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SEMICONDUCTING REGION OF BISMUTH I

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September 1963

Semiconducting Region of Bismuth I

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September 1963

Abstract

Measurements of the electrical resistance have been made on bismuth I between 15 and 35 kilobars at temperatures between 77.4° and 120° K. Above about 150° K, the temperature coefficient of resistance is positive as in a metal. Below 150° K, the coefficient becomes negative as is characteristic of semiconductors. Using the exponential resistance formula, the energy gap on the basis that bismuth is a semiconductor is found to be 0.006 ev at 15 kbars with a steady rise to 0.018 ev at 35 kbars. At higher pressures, bismuth I transforms into a metallic modification with the normal temperature dependence of the resistance. The energy gap in bismuth I is not visible at room temperature because thermal excitation populates the conduction band and yields metallic behavior.

Bismuth I, the form found under normal conditions, has long been considered a semi-metal. The resistivity is 123.2×10^{-6} ohm-cm (1), very high for a metal. From a study of bismuth-tin alloys, Jones (2) suggested that all five of bismuth's valence electrons lie in a single energy zone (valence band). A slight overlap into a higher zone (conduction band) gives the metallic conduction found in pure bismuth. Since this hypothesis, a large number of experiments (the deHaas-van Alphen effect, cyclotron resonance, galvanometric effects, and the low number of conduction electrons, somewhere between 10^{-2} and 10^{-5} per atom. However, bismuth at one atmosphere shows the positive temperature coefficient of resistance characteristic of a metal (4). Bismuth also shows no crystallographic transition upon cooling to 4.2° K (5).

Some alloy work by Jain (6) has suggested that bismuth might become a semiconductor upon a reduction of volume. Jain finds that the temperature coefficient of resistance becomes negative for bismuth alloys containing more than 5 per cent antimony. Using the exponential resistance formula, he finds a band gap which rises to 0.012 ev at 12 per cent antimony and then drops at higher concentrations, becoming a metal again at 40 per cent antimony. Jain also finds from x-ray work that the lattice parameters decrease upon continued addition of antimony. Therefore, the addition of a slight amount of antimony to bismuth is roughly equivalent to a reduction of volume by pressure. The assumption is made that antimony, with the same crystal structure and the same number of valence electrons as bismuth, produces no effect in the alloy other than reducing the lattice paramenters. By reducing the atomic volumes through alloying, therefore, Jain has produced a semiconductor. Beyond 12 per cent antimony, the approximation to volume reduction by pressure breaks down. The antimony now contributes its own properties to the alloy. Since antimony is itself a metal, the alloy must finally become a metal as the percentage of antimony is increased.

The results from work on the direct compression of bismuth confirm that the application of pressure apparently decreases the metallic properties. At room temperature, the resistivity increases 50 per cent with pressure to 25.5 kbars, where the crystallographic transition to the metallic bismuth II occurs (7). Experiments on bismuth to 1.7 kbars at 77.4° K (8) and to 5 kbars at 4.2° K (9) show the same increase of resistance with pressure observed at room temperature. Work on the Hall effect at room temperature (10) shows a decrease in carrier concentration by a factor of three as the pressure is raised from one atmosphere to the I-II transition. Magnetic susceptibility work to one kbar (11) shows a decrease with pressure of the Fermi energy, and consequently of the overlap of valence and conduction bands. This decrease of the metallic properties of bismuth has led to a prediction by Kan and Lasarev that somewhere in the bismuth I phase, there will be semiconducting behavior (12). It is not clear that Kan and Lasarev actually found such semiconducting behavior. However, by cooling and compressing bismuth, we have found it to act like a semiconductor in that there is a reversal in the temperature coefficient of resistance at constant pressure.

The bismuth (13) was supposedly 99.999 per cent pure. Spectral analysis (14) showed five parts per million each of copper, magnesium, and silicon. The magnesium may have come from the spectrometer arc.

The bismuth was extruded into wire 0.003 inch in diameter. The Bridgman anvils and the method of mounting the samples have been described elsewhere (15). The pressure measurement and calibration, as well as the resistance and temperature measurement, have also been described in a previous paper (16).

The electrical resistance of bismuth was studied at pressures between 15 and 35 kbars over the temperature range 77.4° to 120° K. One series of runs at three pressures was made by cooling the exposed anvils to liquid nitrogen temperature. Measurements were taken upon heating of the anvils as the liquid nitrogen evaporated. The technique yields a temperature difference of as much as 20° between the top and bottom anvils. Moreover, cooling runs cannot be taken since the liquid nitrogen drops the sample temperature too abruptly for measurement.

