent. However, this dependence is significant only in the immediate proximity of $T = T_c$, where $\Delta \sim (1 - T/T_c)^{1/2}$. For $T < T_c$ the gap Δ rapidly attains the value Δ_0:

$$\Delta = \Delta_0(1 - \beta e^{-\Delta_0/T})$$

where $\beta \sim 1$.

Therefore, the temperature dependence of σ for an EI formed on the basis of a semimetal must have the characteristic form illustrated in Figs. 3a and 3b. The dashed curve in Fig. 3a depicts the dependence of σ on T in the case $\delta > 1$ and $\sigma_0 \neq 0$.

The small values of the "overlap-gap" G required for the onset of the EI phase in a strong magnetic field can be obtained in $Bi_{1-x}Sb_x$ alloys under pressure, in a magnetic field, or by variation of the Sb concentration. The latter technique is exceedingly impractical, first because it requires the preparation of an extremely perfect alloy with a predetermined Sb concentration confined to a very narrow interval and, second, because it does not allow G at $H = 0$ to be varied continuously throughout the course of the experiment.

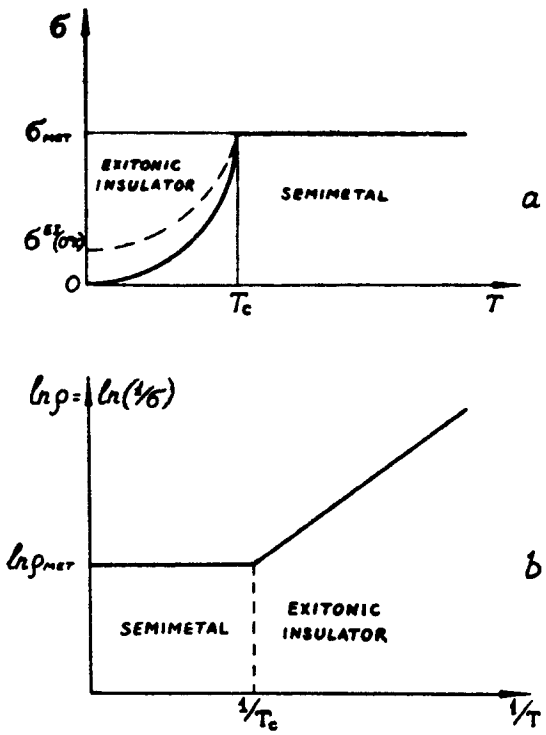

Fig. 3. (a) Electrical conductivity σ of the excitonic insulator phase vs. temperature T. The initial system is a semimetal. The dashed curve indicates the dependence $\sigma(T)$ for[8] $H = 0$ and $\delta = \Delta_{st}/\Delta_0 > 1$ or $H \neq 0$ and $\sigma_0 \neq 0$. (b) Resistivity $\rho = 1/\sigma$ of an excitonic insulator vs. the temperature in coordinates $\ln \rho$, $1/T$. The initial system is a semimetal.

Of practical interest are semiconductor–metal transitions in a magnetic field, as well as metal–semiconductor transitions both under pressure and in a magnetic field. The latter type of transition, however, must be discarded at the outset, because the gap G in the semiconducting state in this case varies qualitatively in a magnetic field (increases) as the EI gap Δ. This prohibits the reliable separation of the two effects and registration of the formation of the EI phase. Fenton, Jan, and Karlsson[21] have used the semiconductor–metal transition in a magnetic field. We know from the work of Brandt and Svistova[26] that this transition at normal pressure is observed only with H oriented along the trigonal axis C_3 in $Bi_{1-x}Sb_x$ alloys with an Sb concentration confined to the narrow interval $0.065 < x \lesssim 0.12$, in which the level $T_{\overline{45}}$ is between the levels L_a and L_s or somewhat below L_s. The indicated transition in this case occurs near the formation

of the gapless state in a magnetic field, in which state the levels L_a and L_s come into contact and invert. This fact greatly complicates the interpretation of the field dependence of the energy gap in connection with formation of the EI state during the semiconductor–metal transition. The mutual proximity of the extrema $T_{4\bar{5}}$, L_s, and L_a in the transition region leads to the formation of a double-gap semiconductor, whose nearly equal energy gaps vary at different rates and in different directions. If we also recognize the fact that the ratio of the densities of states at L and T in this case vary appreciably due to variation of the electron masses at the bottom of the band at L, the identification of the EI phase from the temperature dependences of the magnetoresistance proves to be practically impossible. Moreover, the magnetic field is a factor which, when increased, at first decreases G in the semiconducting state and then increases it in the semimetal state. The region in which the EI can be formed corresponds to a relatively small field interval. It is difficult in this interval to segregate the effects associated with variation of the EI characteristics in a magnetic field from those associated with variation of the unrearranged spectrum of the system. The absence in experiments of a second parameter independent of H, which would make it possible to "adjust" the initial state of the spectrum of the alloy so as to generate the condition $G \simeq 0$ for various values of H, renders the semiconductor–metal transition in a magnetic field exceedingly useless for the observation of the EI phase. The indicated characteristics of this transition explain why the EI phase could not be reliably detected in the experiments of Fenton, Jan, and Karlsson.[21]

The best conditions for registration of the EI phase in $Bi_{1-x}Sb_x$ alloys, in our opinion, can be established in the metal–semiconductor transition under pressure in the presence of a strong magnetic field oriented in such a way as to produce a gradual reduction of the gap G in the semiconducting state or a gradual growth of the overlap $-G$ in the semimetal state. The pressure p in this case affords a workable parameter for obtaining small values of $|G|$.

The indicated choice of orientation of H ensures a qualitative difference between the variation of G in a magnetic field and the hypothesized variation of Δ with the system subjected to the same influence. Thus, it is possible to create any value of $|G|$ for different values of H and to investigate the EI phase over its entire probable region of existence.

The conditions described above are realized in $Bi_{1-x}Sb_x$ alloys near the transition pressure $p = p_k$ with the magnetic field H oriented along the binary axis C_2. For this orientation of H the levels L_s and L_a, which are separated by the direct gap ε_g, approach one another at the rate $\partial\varepsilon_g/\partial H \simeq -0.08$ meV/kOe. The top of the valence band at T (the level $T_{4\bar{5}}$) gradually drops in this case relative to the middle of the gap ε_g, so that the gap G

between L and T varies at the rate $\partial G/\partial H \simeq -0.005$ meV/kOe $\simeq -0.06$ K/kOe.[22,26]

The metal–semiconductor transitions in $Bi_{1-x}Sb_x$ alloys under these conditions were first investigated by the authors,[27] and the detection of the EI phase in a magnetic field was reported.

