

Resistivity of Antimony-Tin Single Crystals at Low Temperatures

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The electrical resistivity of single crystals of pure antimony and alloys of antimony containing small amounts of tin has been determined in the temperature range from 300°K to 4.2°K. In all cases the crystals were orientated such that [111] was perpendicular to the electric field, and various amounts of tin up to about three atomic percent were employed. All the alloys showed normal metallic properties, i.e., the resistivity decreased as the temperature was lowered. However, the average temperature coefficient of resistance between 4.2°K and 77.3°K decreases sharply with increasing tin content and assumes a small constant value at three atomic percent tin. While the addition of tin at room temperature changes the resistivity only slightly, the effect at liquid helium temperature is very large. This "residual" resistivity is approximately a parabolic function of the tin concentration. Qualitative comparison of these results with the Bloch theory of metals is made.

THE three metals, arsenic, antimony, and bismuth are well known to be relatively poor conductors of electricity and are among the few metals whose resistance in the liquid state is less than that for the solid. It has been shown that a Brillouin zone characteristic of the crystal structure of these metals will contain just five electronic states per atom, and the atoms of these metals contain just five electrons beyond the closed d shells (valency electrons). Since, however, these metals are not insulators, the inference is that some electrons overlap into a higher zone leaving an equal number of vacant states or positive holes in the first-mentioned zone. Since, as has been mentioned, the conductivity is small, the number of such overlapping electrons must likewise be small, and when the zone structure is destroyed by melting the lattice, the conductivity becomes comparable with that of the divalent metals.

In particular, if small amounts of tin are added to pure antimony, we should expect that the number of overlapping electrons would be reduced for the following reasons. First, tin, in small amounts, forms a simple substitutional solid solution with antimony, and hence the crystal parameters of the alloys are essentially the same as those for pure antimony. Hence, the antimony zone structure is preserved in the alloys. Second, due to the fact that tin has a valency of four, each added atom of this metal will remove one electron from the antimony structure.

Previously S. H. Browne and one of us have reported the effect on the magnetic properties of antimony of variation in the electron concentration by the above means.¹ The results of this investigation indicated that the overlap in antimony was approximately 10^{-2} electron per atom. In the present investigation the effect of varying the overlap on the temperature dependence of the electrical resistivity has been studied.

EXPERIMENTAL DETAILS

The single crystals were produced from the same materials and in the same manner as those used in the previous work referred to in reference 1. In some instances the same crystals were used again. As previously, no chemical analysis was made of the crystals, and the ingredients were accurately weighed and thoroughly mixed in a quartz crucible, under a hydrogen atmosphere, well above the melting point of antimony. The crystals averaged about three inches in length and one-eighth inch in diameter.

Current and potential leads of No. 40 copper wire were spot welded to each crystal. This was done by placing the crystal, the wire, and a ballast resistor of about 25 ohms in series with a d.c. source of potential of 24 volts and touching the wire momentarily to the crystal. Under a low power microscope the wire was seen to have melted into the crystal at the point of contact. In this way and because of the fineness of the wires,

¹S. H. Browne and C. T. Lane, Phys. Rev. **60**, 899 (1941).

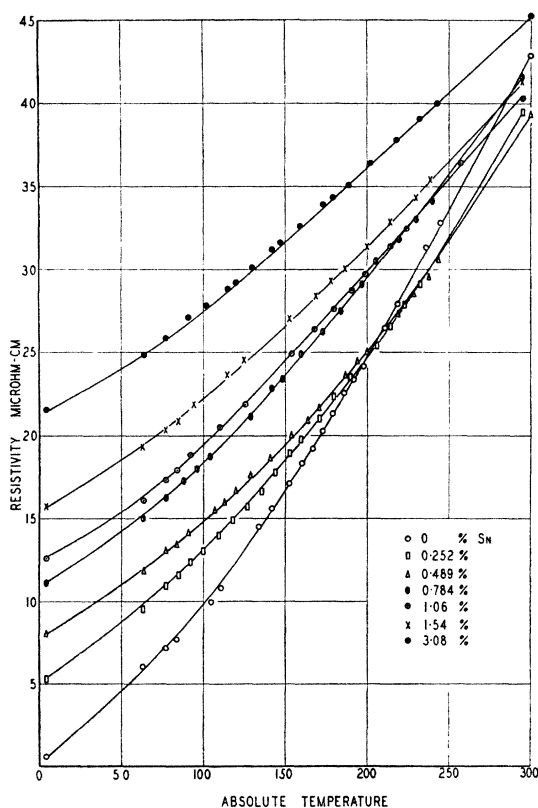


FIG. 1. Resistivity of antimony-tin single crystals from room temperature to 4.2°K.

electrical connection was established with as little disturbance as possible to the specimens.