To better equilibrate the system, heavy cooper blocks were fitted sungly around the anvils and the blocks backing up each anvil. All cracks were plugged with Duxseal. With this method the liquid nitrogen cannot reach the anvils but must first cool down the massive cooper blocks. Both heating and cooling runs can be made with this system. The temperature difference between the top and bottom anvils is decreased to 2 to 6°. Two series of runs at various pressures were made by this method. With either method, the temperature of the bismuth is assumed to be the mean between the top and bottom anvil temperatures.

Figure 1 shows the resistivity of bismuth as a function of temperature at a pressure of 15 kbars. From room temperature to 155° K, the resistivity drops with decreasing temperature as is expected of a metal. But from 155° down to 77.4° K, the resistivity rises with decreasing temperature, as is characteristic of a semiconductor. The measured resistance of bismuth has been converted to resistivity by using the room temperature-one atmosphere value of 123.2×10^{-6} ohm-cm (17) and Bridgman's pressure-resistance data for bismuth (18). The inversion of the temperature coefficient is found at all pressures between 15 and 35 kbars in bismuth I.

In semiconductors, the resistance follows the formula,

$$R = Ae^{E_g/2kT}$$

where E_g is the energy gap. The energy gaps resulting from the application of the simple formula are shown in figure 2, where they are plotted as a function of pressure. The series of points taken with bare anvils are from heating runs only. For the two sets of copper block runs, heating and cooling values are averaged at each pressure. The gap values taken by cooling are about 0.003 ev higher than those taken by heating.

The energy gap in figure 2 is 0.006 ev at 15 kbars and it rises to 0.018 ev at 35 kbars. A linear extrapolation of the energy gap to one atmosphere yields a value of -0.004 ev. This negative value, if it were correct, would represent the overlap energy of the valence and conduction bands. Other estimates of the one atmosphere overlap energy are much larger, however, ranging from -0.012 to -0.035 ev (19) at low temperatures. The semiconductor formula from which the energy gaps are derived is accurate only if the gap is greater than kT.

Since kT is 0.007 ev at 77.4° K and several gap values are smaller, the formula does not apply accurately, and the gap values must be considered qpproximate. The smallness of the energy gap explains why work around room temperature fails to show the semiconducting properties of bismuth. At room temperature, the gap is less than kT and bismuth appears to be a metal. To observe this energy gap, the temperature must be reduced to the point where the gap is of the order or less than kT. At about 41 kbars and 77.4° K, bismuth I rearranges to the metallic bismuth III phase. The resistance drops by a factor of about fifty at this transition.

Despite the large amount of work on bismuth, the band structure is not well known. The metallic behavior of bismuth under normal conditions indicate that the valence and conduction bands overlap. But one deHaas-van Alphen study (20) and several magneto-optical experiments (21) have shown the presence of an energy gap at one atmosphere of 0.015-0.06 ev. It has been suggested that there are two valence bands (22): one which overlaps the conduction band and one which does not. The former makes bismuth metallic at one atmosphere, while the latter provides the energy gap seen in the magneto-optical work. A second valence band has been reported in only a few experiments (23), and there is opposition to its existence (24). An energy gap appears in the electrical resistance only if there is no overlap between any valence band and any conduction band. It is this gap which defines a semiconductor. The gap found by magneto-optical work must be something different. Its discovery is an indication that the band structure of bismuth is more complicated than the elementary parabolic two-band model.

It is interesting to note the wide range of behavior shown by the element bismuth upon compression to 30 kbars. In phase I, it is poorly metallic to semiconducting, but not superconducting (25). Phases II and III, formed under pressure, are both purely metallic, with III and possibly II both being superconducting (26).

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Figure Captions

Figure 1. Resistivity-temperature curve for bismuth at 15 kilobars pressure.

Figure 2. Energy gap of bismuth as a function of pressure. Circles refer to runs without copper blocks; squares and triangles refer to runs with copper blocks.