It was shown in Abrikosov's analysis of the EI phase in a semimetal of the Bi type in a magnetic field that second-order dielectric pairing is possible, in principle, if there are several (more than one) electron ellipsoids equivalently situated with respect to H. In particular, Abrikosov considered the case $H \| C_3$, for which all three electron ellipsoids at the L points of the Brillouin zone are equivalent to one another with respect to H. In the strong magnetic field limit, when the electrons at L and holes at T are "precipitated" into the last Landau levels, the hole Fermi momentum is three times the electron Fermi momentum. Under these conditions both first- and second-order pairing are possible, depending on whether electron–phonon or Coulomb coupling prevails.

In the case $H \| C_2$ two of the three electron ellipsoids are equivalently situated relative to H (for the third ellipsoid, H is perpendicular to the direction of elongation). The magnetic field direction $H \| C_2$ corresponds to equal cross sections (near the minimum) in the equivalent ellipsoids and the maximum cross section in the nonequivalent one. It is known that in Bi and $Bi_{1-x}Sb_x$ alloys the spin splitting exceeds the orbital splitting for small electron cross sections, whereas the situation is reversed for a large cross section.[22,26] As a result, the last Landau level, which is identically situated in each of the equivalent ellipsoids, turns out to be below the last Landau level in the nonequivalent ellipsoid. Consequently, in a strong magnetic field all the electrons are transferred over into the two equivalent ellipsoids, thus emptying the nonequivalent ellipsoid. Thus, the situation for $H \| C_2$ is exactly identical to the one treated by Abrikosov, the only difference being that now only two equivalent electron ellipsoids are involved and the hole Fermi momentum is twice the electron Fermi momentum in the strong magnetic field limit. This changes the numerical coefficients in the final equations, but does not qualitatively affect the pairing scheme.

5. CHARACTERISTICS OF METAL–SEMICONDUCTOR TRANSITIONS IN BISMUTH–ANTIMONY ALLOYS IN A STRONG MAGNETIC FIELD

We have investigated the dependence of the longitudinal magnetoresistance ρ_{22} of semimetal alloys $Bi_{1-x}Sb_x$ on the temperature and magnetic field H in the metal–semiconductor transition region under pressure. The

measurements were performed in samples having Sb concentrations $x = 0.0275$, 0.049, and 0.055. The alloys had the following concentrations of alloying impurities: $\sim 2 \times 10^{15}\,\mathrm{cm}^{-3}$ (n type); $\sim 6 \times 10^{13}\,\mathrm{cm}^{-3}$ (n type); $1 \times 10^{14}\,\mathrm{cm}^{-3}$ (p type). The corresponding critical pressures p_k for transition to the semiconducting state were 17.5 ± 0.1 kbar, 10.8 ± 0.05 kbar, and 8.8 ± 0.05 kbar.

The Sb concentration in the alloy was determined with a Cameka x-ray microprobe at $\sim 5\%$ relative error.

The procedure used to create hydrostatic pressures up to 20 kbar and the magnetoresistance and temperature measurement techniques were similar to those to be described in the article in this journal (Vol. 8, Nos. 5/6) on the gapless state in $Bi_{1-x}Sb_x$ alloys.

The concentration N_i of alloying impurities and its type were determined by measuring the components of the magnetoresistance tensor in weak fields at $p \gtrsim p_k$.[25] The hole and electron relaxation times τ_e and τ_h in the region $p \sim p_k$ were calculated from these data. The pressure dependence of the effective masses as determined from the amplitude variation of the Shubnikov–de Haas oscillations with temperature for $p < p_k$ were used in the calculations.

The semiconductor transition pressure p_k was determined by three independent methods: (a) by extrapolation to zero of the pressure dependences of the extremal cross sections of the electron and hole ellipsoids at L and T, respectively, according to the period of the Shubnikov–de Haas oscillations in the semimetal state for[23] $p < p_k$; (b) from the minimum of the pressure dependence of the magnetic field $H = H_m$ at which the longitudinal magnetoresistance ρ_{22} for $i \| H \| C_2$ (i is the current in the specimen) passes through a maximum[23]; it has been shown in Ref. 23 that H_m is proportional in the semimetal state ($p < p_k$) to the extremal cross section S_e of the electron ellipsoid at L and in the semiconducting state to the energy gap G between the bands at L and T; for $S_e = 0$ and $G = 0$ ($p = p_k$) the value of H_m passes through a minimum; and (c) by extrapolation to zero of the pressure dependence of the gap G in the alloy as determined from the temperature dependences of the resistance ρ_{22} for various pressures $p > p_k$.

The measurements corresponding to method (c) also enabled us to determine the value of $\partial G/\partial p$ for $p \gtrsim p_k$, which was identical for all the alloys within the experimental error limits, amounting to $\partial G/\partial p \simeq 1.35$ meV/kbar. This value agrees with earlier results.[23,25]

With regard to the determination of the gap G between the bands at L and T from the temperature dependence of ρ_{22}, the following consideration is essential. In the semiconducting state at $p > p_k$ the $Bi_{1-x}Sb_x$ alloys represent double-gap semiconductors, with an indirect gap G between the bands at L and T and a direct gap ε_g between the bands at L. The energy

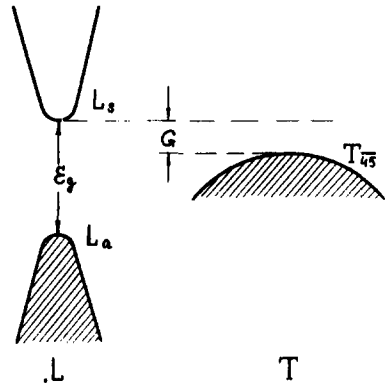

Fig. 4. Diagram of the bands in the energy spectrum of $Bi_{1-x}Sb_x$ alloys in the semiconducting state.

spectrum near the Fermi level is shown for this state in Fig. 4. This and the other gap increase with the pressure in the interval $p > p_k$. However, near $p \simeq p_k$ the gap $G \simeq 0$, whereas the gap ε_g, according to Ref. 23, is greater than or of the order of 10 meV. In the pressure interval in which G is small ($G < 5$–7 meV) the dependences of ρ_{22} on T for $1.8 \leq T < 50$ K clearly exhibit two exponential sections corresponding to the two values of the gaps in the spectrum. In the low-temperature interval ($T < 15$ K) the generation of carriers through the smaller gap G is determinant. The important fact here is that the density of states at the T point exceeds the density of states at the L point because $m_h^* > m_e^*$. Consequently, the gap G can be determined fairly accurately from the low-temperature exponential part of the curve $\rho_{22}(T)$.