The resistance of the specimens was determined potentiometrically by comparison with a one-thousandth ohm standard resistance. The current through the crystals, in most cases, was about 70 ma. Since thermoelectric effects in antimony, especially when different parts of the circuit are at widely different temperatures, are likely to be large, a standard type K potentiometer was adapted to the circuit described by Kapitza and Milner.² In this type of arrangement any unbalanced thermoelectric potential produces only a steady deflection of the galvanometer while actual e.m.f.'s are balanced dynamically, i.e., by observing the absence of galvanometer "kick."

This circuit proved very useful for our purposes, since not only were any spurious thermoelectric effects automatically eliminated, but in addition

the magnitude of the steady galvanometer deflection was a very sensitive measure of any temperature gradients along the specimen.

The specimens were mounted in a hard rubber holder at the bottom of a long narrow dewar flask of soft glass. The resistance was measured at room temperature and at the following fixed points: sublimation point of CO₂ (195°K), boiling point of ethylene (103°K), boiling point of pure oxygen (90.2°K), boiling point of pure nitrogen (77.3°K), near the triple point of nitrogen (ca. 64°K), and finally at the normal boiling point of liquid helium (4.2°K). All the above gases were liquefied by the use of liquid air with the exception of the last one, which was produced by the Kapitza helium liquefier in our laboratory.³

In order to obtain observations at a number of temperatures above that of liquid nitrogen, the dewar flask was allowed to warm up gradually from this temperature, the temperature of the specimen being determined by means of a copper-constantan thermocouple whose junction was cemented to the middle of the specimen. Since the warming-up period was of the order of several hours, a large number of resistance determinations at various temperatures could readily be made. If long (14 inches) and narrow (1½ inches) dewar flasks were used it was found that the temperature change along the specimens never exceeded 1°C at any time. The determinations made in this way were found to be in good agreement with those made at the oxygen, ethylene, and CO₂ fixed points.

In every case the crystallographic orientation of the specimens was such that [111] was perpendicular to the axis of the rod to within one degree. Hence in all instances the current was very approximately perpendicular to [111].

The cross-sectional area of the crystals was determined by observing the height to which a liquid (CCl₄) rose in a fine tube when a known length of crystal was immersed in a wider connecting tube. The apparatus was calibrated by observations on a piece of ⅛-inch drill rod. The distance between the potential leads was determined with a traveling microscope. The individual resistivities are probably accurate to about two percent.

² P. Kapitza and C. Milner, *J. Sci. Inst.* **14**, 165 (1937).

³ C. T. Lane, *Rev. Sci. Inst.* **12**, 326 (1941).

RESULTS AND DISCUSSION

Figure 1 is a plot of the resistivity in microhm cm in the whole temperature range for pure antimony and various alloys. Figure 2 shows the relation between the "residual" resistivity of the alloys as a function of the amount of contained tin. (Curve I). The residual resistance is taken to be equal to the resistance at 4.2°K.⁴ Curve II, Fig. 2, is a plot of the mean temperature coefficient of resistance (θ_{Av}) in the range 4.2°K to 77.3°K, as a function of alloy composition. In this case θ_{Av} is defined as the difference between the resistance at 77.3°K and 4.2°K divided by the resistance at 77.3°K.

An inspection of Fig. 1 shows that all the alloys behave as "normal" metals, that is, the resistance decreases more or less linearly as the absolute temperature is reduced. No negative temperature coefficient, such as has been reported in bismuth alloys,⁵ is observed even though in the last alloy all the overlapping electrons have been removed, if the previous estimate of overlap is correct as we believe it to be. On the model which we are using we should expect an antimony alloy in which the overlap has disappeared to behave more like a semi-conductor than a metal. This is brought out more clearly by the plot in Curve II, Fig. 2. A true semi-conductor should have a negative temperature coefficient. For these alloys, however, the mean temperature coefficient appears to approach a small constant value at the higher percentages of tin and gives no indication of becoming negative anywhere up to the solubility limit for the solid solution (about 6 percent tin).

The case of the residual resistivity, Curve I, Fig. 2, is of some interest. For the case of random solid solutions of monovalent metals Nordheim⁶ has shown that the part of the residual resistivity due to scattering of the electron waves by foreign atoms is given by

$$\rho_0 = \frac{h}{2e^2\Omega_0 N^{\frac{1}{2}}} \left(\frac{3}{\pi}\right)^{\frac{1}{2}} Q,$$

⁴ Some rough measurements on pure antimony indicated that the resistivity was substantially constant between 4.2°K and 1.6°K.

⁵ N. Thompson, Proc. Roy. Soc. **A155**, 111 (1936).

⁶ L. Nordheim, Ann. d. Physik **9**, 641 (1931).

