DEPENDENCE OF THE ELECTRIC AND THERMOELECTRIC PROPERTIES OF
ANTIMONY ON PRESSURE

E. L. BROIDE

Ural Scientific Center of the Metal Physics Institute, USSR Academy of Sciences

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The diagonal components of the specific resistance tensor (\(\rho_{11}\) and \(\rho_{22}\)) for Sb are measured at a temperature \(T \sim 80^\circ K\) and a pressure \(P\) up to 10 kbar. Measurements are also made of the diagonal components of the specific thermal e.m.f. \(\sigma_{22}(0)\) and \(\sigma_{22}(0)\) at \(T_{AV} \sim 97^\circ K\) and \(T_{AV} \sim 300^\circ K\) and pressures \(P\) up to 14.5 kbar; the variation of the thermal e.m.f. tensor components in a transverse magnetic field (longitudinal Nernst-ETtingshausen effect) \(\xi_{11}(H_j)\) at \(T_{AV} \sim 97^\circ K\) and \(P\) up to 12 kbar; the temperature dependence of resistivity in a temperature range of 80–120°K at various pressures. The baric coefficient for variation of \(\rho_{33}\), \(\sigma_{33}(0)\), and \(d\rho_{33}/dT\) on pressure is greater than that for \(\rho_{22}\), \(\sigma_{22}(0)\), or \(d\rho_{22}/dT\) (the 3 refers to the trigonal axis and 2 to the bisector axis). The sign of \(\xi_{22}(H_j)\) changes at a pressure \(P \sim 4\) kbar and that of \(\xi_{33}(H_j)\) changes at a pressure \(P \sim 1.5\) kbar. \(\xi_{33}(H_j)\) does not change its sign in the pressure range studied.

Antimony belongs to the class of semimetals of group IV (Bi, Sb, As) which have a unit cell with two atoms located on a threefold axis. A structure of the Bi type is characterized by three parameters: the rhombohedral angle \(\alpha\), the cell parameter \(a\), and the distance \(u\) between the atoms along the threefold axis. Hydrostatic compression changes \(\sigma\), \(a\), and \(u\) of Sb in such a way that its structure gradually approaches the cubic one \(^{1,2}\). The elastic deformation of the energy spectrum of the carriers was calculated theoretically by Falicov \(^3\). A decrease in the overlap of the conduction and valence bands was predicted on the basis of the theory \(^{4,5}\). Moreover, according to the theory \(^{6,7}\), semimetals of group IV are promising crystals for use as thermal generators, in view of the anisotropy of the rhombohedral lattice. The figure of merit of the device increases strongly when placed in a magnetic field. Particularly vital is the region of magnetic fields and temperatures in which the properties change in \(a\) and \(a\). The experimental data on the deformation of the energy spectrum in Sb are scanty and quite contradictory \(^{8,9}\). The elastic deformation of the energy spectrum in Sb are scanty and quite contradictory \(^{8,9}\). Moreover, according to the theory \(^{10,11}\), semimetals of group IV are promising crystals for use as thermal generators, in view of the anisotropy of the rhombohedral lattice. The figure of merit of the device increases strongly when placed in a magnetic field. Particularly vital is the region of magnetic fields and temperatures in which the properties change in \(a\) and \(a\). The experimental data on the deformation of the energy spectrum in Sb are scanty and quite contradictory \(^{8,9}\).

We have measured the pressure dependences of the following: \(\rho_{11}\) — the resistivity at \(T \sim 80^\circ K\), \(d\rho_{11}/dT\) — the temperature coefficient of resistivity in the interval \(T \sim 77–120^\circ K\), \(\sigma_{11}(0)\) — the specific thermoelectric power at \(T \sim 97^\circ K\) (the longitudinal Nernst-Ettingshausen effect) up to 12 kbar. The subscripts denote the crystallographic directions: 1 — binary, 2 — bisector, and 3 — trigonal axis of the crystal.