In the temperature range $T < 15$ K the experimental curves of $\sigma_{22} = 1/\rho_{22}$ vs. T at $H \geq 5$ kOe are well described by a function of the form $\sigma_{22}(T) - b \sim e^{-G/T}$ with the one unknown parameter b. In other words, the dependence of σ_{22} on T in the coordinates $\ln[\sigma_{22}(T) - b]$, $1/T$ is linearized for a single value of b. The corresponding value of b was found by the method of least squares. The parameter b therefore determines the theoretical value of σ_{22} at $T = 0$ K and is denoted henceforth by $\sigma_{22}(0\text{ K})$.

The temperature dependences of the longitudinal magnetoresistance ρ_{22} for different magnetic fields and different pressures $p \lesssim p_k$ and $p \gtrsim p_k$ exhibit the same qualitative behavior for all three alloys. However, the singular features in the behavior of the alloy in a magnetic field at $p \simeq p_k$, which in our estimation are attributable to the inception of the EI phase, are the most pronounced for the purest alloy, $Bi_{0.951}Sb_{0.049}$. The data for this alloy make it possible to determine certain quantitative parameters of the EI (Δ, T_c, the critical values of the magnetic field, etc.). For brevity, therefore, the quantitative laws having a character common to all the alloys are given here only for $Bi_{0.951}Sb_{0.049}$.

The resistance ρ_{22} is observed to decrease as the magnetic field is increased ($\partial\rho_{22}/\partial H < 0$) for the alloys of all concentrations in regions sufficiently far removed from the metal–semiconductor transition (with respect to the pressure, by more than $\sim$0.07 kbar for $p > p_k$ or $p < p_k$, corresponding at $H = 0$ to a value of $|G| \sim 1.0$ meV) for $H > 5$–10 kOe at a fixed temperature.

This experimental fact corresponds to an increase in the carrier concentration in a strong magnetic field H due to an increase in the statistical degeneracy of the Landau levels and to the motion of the band boundaries at L and T for the selected orientation of H. We recall that for $H \| C_2$ the gap G decreases in the field in the semiconducting state ($p > p_k$), while in the semimetal state ($p < p_k$) the band overlap $-G$ increases.

Curves of ρ_{22} as a function of T^{-1} for various values of H from 10 to 70 kOe in the pressure interval "far" from $p = p_k$ are shown for $Bi_{0.951}Sb_{0.049}$ in Fig. 5 ($p = 10.3$ kbar $< p_k = 10.8$ kbar) and Fig. 6 ($p = 11.6$ kbar $> p_k = 10.8$ kbar). Figure 6 is plotted in coordinates of $-\ln[\sigma_{22}(T) - \sigma_{22}(0\text{ K})] + \text{const}$ vs. T^{-1}. Figure 5 corresponds at $H = 0$ to the semimetal state with a band overlap $-G \simeq 7.5$ K. Figure 6 corresponds at $H = 0$ to the semiconducting state with a gap $G = 12.5$ K. The curves of ρ_{22} as a function of T^{-1} for $Bi_{0.951}Sb_{0.049}$ at $p < 10.3$ kbar and at $p > 11.6$ kbar are qualitatively

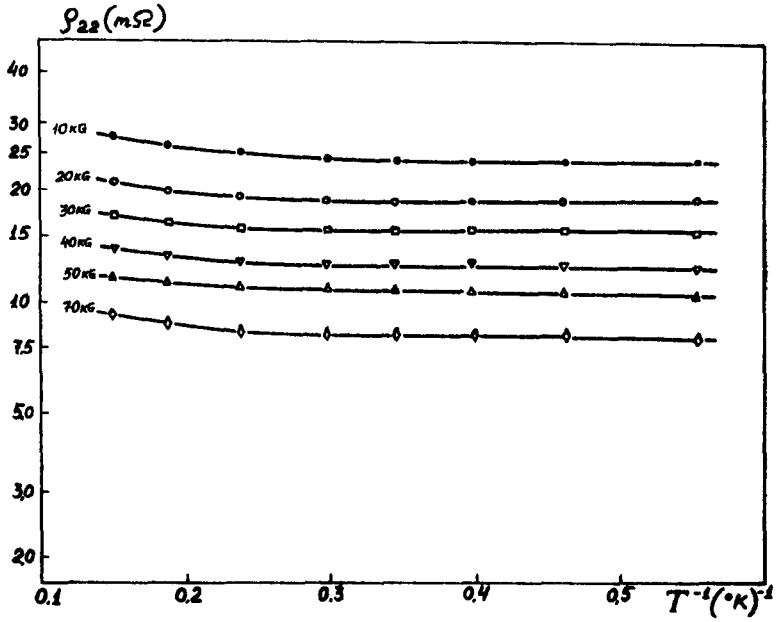

Fig. 5. Longitudinal magnetoresistance ρ_{22} (log scale) vs. T^{-1} for the alloy $Bi_{0.951}Sb_{0.049}$ at a pressure $p = 10.3$ kbar ($p < p_k$, "far" pressure zone) for various values of the magnetic field H parallel to the axis C_2.

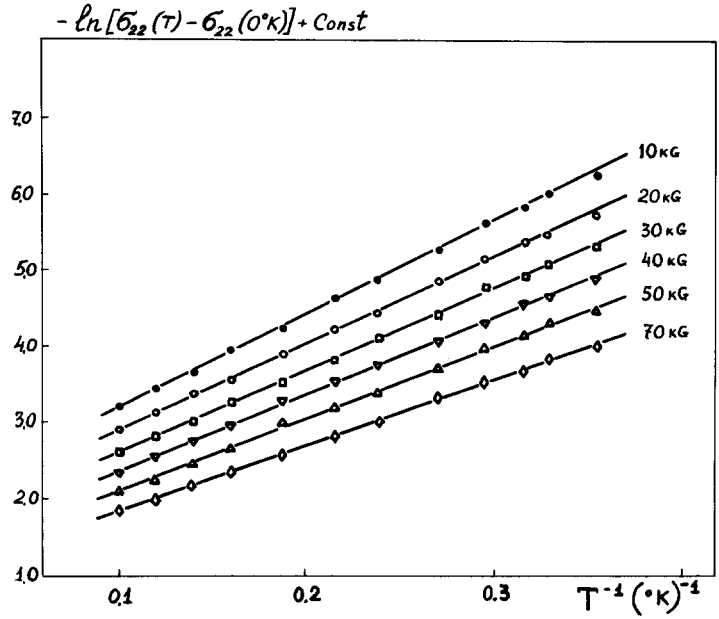

Fig. 6. Curves of $-\ln[\sigma_{22}(T) - \sigma_{22}(0\,\mathrm{K})] + \mathrm{const}$ vs. T^{-1} for the alloy $Bi_{0.951}Sb_{0.049}$ at a pressure $p = 11.6$ kbar ($p > p_k$, "far" pressure zone) for various values of the magnetic field H parallel to the axis C_2 (semiconducting state).

similar to the corresponding curves of ρ_{22} as a function of T^{-1} in Figs. 5 and 6.