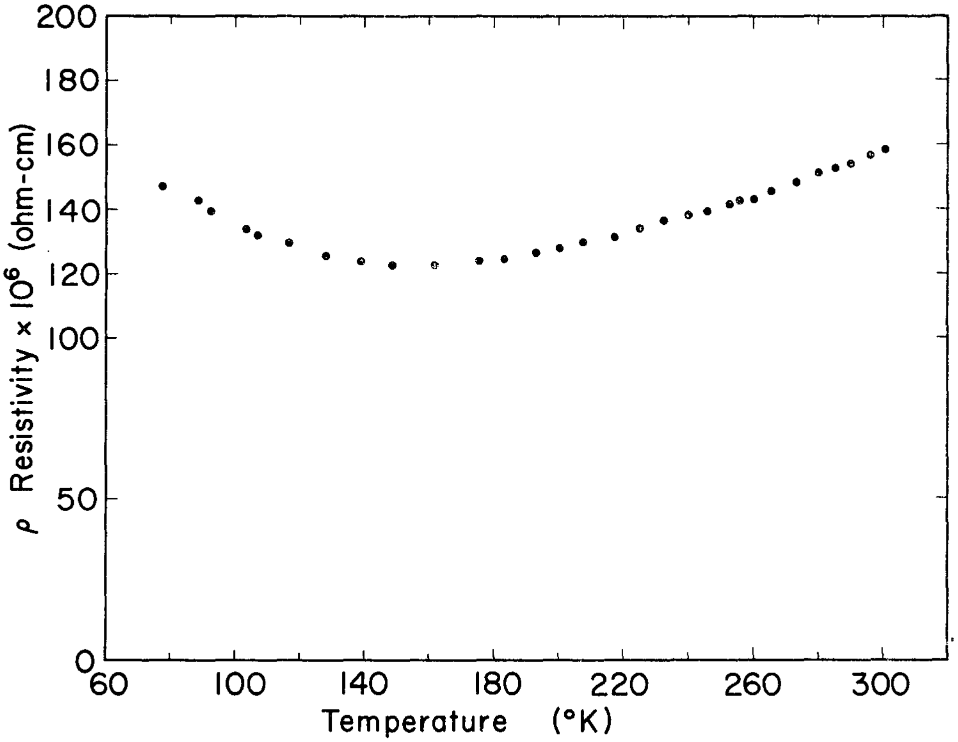

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Fig. 1

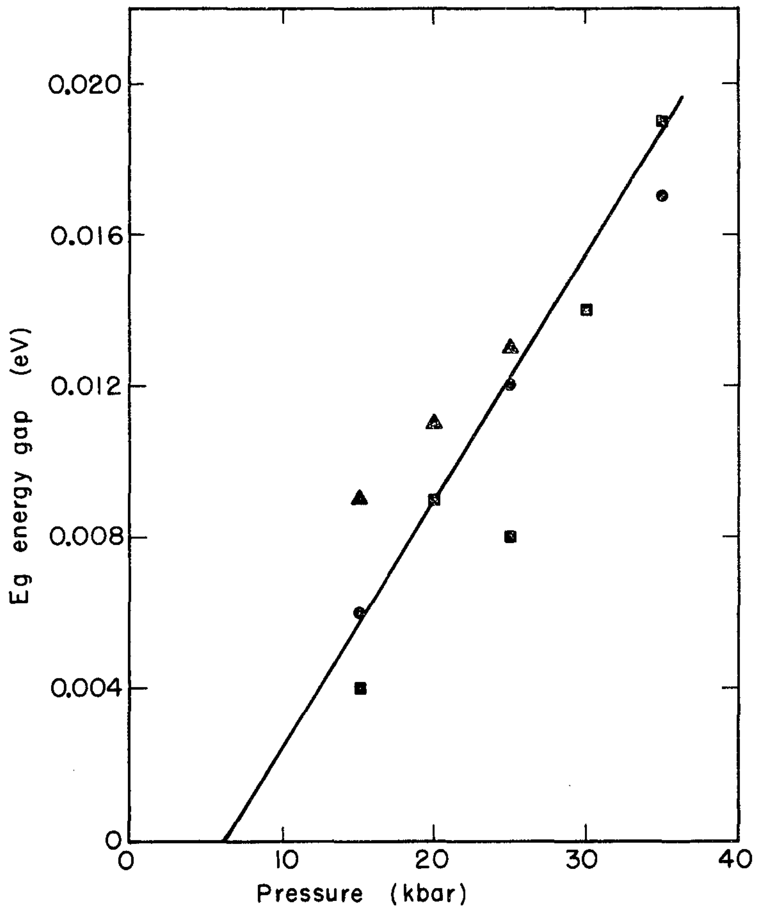

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Fig. 2

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