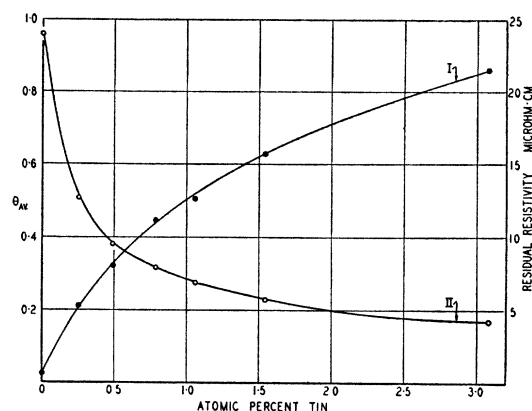


FIG. 2. Curve I—Residual resistivity of antimony-tin single crystals as a function of tin content. Curve II—Mean temperature coefficient between 4.2°K and 77.3°K as a function of tin content.

where N is the effective number of free electrons per cc and Ω_0 is the atomic volume. In the case of a binary alloy the quantity Q is given by

$$Q = \frac{1}{2}(1-Z)ZQ_{12},$$

where Z is the atomic fraction of the solute and Q_{12} may be thought of as the effective scattering cross section of each atom of the solute.

In the present experiment Z is always a very small quantity and therefore Q and hence ρ_0 should be a linear function of Z . This, however, is not the case. The residual resistivity is roughly a parabolic function of Z . Two possible reasons for this discrepancy suggest themselves. First, tin may not form a true random solid solution with antimony. This seems unlikely except for extremely small values of Z (around 0.01 percent) where there is some evidence that groups of foreign atoms segregate in the (111) planes of the crystal, at least in the allied element bismuth.⁷

A second more likely possibility lies in the fact that as Z is increased the effective number of free electrons is reduced. It is difficult, however, to form an estimate of this effect since some of the conduction in antimony is undoubtedly due to positive holes.⁸

While the numbers of overlapping electrons and positive holes are equal in pure antimony, this is no longer true when a tetravalent impurity

⁷ A. B. Focke, Phys. Rev. **46**, 623 (1934).

⁸ The Hall coefficient in polycrystalline antimony is positive.

is added. The difference is⁹

$$N^{(+)} - N^{(-)} = Z/\Omega_0. \quad (1)$$

Further, Jones has shown that, if one assumes complete circular symmetry about [111] (actually it is trigonal) then the conductivity perpendicular to the principal axis (our case) is given by

$$\sigma_{\perp} = \sigma_{\perp}^{(-)} + \sigma_{\perp}^{(+)}, \quad (2)$$

where

$$\sigma_{\perp}^{(-)} = \frac{e^2 \tau^{(-)} N^{(-)}}{c^2 m^{(-)}},$$

$$\sigma_{\perp}^{(+)} = \frac{e^2 \tau^{(+)} N^{(+)}}{c^2 m^{(+)}}.$$

⁹ H. Jones, Proc. Roy. Soc. **A155**, 653 (1936).

Here τ is the relaxation time and m the reduced mass.

It appears from (1) combined with (2) that the effect of reducing the overlap would be to add an additional term to ρ_0 over and above the linear term due to the random atomic scattering. The experimental results, however, indicate just the opposite effect. It appears, therefore, that one must suppose that the low temperature conductivity is due mainly to positive holes, and further that as the overlap is reduced the density of such holes sharply increases.

In conclusion we should like to express our thanks to Dr. S. H. Browne for providing some of the crystals used in this experiment. This work was supported, in part, by a grant from the George Sheffield Fund.

Theory of Complex Spectra. I

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This paper gives a closed formula which entirely replaces for the two-electron spectra the previous lengthy calculations with the diagonal-sum method. Applications are also made to some configurations with three or more electrons and to the p'' configurations of the nuclei.

§1. INTRODUCTION

THE first-order perturbation energy for the terms of a given configuration was calculated at first by Slater.¹ In his classical paper he showed that the electrostatic interaction between two electrons depends on a very few integrals F^k and G^k , and he developed the diagonal-sum procedure for calculating the coefficients of these integrals; with this procedure he obtained numerical tables of coefficients for the two-electron configurations involving s , p , or d electrons. These tables were extended by several authors² to f electrons and to some configurations with three or more electrons.

But the diagonal-sum procedure has some deficiencies. Firstly, when two terms of a kind occur in a given configuration, this procedure will determine only the sum of their energies, and they can be separated only by other methods. Secondly, this method does not give general formulas, but only numerical tables; it is therefore impossible to make generalizations, and one must begin again for each new case with new and more complex calculations.³

It is the purpose of this paper to substitute for the numerical methods of Chapters VI and VII of TAS more general methods and more conformable to Chapter III of the same book.

¹ J. C. Slater, Phys. Rev. **34**, 1293 (1929).

² See E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge 1935), (which we shall denote by TAS) Chapters VI and VII, for definitions, notations and bibliographical indications.

³ G. H. Shortley and B. Fried, Phys. Rev. **54**, 739 (1938).