The data of Fig. 6 can be processed to calculate the gap G for various values of H. The dependence of G on H for $Bi_{0.951}Sb_{0.049}$ at $p = 11.6$ kbar is shown in Fig. 7. The linear decrease of G in the magnetic field is characterized by the derivative $\partial G/\partial H$. This quantity is practically independent of the pressure for the alloys of every concentration in the interval $p > p_k +$ (0.7–1) kbar, amounting to $\partial G/\partial H \simeq -0.06$ K/kOe. The value obtained for $\partial G/\partial H$ is in good agreement with the corresponding value of ~ -0.05 K/kOe found for $H \| C_2$ in the case of semiconducting alloys $Bi_{1-x}Sb_x$ on the basis of the data of Ref. 26.

In the immediate vicinity of the transition point $p = p_k$ all the investigated alloys disclosed a qualitative change in the magnetic field dependence of ρ_{22}. This singular feature is visibly illustrated in Figs. 8a and 9a, which show the dependence of ρ_{22} on T for $Bi_{0.951}Sb_{0.049}$ at $p = 10.65$ kbar and $p = 11.1$ kbar, respectively. The interval of pressures "near" $p = p_k$ is marked by the fact that the "overlap-gap" $|G|$ does not exceed ~ 10 K at $H = 0$. In this interval ρ_{22} decreases in a magnetic field only for $H < 30$ kOe, over the

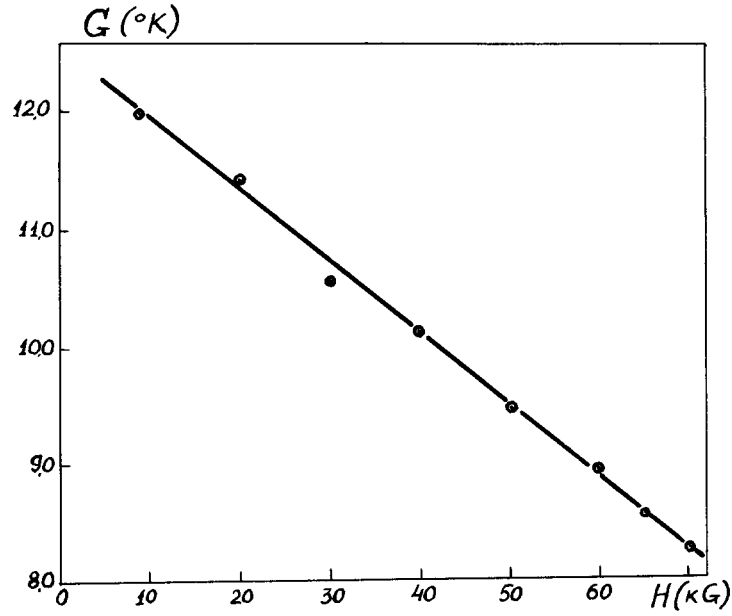

Fig. 7. Semiconductor gap G vs. the magnetic field $H \| C_2$ for the alloy $Bi_{0.951}Sb_{0.049}$ at a pressure $p = 11.6$ kbar.

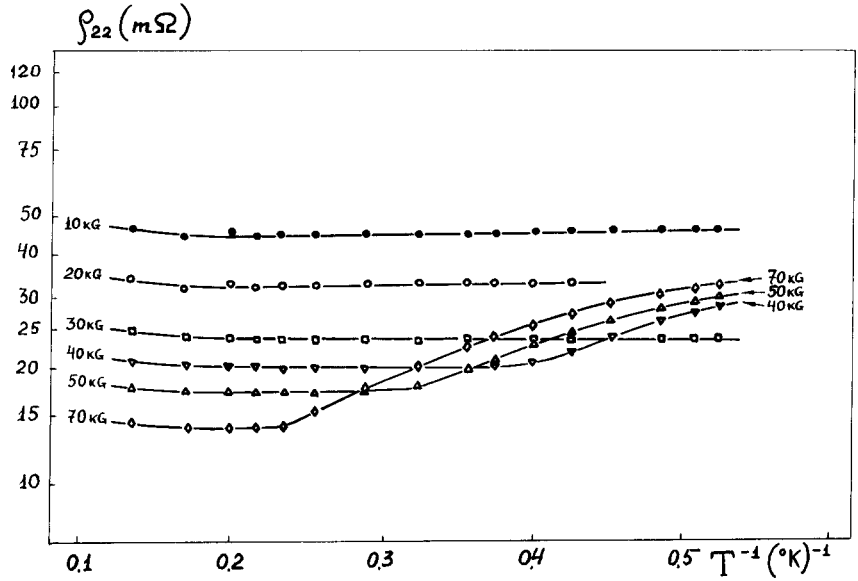

Fig. 8a. Longitudinal magnetoresistance ρ_{22} (log scale) vs. T^{-1} for the alloy $Bi_{0.951}Sb_{0.049}$ at a pressure $p = 10.65$ kbar ($p < p_k$, "near" pressure zone) for various values of the magnetic field H parallel to the axis C_2.

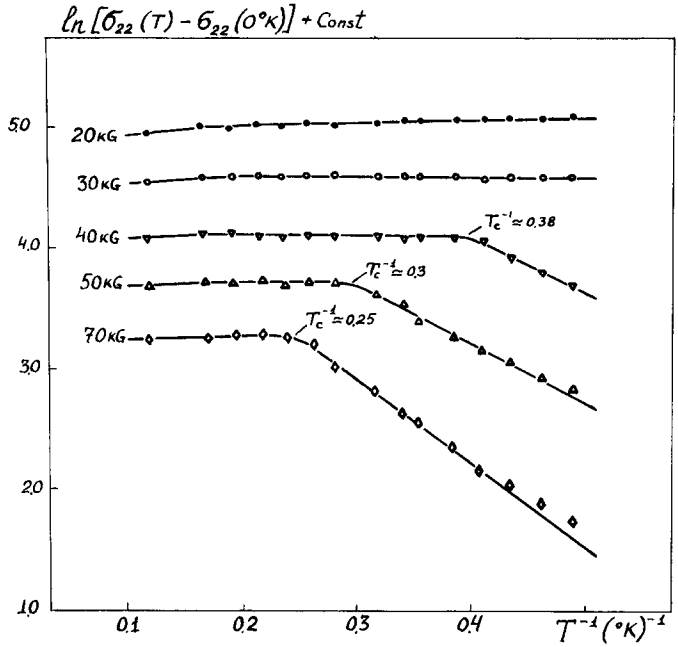

Fig. 8b. Curves of $\ln[\sigma_{22}(T) - \sigma_{22}(0\,\mathrm{K})] + \mathrm{const}$ vs. T^{-1} for the alloy $Bi_{0.951}Sb_{0.049}$ at a pressure $p = 10.65$ kbar ($p < p_k$, "near" pressure zone) for various values of the magnetic field H parallel to the axis C_2. The ordinate positions of the individual curves is arbitrary (for $H = 20$ and 30 kOe the curves represent the dependence of $\ln[\sigma_{22}(T)] + \mathrm{const}$ on T^{-1}).

