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CONCERNING THE EFFECT OF PRESSURE ON THE ENERGY SPECTRUM OF THE ELECTRONS IN BISMUTH-ANTIMONY ALLOYS

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The effect of uniform compression at pressures up to 23 katm on the temperature dependence of the electrical resistance ρ and the Hall emf U_H is investigated in single crystals of bismuth-antimony alloys containing up to 12 at.% antimony. The study was carried out in various crystallographic directions and at temperatures between 2 and 295° K. It was found that alloys containing less than 5 at.% of antimony change under pressure from the semimetallic to a semiconductor phase; the energy gap thus produced increases with increasing pressure. The energy gap also increases with the pressure in alloys containing from 5 to 12.5 at.% of antimony. In the $Bi_{87.5}Sb_{12.5}$ alloy at a pressure of 18.5 katm the energy gap is $E_0 \approx 0.038$ eV. A maximum which shifts with increasing pressure to the low-temperature region is observed on the U_H temperature dependence curves for the $Bi_{87.5}Sb_{12.5}$ alloy.

THE electrical and galvanomagnetic properties of bismuth-antimony alloys have been investigated in a large number of papers.[1-6] Nonetheless, the energy spectrum of these alloys and the nature of their change with increasing antimony concentration remain to a large extent unclear. To obtain additional information on the energy spectrum of bismuth-antimony alloys, it is convenient to investigate the effect of uniform compression on the galvanomagnetic properties of these alloys. A similar technique was already applied in a study of oscillatory and galvanomagnetic effects in bismuth,[7-9] where it was established that uniform compression decreases the overlap ϵ_{OV} of the electron energy bands in bismuth. Measurements of the electrical resistance ρ of bismuth in a broad range of pressures[10-12] showed that with increasing pressure p the temperature dependence of the resistance of bismuth $\rho(T)$ assumes a "semiconducting nature."

An increase in the antimony concentration in bismuth also leads to decreasing overlap of the bands. Thus an admixture of about 1.65 at.% antimony decreases the overlap by a factor of 1.6.[1,2] At an antimony content of about 5 at.% the overlap ϵ_{OV} ceases; at higher antimony concentrations (up to 50 at.%) the alloy exhibits semiconducting properties in a broad range of temperatures.[3-6]

To explain the structure of the energy spectra in bismuth-antimony alloys, it is important to establish how far the analogy between the effect of antimony admixture and uniform compression extends. For this purpose we investigated the effect of the pressure on the galvanomagnetic properties of bismuth-antimony alloys up to antimony concentrations of 12.5 at. %. The alloys were prepared from 99.9999% pure bismuth and from spectrally pure antimony by zone leveling. The measurements were carried out on single-crystal samples 0.8–1 mm in diameter and 2.3–2.5 mm long with various orientations of the crystallographic axes, by a method described in [12], the pressures being produced by methods 2), 3), and 4) of that reference. The electrical measurements were carried out with direct current by the usual potentiometer method.

Figure 1 shows some curves of the temperature dependence of $\rho(T)/\rho_{295}$ for bismuth-antimony alloys of various concentrations at various pressures. An analysis of the curves shows that in a certain intermediate range of temperatures, 80–100 deg wide, the temperature dependence of the resistance of the alloys $Bi_{98.35}Sb_{1.65}$, $Bi_{95.9}Sb_{4.1}$ and $Bi_{95}Sb_5$ is of a semiconducting character at pressures above 14.5, 6, and 1 katm respectively, and for the alloys $Bi_{93.5}Sb_{6.5}$ and $Bi_{87.5}Sb_{12.5}$ in the entire pressure range.

The temperature corresponding to the lower boundary of this region increases with increasing pressure and antimony concentration and lies within the limits of 50 to 110° K. At lower temperatures the increase in the resistance is replaced by saturation which becomes particularly noticeable when the concentration of antimony is increased.

