EFFECTS OF BORONATION ON THE TRANSPORT PROPERTIES OF SP-1 GRAPHITE*

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The Fermi surface of a solid can most easily be studied by varying the number of charge carriers it contains. This variation can be produced by the creation of lattice defects or by the introduction of impurities. However, one must avoid unduly perturbing the host lattice in order that the initial energy bands are left intact so the gradual progression from the pure case can be studied. In general, for semi-metals, the density of electronic states near the top of the Fermi distribution is low as compared to metals and thus the addition of any defect which changes the number of carriers can alter the Fermi level. The electronic properties of a small band overlap material such as graphite become very responsive to this shift. The measurements of greatest interest are those which are sensitive to the difference in electron and hole behavior, or more fundamentally, those that see the effect of the individual Fermi surfaces without being unduly influenced by scattering effects. The resulting property changes can give information concerning the band structure and also serve to test the existing models of that structure. In polycrystalline solids, the Seebeck or thermoelectric effect most closely fits these requirements.

It has been known for some time that small amounts of boron have a marked effect on the physical properties of graphite. However, until fairly recently, no further attempts were made to understand the various processes taking place, beyond speculation, that boron: (i) promoted graphitization and thus lowered the electrical resistivity, (ii) had no effect on crystal growth, but simply added current carriers, or (iii) some combination of both processes prevailed.

This paper will present an analysis of previous work on boron doping and the results of a study on the effect of boronation of compacted natural graphite (SP-1) on the electrical resistivity (ρ), the thermoelectric power (α), their temperature dependence, the Hall constant and the magneto-resistance. Boron was chosen as a relatively ideal acceptor because of its size (comparable to graphite) and because it has one less valence electron than carbon. Boron powder was mixed with SP-1 graphite to roughly give B/C atom ratios of 1, 10, 100, 500, 1000, 2000, 5000, and 10,000 (1%) ppm. Samples were pressure compacted into 15g rectangular parallelepipeds at 7×10^3 kg/cm^2. Each sample was then machined to fit the apparatus geometry. In order to both clean and anneal the graphite and to dope the lattice with

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boron, the samples were inductively heated to about 2500°C. Boron contents were determined by infrared spectroscopy, mass spectroscopy and in certain cases, chemical analysis. Each sample appeared to be homogeneous in its boron content. Some boron was lost in the course of heat treatment, but this could not be correlated with any other information. The samples had bulk densities of the order of 2.20±0.03 g/cc and helium densities of 2.25±0.01 g/cc.

Orientation analyses, using x-ray reflection techniques and measuring relative beam intensities, have shown that the compacted, heat-treated samples have approximately the same degree of orientation as the better grades (highest deposition temperatures) of as-deposited pyrolytic graphite.

Thermoelectric power (α) and electrical resistivity (ρ) measurements were made in a specially constructed vacuum cryostat and covered the temperature range from 77 to 570°K. Hall effect and magneto-resistance measurements were made at room temperature.

Studies on the undoped SP-1 graphite show that as the temperature decreases α, which is initially negative at room temperature, rises and eventually becomes positive at about 250°K. Above 300°K α becomes more negative. The room temperature value of α is about -1.5 μV/°K. Room temperature resistivity is of the order of 9×10^{-4} ohm-cm and shows only slight temperature dependence.

The effect of boron on α is quite marked. At about 10 ppm B/C, the magnitude of α at all temperatures is decreased. Boron anneals many of the electron trapping defect states. At 100 ppm, α (which had been negative at temperatures above 250°K) becomes positive at all temperatures and the slope of $d\alpha/dT$ becomes positive over most of the temperature range from 70 to 600°K, with a low temperature minimum and a high temperature maximum. With further boronation, α increases for all temperatures while the extrema shift to lower and higher temperatures respectively.

The addition of boron has no marked effect on the resistance or its temperature dependence except at high boron concentrations.

Hall constant and magneto-resistance data are in agreement with the results previously reported by D. Soule.

Another aspect of the work with boron is what is believed to be the resolution of the controversy over where the boron goes in the graphite lattice. There are only a few possibilities after heat treatment: (a) There is no boron present, (b) boron is located in interstitial sites, (c) boron is on edge sites, and (d) boron is in substitutional lattice sites. The results of this study accord with the view expressed in (c) and (d).