entire range of investigated temperatures. For $H > 30$–40 kOe and high temperatures a decrease in ρ_{22} continues to be observed, whereas at low temperatures ($T \sim 1.8$–2.0 K), all other conditions being equal, an increase in ρ_{22} is observed in the magnetic field ($\partial\rho_{22}/\partial H > 0$). This behavior of ρ_{22} as a function of H and T in the "near" pressure zone (10.65 kbar $\leq p \leq$ 11.1 kbar for $Bi_{0.951}Sb_{0.049}$) is in exact opposition to the value determined by variation of the carrier concentration in a magnetic field in the semimetal or semiconducting state and evinces the inception of a gap, which increases with H, in the energy spectrum of the alloy. This conclusion is purely qualitative and does not rest on any assumption as to the particular form of the temperature dependence of ρ_{22} or on the method of calculating the gap in the spectrum.

It is evident in Fig. 8a that ρ_{22} depends only weakly on the temperature at $p = 10.65$ kbar in weak fields, $H \leq 30$ kOe (semimetal state). In a magnetic field $H \gtrsim 40$ kOe, however, the dependence of $\ln \rho_{22}$ on T^{-1} acquires characteristic "kinks." In the vicinity of a kink the parameter σ_{22} (0 K) was determined from the low-temperature part of the curve. The temperature

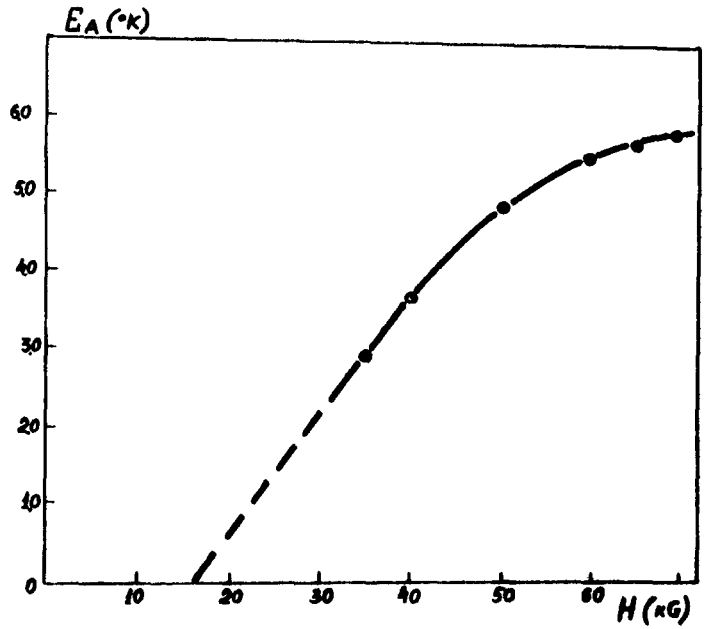

Fig. 8c. Activation energy E_A vs. magnetic field in the alloy $Bi_{0.951}Sb_{0.049}$ at a pressure $p = 10.65$ kbar and temperature $T = 2.0$ K.

T_c at which the kink occurs increases in the magnetic field. The ratio of the conductivity σ_{22} for T higher than T_c to σ_{22} (0 K) is ~2.5–4.5. The activation energy E_A referring to the temperature interval above the kink can be determined from the sloping parts of the curves of $\ln [\sigma_{22}(T) - \sigma_{22}(0\text{ K})]$ vs. T^{-1} for $T < T_c$ (Fig. 8b). The dependence of E_A on H for the alloy $Bi_{0.951}Sb_{0.049}$ at $p = 10.65$ kbar is illustrated in Fig. 8c.

It is obvious from Fig. 9a that the dependence of $\ln \rho_{22}$ on T^{-1} at $p = 11.1$ kbar and $H \leq 20$ kOe corresponds to the semiconducting state of the alloy with a positive activation energy E_A. For $H \geq 30$ kOe the curves of $\ln \rho_{22}$ vs. T^{-1} also acquire kinks, implying that a certain temperature T_c depending on H a change occurs in the activation energy E_A in the alloy. The temperature T_c also increases in the magnetic field. Each kink represents a transition from a smaller value of E_A at $T > T_c$ to a larger value of E_A at $T < T_c$. Moreover, after the kinks appear for $H \geq 30$ kOe, the slope of the low-temperature (below T_c) parts increases, while the slope of the high-temperature (above T_c) parts decreases with an increase in the magnetic field. This behavior on the part of the slope clearly ties the high-temperature parts in with the semiconducting state, the low-temperature parts with the excitonic insulator state.

The dependence of the activation energy E_A on H for the low-temperature parts of the curves in Fig. 9a is given in Fig. 9b.

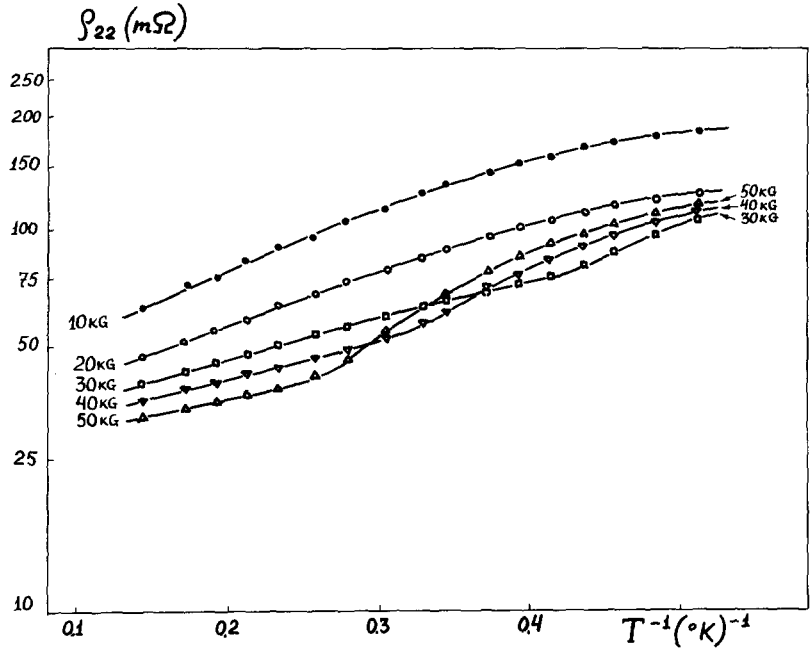

Fig. 9a. Longitudinal magnetoresistance ρ_{22} (log scale) vs. T^{-1} for the alloy $Bi_{0.951}Sb_{0.049}$ at a pressure $p = 11.1$ kbar ($p > p_k$, "near" pressure zone) for various values of the magnetic field H parallel to the axis C_2.

