## DEPENDENCE OF THE ELECTRIC AND THERMOELECTRIC PROPERTIES OF

ANTIMONY ON PRESSURE

## E. L. BROÏDE

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

Submitted February 2, 1972

Zh. Eksp. Teor. Fiz. 63, 579-582 (August, 1972)

The diagonal components of the specific resistance tensor  $(\rho_{33}^3 \text{ and } \rho_{22})$  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.  $\alpha_{33}(0)$  and  $\alpha_{22}(0)$  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  $80-120^{\circ}$  K at various pressures. The baric coefficient for variation of  $\rho_{33}$ ,  $\alpha_{33}(0)$  and  $d\rho_{33}/dT$  on pressure is greater than that for  $\rho_{22}$ ,  $\alpha_{22}(0)$  or  $d\rho_{22}/dT$  (the 3 refers to the trigonal axis and 2 to the bisector axis). The sign of  $\xi_{22}(H_1)$  changes at a pressure P  $\sim 4$  kbar and that of  $\xi_{22}(H_3)$  changes at a pressure P  $\sim 1.5$  kbar.  $\xi_{33}(H_j)$  does not change its sign in the pressure range studied.

 $\mathbf{A}$  NTIMONY 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  $\alpha$ , a, and u of Sb in such a way that its structure gradually approaches the cubic one<sup>[1,2]</sup>. The elastic deformation of the energy</sup> spectrum of the carriers was calculated theoretically by Falicov<sup>[3]</sup>. A decrease in the overlap of the conduction and valence bands was predicted on the basis of the changes in  $\alpha$  and a. The experimental data on the deformation of the energy spectrum in Sb are scanty and quite contradictory [4-8]. Moreover, according to the theory<sup>[9-11]</sup>, 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 are strongly anisotropic. In Sb, this region occurs at liquid-nitrogen temperature [12]. It is therefore of interest to investigate the influence of hydrostatic compression on the components of the tensors of the kinetic coefficients in this intermediate region.

We have measured the pressure dependences of the following:  $\rho_{ii}$ -the resistivity at T ~ 80°K,  $d\rho_{ii}/dT$ the temperature coefficient of resistivity in the interval T = 77-120°K,  $\alpha_{ii}(0)$ -the specific thermoelectric power at T ~ 97°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 was plotted at fixed pressures 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  $\rho_{33}$ ,  $\alpha_{33}(0)$ , and  $d\rho_{33}/dT$  vary more strongly with pressure than  $\rho_{22}$ ,  $\alpha_{22}(0)$ , 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 Umkehreffekt in this region of temperatures and magnetic fields, the quantity  $\xi_{ii}(H_i)$  (the change of the thermoelectric power in the magnetic field) was defined as

$$\xi_{ii}(H_j) = \frac{\Delta \alpha_{ii}(H_j^+) + \Delta \alpha_{ii}(H_j^-)}{2\alpha_{ii}(0)}$$

where  $\Delta \alpha_{ii} = \alpha_{ii}(H_j^{\sharp}) - \alpha_{ii}(0)$ . The values of  $\xi_{ii}(H_j)$ were measured at a temperature  $T_{av} \sim 98^{\circ}$ K and at H = 3000 Oe.

It is seen from Fig. 3 that  $\xi_{22}(H_1)$  and  $\xi_{22}(H_3)$  are positive at the pressure P = 0 while  $\xi_{33}(H_1)$  and  $\xi_{33}(H_2)$ are negative. With increasing pressure, the signs of  $\xi_{22}(H_1)$  and  $\xi_{22}(H_3)$  are reversed at  $P \sim 4$  and 1.5 kbar, respectively.  $\xi_{33}(H_1)$  and  $\xi_{33}(H_2)$  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  $d\rho_{ii}/dT$ in Sb, T = 77-120°K, II- $d\rho_{22}/dT$ , III- $d\rho_{33}/dT$ . The ordinates represent the slope of  $\rho_{ii}(\Omega$ -cm) with respect to T. b-Relative pressure variation, at T ~ 83°K, of the resistivity  $\rho_{ii}(P)/\rho_{ii}(0)$ . Curves II- $\rho_{22}(P)/\rho_{22}$ (0), III- $\rho_{33}(P)/\rho_{33}(0)$ .