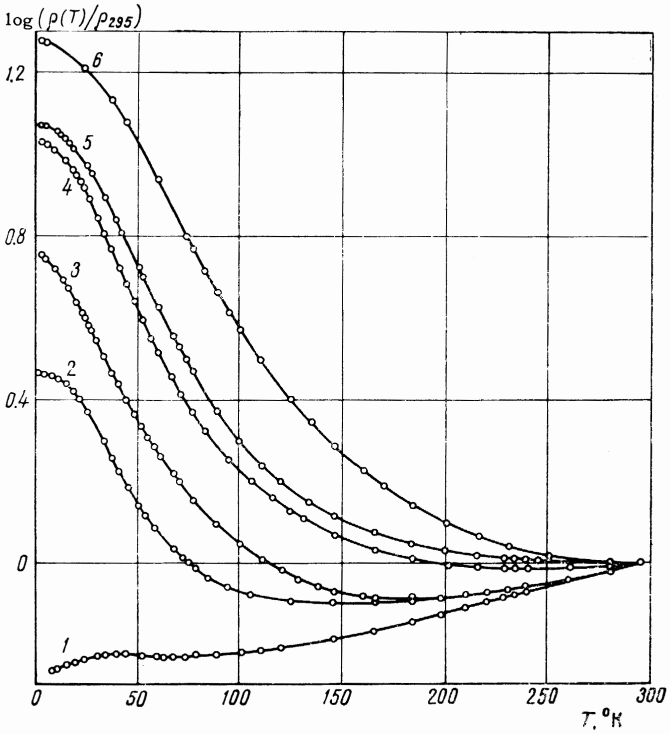

FIG. 1. Temperature dependence of the relative electrical resistance $\rho(T)/\rho_{295}$ in bismuth-antimony alloys: 1 – $Bi_{98.35}Sb_{1.65}$, no pressure; 2 – $Bi_{93.5}Sb_{6.5}$, p = 7.1 katm; 3 – $Bi_{98.35}Sb_{1.65}$, p = 21.8 katm; 4 – $Bi_{95.9}Sb_{4.1}$, p = 20.1 katm; 5 – $Bi_{93.5}Sb_{6.5}$, p = 18.3 katm; 6 – $Bi_{87.5}Sb_{12.5}$, p = 18.5 katm.

In the alloys $Bi_{98.35}Sb_{1.65}$, $Bi_{95.9}Sb_{4.1}$, and $Bi_{95}Sb_5$ at pressures below 14.5, 6, and 1 katm respectively, the $\rho(T)$ curves can be well described in a broad range of temperatures by a power-law dependence which is characteristic of band overlap.[12]

The temperature dependences of the Hall emf U(T) of the first three alloys, obtained in weak magnetic fields, also saturate at low temperatures; in $Bi_{87.5}Sb_{12.5}$ there appears a maximum in the U(T) curves and shifts with increasing pressure to low temperatures (Fig. 2). (The sign of the Hall coefficient is negative throughout.)

In the alloys $Bi_{98.35}Sb_{1.65}$, $Bi_{95.9}Sb_{4.1}$, and $Bi_{95}Sb_5$, in which without pressure there is overlap of the bands, the energy gap E_0 appearing under pressure was estimated by dividing the investigated $\rho(p, T)$ curve by the $\rho(0, T)$ curve obtained after the pressure was relaxed (see [12]). It was also assumed that the temperature dependence of the mobility for these curves at temperatures above 50° K is identical:

$$\rho(p, T) / \rho(0, T) \sim T^{3/2} U(0, T) / T^{3/2} \exp[-E_0/2kT] U(p, T)$$
$$\sim \exp[E_0/2kT].$$

For the alloys $Bi_{93.5}Sb_{6.5}$ and $Bi_{87.5}Sb_{12.5}$ the gap was estimated according to the formula[3-6]

$$\rho = \rho_0 \exp[E_0/2kT].$$

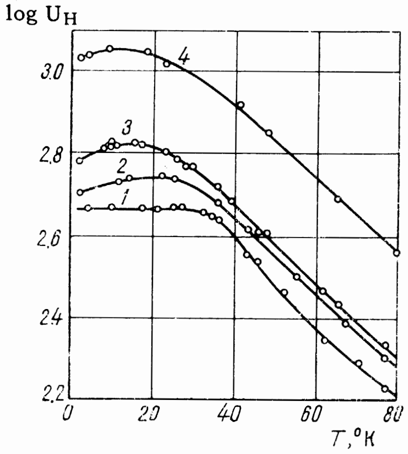

FIG. 2. Temperature dependence of the Hall emf in the alloy $Bi_{87.5}Sb_{12.5}$: curve 1 – p = 0; 2 – p = 2.1 katm; 3 – p = 4.6 katm; 4 – p = 18.5 katm.

Figure 3 illustrates the pressure dependence of the band overlap ϵ_{ov} and of the energy gap E_0 between the maximum of the valence band and the minimum of the conduction band in pure bismuth and in bismuth-antimony alloys. The band overlap ϵ_{ov} for pure bismuth at zero pressure (Δ) is taken to be 0.039 eV (nonquadratic dispersion law) and at 6.8 katm (□) it is calculated from results obtained in [8]. The values of ϵ_{ov} for alloys with antimony concentrations of 1.65, 4.1, and 5 at. % at zero pressure (∇) are calculated from data taken from [1, 2]. The zero overlap for pure bismuth (◇) was obtained from [12].