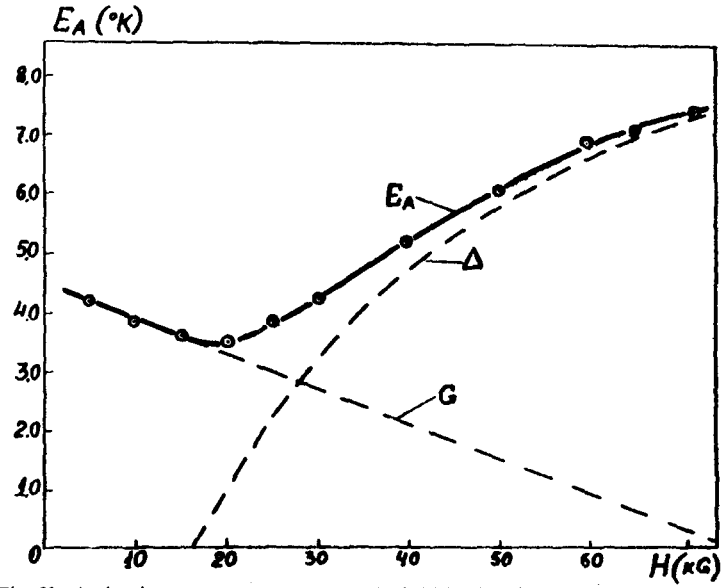

Fig. 9b. Activation energy E_A vs. magnetic field in the alloy $Bi_{0.951}Sb_{0.049}$ at a pressure $p = 11.1$ kbar and temperature $T = 2.0$ K. The dashed curves give the dependence of G on H and the hypothesized dependence of Δ on H.

6. DISCUSSION

We have investigated the longitudinal magnetoresistance of three different $Bi_{1-x}Sb_x$ alloys in the vicinity of the metal–semiconductor transition under pressure. The direction of the magnetic field was intentionally chosen so that the resistance of the alloys would diminish with increasing H ($\partial\rho_{22}/\partial H < 0$) in both the semimetal ($p < p_k$) and semiconducting ($p > p_k$) states. In the immediate vicinity of the transition point (for $|G| \lesssim 1$ meV) in fields $H \gtrsim 30$–40 kOe a change of sign of the derivative $\partial\rho_{22}/\partial H$ was observed. This qualitative singularity, which occurs for small values of the "overlap-gap" G, is independent of the concentration and type of alloying impurity in the alloy and is, in our opinion, primary evidence of the formation of an excitonic insulator in the magnetic field.

The nature of the effect observed in the "near"-transition zone is reminiscent of the carrier "freeze-out" effect in a magnetic field, as first observed by Keyes and Sladek[28] in specimens of n-type InSb. In our situation, however, the freeze-out of carriers would have to be observed over the entire semiconductor domain for $p > p_k$, regardless of the proximity to the transition pressure p_k. Indeed, as we move farther away from p_k toward either decreasing or increasing pressures, the change of sign of $\partial\rho_{22}/\partial H$ occurs in ever-larger fields. An increase in the pressure from p_k to p_k + (0.7 or 0.8) kbar (corresponding at $H = 0$ to a variation of the gap G from 0 to ~ 1 meV) causes the effect to vanish over the entire interval of fields $H \leq 70$ kOe in which the measurements were performed, and $\partial\rho_{22}/\partial H$ to become negative in accordance with the motion of the band boundaries in the spectrum of the initial alloy under the action of the magnetic field. The acutely local character of the freeze-out of carriers in a magnetic field cannot possibly be attributed to variation of the electron mass at the bottom of the band under pressure. It is a well-known fact that the conditions for freeze-out are improved with an increase in the carrier effective mass.[29,30] An increase in the electron effective mass in a semiconductor can lead to the detachment of donor levels from the conduction band, even in the absence of a magnetic field. This "spontaneous freeze-out" effect has been observed in n-type semiconducting alloys $Bi_{1-x}Sb_x$ by Brandt and others.[25] In our case, however, the electron effective mass at the bottom of the band at L increases under pressure, at least for $p > p_k$, owing to the increase in the direct gap ε_g at the L point,[23] so that the conditions for carrier freeze-out in a magnetic field could only be improved, but never worsened, with distance from the transition point on the $p > p_k$ side.

Also characteristic is the fact that for $H = 0$ (as well as in relatively weak fields $H \lesssim 25$ kOe) the system does not exhibit any singularity, but behaves as a semimetal for $p < p_k$ (see the curves for $H = 10$, 20, and 30 kOe

in Fig. 8a) or as a semiconductor for $p > p_k$ (see the curves for $H = 10$ and 20 kOe in Fig. 9a), independently of the proximity to the zero-gap state $G = 0$. These data indicate that the formation of bound states in the system takes place only after a certain threshold magnetic field H_c, the value of which depends on the G of the initial system and on the temperature. In the semiconducting state of the initial spectrum ($p > p_k$) the existence of the threshold value H_c for given G and T can be explained by the fact that the formation of the EI phase is based on satisfaction of inequalities (3) and (8), owing to the increase in the exciton binding energy E_B (11). For the semimetal state of the initial spectrum ($p < p_k$) the threshold field H_c is related to satisfaction of inequalities (8) and (12).