We investigated antimony samples cut by the electric-spark method from a single-crystal ingot grown by the Bridgman method. The crystal was grown from Sb 99.999% pure. The orientation and the cutting of the samples were performed with accuracy \(2\)–\(3^\circ\). The dimensions of the samples were \(\sim 9 \times 1.5 \times 0.8\) mm. Before the measurements, the sample was mounted on a contact panel inside the high-pressure chamber. Two end-face heaters made it possible to produce a temperature gradient up to \(6^\circ\) in the sample, and also to vary the direction of the gradient. The measurements were performed by a null method with sensitivity not lower than \(10^{-7}\) V. The chamber was placed between the poles of a small electromagnet and dropped into a cryostat, where the setup, with fixed pressure, was cooled 3–4 hours to the temperature of liquid nitrogen. The constant magnetic field attained between the poles of the electromagnet did not exceed \(6\) kOe. The temperature dependence of resistivity in the interval \(77–120\) K. The obtained data are shown in Figs. 1 and 2. It is seen from these figures that the quantities \(\rho_{33}, \sigma_{33}(0)\), and \(d\rho_{33}/dT\) vary more strongly with pressure than \(\rho_{22}, \sigma_{22}(0)\), and \(d\rho_{22}/dT\). Figure 3 shows the variation of the thermoelectric power in the magnetic field with pressure for different orientations of the magnetic field relative to the crystallographic axes of the samples. Since Sb is subject to the Umkehrreffekt in this region of temperatures and magnetic fields, the quantity \(\xi_{11}(H_j)\) (the change of the thermoelectric power in the magnetic field) was defined as

\[
\xi_{11}(H_j) = \frac{\Delta a_{11}(H_j) + \Delta a_{33}(H_j)}{2a_{11}(0)}
\]

where \(\Delta a_{11} = a_{11}(H_j) - a_{11}(0)\). The values of \(\xi_{11}(H_j)\) were measured at a temperature \(T_{AV} \sim 98^\circ K\) and \(H = 3000\) Oe.

It is seen from Fig. 3 that \(\xi_{22}(H_j)\) and \(\xi_{33}(H_j)\) are positive at the pressure \(P = 0\) while \(\xi_{22}(H_j)\) and \(\xi_{33}(H_j)\) are negative. With increasing pressure, the signs of \(\xi_{22}(H_j)\) and \(\xi_{33}(H_j)\) are reversed at \(P \sim 4\) and 1.5 kbar, respectively. \(\xi_{33}(H_j)\) and \(\xi_{33}(H_j)\) remain negative in the entire investigated pressure interval.

Since the energy spectrum of the carriers of Sb is characterized by nine parameters and the data on their variation with pressure are limited, it is impossible for the time being to present a quantitative estimate of the observed effects.

If we assume that the relaxation time \(\tau\) is practically
FIG. 1. a—Pressure dependence of the temperature coefficient $\frac{dp_{ii}}{dT}$ in Sb, $T = 77-120^\circ K$, II—$dp_{zz}/dT$, III—$dp_{33}/dT$. The ordinates represent the slope of $p_{ii}(\Omega-cm)$ with respect to $T$. b—Relative pressure variation, at $T = 83^\circ K$, of the resistivity $\frac{\rho_{ii}(P)}{\rho_{ii}(0)}$. Curves I—$\rho_{zz}(P)/\rho_{zz}(0)$, II*$-\frac{\rho_{zz}(P)}{\rho_{zz}(0)}$ at $T_{av} = 300^\circ K$, II$^*$—$\rho_{33}(P)/\rho_{33}(0)$ at $T_{av} = 90^\circ K$.

FIG. 2

FIG. 3

Independent of the pressure, then the growth of $dp_{ii}/dT$ (Fig. 1a) with increasing pressure is due to the growth of the effective masses of the carriers. Such a conclusion agrees with the data of Minina and Lavrova.$^5$

At liquid-nitrogen temperature, antimony is characterized by two mechanisms of carrier-scattering by phonons, intravalley and intervalley.$^{14}$ In spite of the anisotropy of the equal-energy surfaces, as is well known, the relaxation time for these scattering mechanisms can be averaged $(\langle \tau_e \rangle, \langle \tau_p \rangle)$ with sufficient degree of accuracy and can be regarded as isotropic.

Using the expression for $\sigma_{11}$ and $\sigma_{33}$ and the values of the effective masses given in $^{13}$, we can conclude under the condition $\langle \tau_e \rangle \sim \langle \tau_p \rangle$ (scattering by acoustic phonons prevails in this temperature region) that when the pressure is increased the anisotropy of $\rho_{ii}(P)/\rho_{ii}(0)$ (Fig. 1b) increases, thus evidencing that the deformation of the electron ellipsoids exceeds the deformation of the hole ellipsoids. The reversal of the sign of the magnetothermal emf $\xi_{22}(H_1)$ and $\xi_{22}(H_3)$ under pressure cannot be explained.


6 N. B. Brandt and N. Ya. Minina, ZhETF Pis. Red. 7, 264 (1968) [JETP Lett. 7, 205 (1968)].

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