The values of $\partial\epsilon_{ov}/\partial p$ for pure bismuth (at pressures up to 8 katm) and for the alloys $Bi_{98.35}Sb_{1.65}$ and $Bi_{95.9}Sb_{4.1}$ (at pressures up to 6 katm) are of the form

Samples	Bi	$Bi_{98.35}Sb_{1.65}$	$Bi_{95.9}Sb_{4.1}$
$(\partial\varepsilon_{ov}/\partial p) \cdot 10^6$, eV/atm:	−1.85 [9] −1.9 [8]	−1.95 1) −1.55 2)	— −1.4 2)

For pure bismuth the value of $\partial\epsilon_{ov}/\partial p$ was taken from [9] and also calculated from the data of [8]. For the alloys indicated above the values of $\partial\epsilon_{ov}/\partial p$ were calculated from the pressure dependence of the Hall coefficient. In the alloys $Bi_{87.5}Sb_{12.5}$, $Bi_{93.5}Sb_{6.5}$, $Bi_{95}Sb_5$, and $Bi_{95.9}Sb_{4.1}$ these values do not depend to a first approximation on the pressure and decrease smoothly with increasing antimony concentration.

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1) Results of the calculation of the pressure dependence of the Hall coefficient obtained in this paper.

2) Values determined from the slope of the curves in Fig. 3.

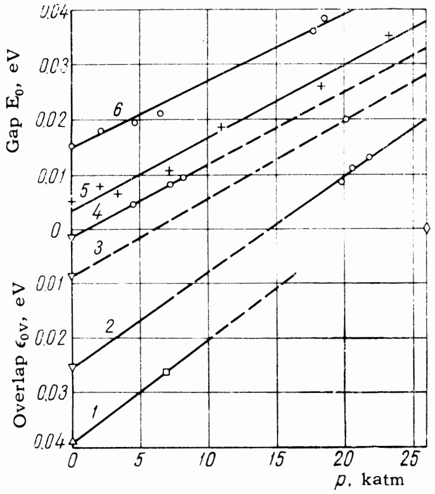

FIG. 3. Pressure dependence of the band overlap ϵ_{0v} and of the energy gap E_0 in pure bismuth and bismuth-antimony alloys: curve 1 – pure bismuth; 2 – $Bi_{98.35}Sb_{1.65}$; 3 – $Bi_{95.9}Sb_{4.1}$; 4 – $Bi_{95}Sb_5$; 5 – $Bi_{93.5}Sb_{6.5}$, 6 – $Bi_{87.5}Sb_{12.5}$.

It should be borne in mind that if bismuth goes over to the semiconducting phase in the region of high pressures, then this transition may be delayed, a circumstance which would lead to a distortion of the dotted line in Fig. 3.

It should be noted that in the processing of the results the relation $\rho = \rho_0 \exp(E_0/2kT)$ must be used with great care if it is assumed that the energy gap is small. Otherwise the effect due to weak overlap may be taken to be a manifestation of "semiconducting properties" of the investigated substance.

The matter is further complicated by the fact that when there is almost no overlap one begins apparently to note at sufficiently high temperatures a considerable contribution to the conductivity by the generation of carriers across the gap E_g, about 0.02 eV for pure bismuth (see also [3]), between the valence and conduction band along the direction of the two-fold axis of the reciprocal lattice. This is confirmed by data from [12] where it is possible to separate from the $\rho(T)$ curve of bismuth at a pressure of 24.5 katm and at a temperature above 75° K a contribution to the carrier concentration

$$\Delta n \sim T^{3/2} \exp(-0.022[\mathrm{eV}]/2kT).$$

It is interesting to note in this connection that in the $Bi_{98.35}Sb_{1.65}$ alloy at pressures of 19.8, 20.6, and 21.8 katm the curves $\log(n/T^{3/2}) = f(1/T)$ exhibit a point of inflection, and above 120° K they have approximately the same slope, which corresponds apparently to $E_g = 0.02$ eV.

According to the model of Jain, Cohen, and Blount[3] the admixture of antimony depresses the maximum of the valence band relative to the minimum of the conduction band, leading to the appearance of an energy gap. At the same time it is assumed that E_g remains constant. The data of this work allow us to assume that E_g increases with increasing antimony concentration.

In addition, a simple shift of the bands with respect to one another cannot explain the saturation effects of $\rho(T)$ and $U(T)$ in the bismuth-antimony alloys at low temperatures. A similar saturation may appear as a result of the insufficient purity of the initial bismuth. Otherwise it must be assumed that in bismuth-antimony alloys additional allowed states are produced in the electron spectrum of bismuth, as a result of which a redistribution of carriers takes place, the equal concentration of electrons and holes being conserved.

In conclusion we take this opportunity to express our sincere gratitude to A. I. Shal'nikov for interest in the work.

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50