FIG. 2. Pressure dependence of the specific thermoelectric power  $\alpha_{ii}(0)$ . II $-\alpha_{22}(0)$ , III $-\alpha_{33}(0)$  at  $T_{av} \sim 300^{\circ}$ K. II $*-\alpha_{22}(0)$ , III $*-\alpha_{33}(0)$  at  $T_{av} \sim 90^{\circ}$ K.

FIG. 3. Pressure dependence of the change on the specific thermoelectric power in a transverse magnetic field at different directions of the magnetic field (H<sub>j</sub>) and of the temperature gradient:  $I-\xi_{22}(H_1)$ ,  $II-\xi_{22}(H_1)$ -sample purity 99.9999%,  $III-\xi_{22}(H_3)$ ,  $IV-\xi_{33}(H_2)$ ,  $V-\xi_{33}(H_1)$ .

independent of the pressure<sup>[4]</sup>, then the growth of  $d\rho_{\rm ii}/dT$  (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<sup>[5]</sup>.

At liquid-nitrogen temperature, antimony is characterized by two mechanisms of carrier-scattering by phonons, intravalley and intervalley<sup>[14]</sup>. In spite of the anisotropy of the equal-energy surfaces, as is well known, the relaxation time for these scattering mechanisms can be averaged  $(\langle \tau_{\mathbf{e}} \rangle, \langle \tau_{\mathbf{p}} \rangle)$  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<sup>[13]</sup>, we can conclude under the condition  $\langle \tau_{\rm e} \rangle \sim \langle \tau_{\rm h} \rangle$  (scattering by acoustic phonons prevails in this temperature region) that when the pressure is increased the anisotropy of  $\rho_{\rm ii}({\rm P})/\rho_{\rm ii}(0)$ (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  $\xi_{22}({\rm H}_1)$  and  $\xi_{22}({\rm H}_3)$  under pressure cannot be explained.

The author thanks A. N. Mezentsev, G. A. Kharus, and Ya. G. Ponomarev for a discussion of the results and N. B. Brandt for a useful discussion.

<sup>1</sup>L. F. Vereshchagin and S. S. Kabalkina, Zh. Eksp. Teor. Fiz. 47, 414 (1964) [Sov. Phys.-JETP 20, 274 (1965)].

 $^{2}$  B. Morosin and J. E. Shirber, Phys. Lett. 30A, 512, 1969.

<sup>3</sup> L. M. Falicov, Physics of Solid at High Pressures, ed. C. T. Tomisuka and Emrik, Acad. Press, 1965, p. 30.

<sup>4</sup> V. V. Kechin, Fiz. Tverd. Tela 9, 3595 (1967) [Sov. Phys.-Solid State 9, 2828 (1968)].

<sup>5</sup> N. Ya. Minina and V. V. Lavrova, Zh. Eksp. Teor. Fiz. 57, 354 (1969) [Sov. Phys.-JETP 30, 194 (1970)].

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

<sup>7</sup>J. E. Shirber and W. J. O'Sulliwan, Solid State Comm. 7, 709, 1969.

<sup>8</sup>S. Tanuma, S. Minomura, G. Fujii and W. R. Datars, Proc. of the XII Intern. Conf. on Low Temper. Phys.,

Kyoto, Japan, 1970, Acad. Press of Japan, 597, 1971.

<sup>9</sup>R. Wolf and G. Smith, Phys. Rev. **129**, 1086, 1963. <sup>10</sup>R. Wolf and G. Smith, J. Appl. Phys. Lett. **1**, 5, 1962.

<sup>11</sup>A. G. Samoilovich and I. I. Pinchuk, Fiz. Met. Metallov. 22, 32 (1966).

<sup>12</sup> Yu. A. Bogod and V. V. Eremenko, Zh. Eksp. Teor. Fiz. 53, 473 (1967) [Sov. Phys.-JETP 26, 311 (1968)].

<sup>13</sup> K. Tanaka, S. K. Suri and A. L. Jain, Phys. Rev. 170, 3, 1968.

<sup>14</sup> M. S. Bresler and N. A. Red'ko, Zh. Eksp. Teor. Fiz. 61, 287 (1971) [Sov. Phys.-JETP 34, 149 (1972)].

Translated by J. G. Adashko 60