The data obtained in magnetic fields up to 70 kOe reveal that as H is increased the interval of values of $|G|$ in which bound states occur expands continuously. However, these data are not sufficient to explain whether the interval of existence of the EI phase merely increases with H or whether, after a certain value of H, begins to decrease (as would be expected on the basis of Abrikosov's study for the case of an unrearranged semimetal system). A detailed analysis of Figs. 8a, 8b, and 9a indicates that in a magnetic field a system having properties similar to those of an EI occurs in the "near" zone to $p = p_k$. Figures 8a and 8b clearly demonstrate the fact that in the alloy $Bi_{0.951}Sb_{0.049}$ at pressures $p = 10.65$ kbar in magnetic fields $H > 30$ kOe a variation (decrease) of the temperature induces phase transitions from a state with zero activation energy (semimetal) to a state with a finite activation energy (EI). It is evident in Figs. 8a and 8b that the transition temperature T_c and activation energy E_A increase with the magnetic field. Thus, for $H = 50$ kOe we have $E_A \simeq 4.8$ K and $T_c \simeq 3.3$ K, while for $H = 70$ kOe we have $E_A \simeq 5.9$ K and $T_c \simeq 4.1$ K. The reasonably linear behavior of the dependence of $\ln[\sigma_{22}(T) - \sigma_{22}(0\,\mathrm{K})]$ on T^{-1}, beginning almost immediately for $T < T_c$, indicates that E_A (or Δ in the EI case) is practically independent of T for $T < T_c$ and falls rapidly to zero for $T \sim T_c$. This corresponds to the theoretical similarity of the EI and superconductor spectra. On the other hand, Figs. 8a and 8b show that if the magnetic field is increased and the temperature held constant a phase transition takes place in the system from a state with zero activation energy E_A to a state with a finite value of E_A. At each temperature T it is possible to determine the critical value H_c at which bound states set in. This means, in fact, that for a given value of G in a zero field it is possible to plot the dependence of T_c on H corresponding to the critical field curve for a superconductor (we point out, however, that in the case of the EI, unlike the superconductor, for which T_c decreases as the magnetic field is increased, an increase in T_c is observed). For the EI this curve is strongly dependent on the value of G in the spectrum of the unrearranged system. Figure 8c illustrates the mag-

netic field dependence of the activation energy E_A (gap Δ for the EI) corresponding to Figs. 8a and 8b. The values of E_A are found from the slope of the low-temperature parts of $\ln [\sigma_{22}(T) - \sigma_{22}(0\,\mathrm{K})]$. The form of the curve of E_A vs. H distinctly illustrates the existence of the threshold field H_c at which the EI phase is initiated in a semimetal with a band overlap $-G$ for $H = 0$. The initial growth of E_A, which is almost linear, is slowed down in strong fields. This is consistent with Abrikosov's theoretical analysis,[20] according to which the EI gap Δ increases linearly at first, passes through a maximum at a certain H value, and then decreases.

Figure 9a shows the formation of the EI phase in the unrearranged semiconductor spectrum. It is clear that for $T < T_c$ the activation energy increases with the magnetic field, a situation that must be extremely probable in the EI. The activation energy for $T > T_c$ decreases as the magnetic field is increased, consistent with the behavior of a semiconductor system. Thus, a kink occurs at the phase transition from semiconductor to EI. For $T \sim T_c$ the activation energy changes from a value $E_A = G$ (in the semiconductor) to a value $E_A = \sqrt{G^2 + \Delta^2}$ (in the EI).[18] For example, for $H = 30$ and 40 kOe and the corresponding temperatures ~ 2.3 and ~ 3.3 K the EI is annihilated, becoming transformed to a semiconductor with G equal to ~ 2.7 and ~ 2.1 K. The curves of Fig. 9a also indicate that the EI gap Δ varies rapidly with the temperatures at $T \sim T_c$ and then has a weak dependence on T for $T < T_c$. The activation energy corresponding to the low-temperature parts of the curves in Fig. 9a decreases slightly at first with increasing H, passes through a minimum at $H \sim 20$ kOe, and then increases (Fig. 9b). This behavior on the part of E_A vs. H can be attributed to the fact that it describes two effects: a decrease in the semiconductor gap G in fields smaller than a certain threshold value ($E_A = G$), and then the combination of the decreasing semiconductor gap G with the growing EI gap Δ ($E_A = \sqrt{G^2 + \Delta^2}$). The postulated form of the dependence of Δ and G on H is represented by the dashed curve in Fig. 9b.

Finally, we have in concurrence with the theoretical conception of the EI phase the qualitative fact that for each value of H the temperature T_c is smaller than Δ. The proportionality factor $\alpha = T_c/\Delta$ can be determined from the data. The approximate value of α is ~ 0.7 for both the unrearranged semimetal spectrum and the semiconductor spectrum. We point out the curious fact that this value of α practically coincides with the value of $\alpha = 0.72$ obtained in Ref. 6 for an EI at $H = 0$ in the case of an isotropic unrearranged spectrum for $m_e^* \ll m_h^*$. The latter inequality is satisfied in $Bi_{1-x}Sb_x$ alloys, both for the effective masses in the direction of the axis C_2 and for the cyclotron masses with $H \| C_2$. As stated earlier, in the ultraquantum limit the anisotropy of the spectrum no longer plays any part. Consequently, the behavior of the $Bi_{1-x}Sb_x$ alloy in a strong magnetic field

becomes analogous to the behavior of a system with an isotropic spectrum for $m_e^* \ll m_h^*$. It may be assumed that this fact establishes a basis for agreement of the experimental and theoretical value of α, provided, of course, that the application of the magnetic field does not alter the coefficient α in relation (5). As shown by Abrikosov, for an EI formed in a magnetic field from a semimetal base by first-order pairing the value of α, as for a superconductor, is $\simeq 0.577$. This value is somewhat smaller than the experimental value $\alpha \simeq 0.7$.

Consequently, the experimental data are not contradictory, and we feel certain that the only way they can be explained is by postulating the formation of an excitonic insulator phase near the metal–semiconductor transition point in $Bi_{1-x}Sb_x$ alloys in a magnetic field. If the exciton insulator concept is rejected, the whole body of data sharply contradicts our cumulative notions concerning the band structure of $Bi_{1-x}Sb_x$ alloys and its magnetic-field- and pressure-induced changes.

The formation of the EI phase in a magnetic field in the alloy $Bi_{0.951}Sb_{0.049}$ is illustrated by the phase diagram of $\Delta_0(G)$ (Fig. 10). The arrows underneath the horizontal axis of Fig. 10 indicate the values of G (for $H = 0$) corresponding to the values of p at which the measurements were conducted. The experimental values of Δ were used to plot the gap functions for different values of H. The shift of the EI gap functions with increasing H corresponds to the predetermined motion of the band boundaries in the alloy under the influence of a magnetic field. At $p = 11.1$ kbar and $H = 70$ kOe the gap G of the unrearranged spectrum for the alloy is close to zero, so that the activation energy $E_A \simeq 7.5$ K determined under these conditions for the lowest temperature $T = 1.9$ K coincides with the maximum value Δ_{00} of the EI gap.

We now consider the type of pairing involved in light of the existing experimental data. According to the data of Ref. 23, the electron and hole cyclotron masses $(m_e^*)_c$ and $(m_h^*)_c$ in $Bi_{1-x}Sb_x$ alloys with $x < 0.065$ are $\sim(3\text{–}5) \times 10^{-3} m_0$ and $\sim 0.2 m_0$, respectively, in the metal–semiconductor transition region for $H \| C_2$. For an overlap energy $|G| \sim 1$ at $H = 0$ the electron cyclotron energy $\hbar\omega_e$ becomes of the same order as the electron Fermi energy ε_F^e in fields $H \sim 0.5$ kOe, whereas for holes the condition $\hbar\omega_h \sim \varepsilon_F^h$ is satisfied only in fields $H \sim 15\text{–}25$ kOe. It is in this field range, however, that the formation of bound states is observed for $p < p_k$. Consequently, the EI phase does not set in until after not only electrons at the L point, but also holes at the T point are precipitated to the last Landau level and inequality (12) holds for carriers of either type. This fosters the assumption that first-order pairing takes place in $Bi_{1-x}Sb_x$ alloys in a magnetic field, with the participation of electrons at L and holes at T. The same conclusion is inferred from an analysis of the ratio of the semimetal and EI

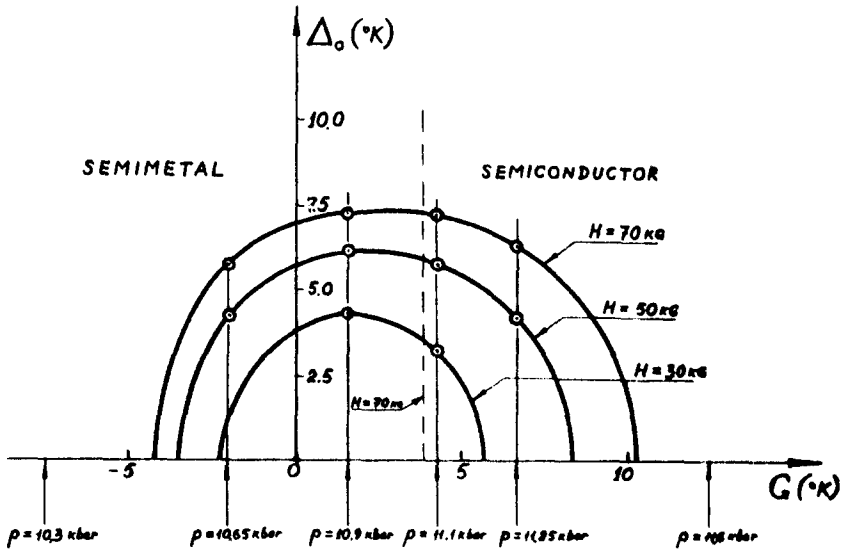

Fig. 10. Schematic diagram of the exciton insulator gap Δ_0 for various values of the magnetic field H vs. the "overlap-gap" G at $H = 0$ in the unrearranged spectrum of the alloy $Bi_{0.951}Sb_{0.049}$ ($T = 2.0$ K). The circles indicate the values of Δ_0 calculated for $p = 10.65$, 10.9, 11.1, and 11.3 kbar. The dashed line corresponds to the metal–semiconductor transition ($G = 0$) in the unrearranged system at $H = 70$ kOe.

conductivities (at $T = 0$ K) for different types of pairing. These arguments are developed in detail in Abrikosov's work.

ACKNOWLEDGMENTS

We wish to express our sincere appreciation to Profs. A. A. Abrikosov and L. V. Keldysh for their interest in the present study and for rewarding discussions.

REFERENCES

1. N. F. Mott, *Proc. Phys. Soc.* (*London*) **A62**, 416 (1949).
2. L. V. Keldysh and Yu. V. Kopaev, *Fiz. Tverd. Tela* **6**, 2791 (1964).
3. Yu. V. Kopaev, *Fiz. Tverd. Tela* **7**, 2902 (1965).
4. A. N. Kozlov and L. A. Maksimov, *Zh. Eksperim. Teor. Fiz.* **48**, 1184 (1965).
5. Yu. V. Kopaev, *Fiz. Tverd. Tela* **8**, 233 (1966).
6. A. N. Kozlov and L. A. Maksimov, *Zh. Eksperim. Teor. Fiz.* **49**, 1284 (1965).
7. D. Jerome, T. M. Rice, and W. Kohn, *Phys. Rev.* **158**, 462 (1967).
8. J. Zittars, *Phys. Rev.* **162**, 752 (1967).
9. J. Zittars, *Phys. Rev.* **164**, 575 (1967).
10. B. I. Halperin and T. M. Rice, *Rev. Mod. Phys.* **40**, 755 (1968).
11. L. V. Keldysh and A. N. Kozlov, *Zh. Eksperim. Teor. Fiz.* **54**, 978 (1968).

12. Yu. V. Kopaev, *Zh. Eksperim. Teor. Fiz.* **58**, 1012 (1970).
13. E. F. Gross, *Usp. Fiz. Nauk* **63**, 575 (1957)
14. B. P. Zakharchenya and R. P. Seisyan, *Usp. Fiz. Nauk* **97**, 193, (1969).
15. *Excitons in Semiconductors* (Collected Papers) (Izd. Nauka, Moscow, 1971).
16. R. J. Elliott and R. Loudon, *J. Phys. Chem. Solids* **8**, 382 (1959); **15**, 196 (1960).
17. H. Hasegawa and R. E. Howard, *J. Phys. Chem. Solids* **21**, 179 (1961).
18. Y. Yafet, R. W. Keyes, and E. N. Adams, *J. Phys. Chem. Solids* **1**, 137 (1956).
19. E. W. Fenton, *Phys. Rev.* **170**, 816 (1968).
20. A. A. Abrikosov, *J. Low Temp. Phys.* **2**, 37 (1970); **2**, 177 (1970).
21. E. W. Fenton, J.-P. Jan, and Å. Karlsson, *J. Low Temp. Phys.* **3**, 147 (1970).
22. G. E. Smith, G. A. Baraff, and J. M. Rowell, *Phys. Rev.* **135A**, 1118 (1964).
23. N. B. Brandt and S. M. Chudinov, *Zh. Eksperim. Teor. Fiz.* **59**, 1494 (1970).
24. W. S. Boyle and A. D. Brailsford, *Phys. Rev.* **120**, 1943 (1960).
25. N. B. Brandt, Kh. Dittmann, and Ya. G. Ponomarev, *Fiz. Tverd. Tela* **13**, 2860 (1971).
26. N. B. Brandt and E. A. Svistova, *J. Low Temp. Phys.* **2**, 1 (1970).
27. N. B. Brandt and S. M. Chudinov, *ZhETF Pis. Red.* **13**, 146 (1971).
28. R. W. Keyes and R. J. Sladek, *J. Phys. Chem. Solids* **1**, 143 (1956).
29. E. W. Fenton and R. R. Haerring, *Phys. Rev.* **159**, 593 (1967).
30. M. V. Ortenberg and G. Landwehr, *Phys. Stat. Sol.* **37**, K69 (1970).