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THE CONDUCTIVITY OF GRAPHITE-ALKALI-METAL-HYDROGEN TERNARY SYSTEMS

Mizuka SANO* and Hiroo INOKUCHI
Institute for Molecular Science, Okazaki 444

The effect of hydrogen on the basal-plane electrical resistivity was studied for C_8K, $C_{24}K$, C_8Cs and $C_{24}Cs$ intercalation compounds. The admission of hydrogen onto cooled C_8K and $C_{24}K$ induced a reversible change in the resistivity below 200 K, and an irreversible increase in the resistivity at room temperature.

Graphite, the prototype layered solid, can form intercalation compounds with various kinds of chemical substances. The compounds of alkali metals, that have been reported to be C_8M and $C_{12n}M$ ($n \geq 2$), where M represents either potassium, rubidium, or cesium, are regarded as synthetic metals.$^{1,2)}$ When potassium, for example, is intercalated between the hexagon layers of carbon atoms, the distance between the layers has been reported to expand from 3.35 to 5.40 A, and the distance between the potassium atoms is 4.91 A even for the potassium richest compound, C_8K.$^{3)}$ This means that many vacancies, which are supposed to be situated under some special electric field, are newly formed between the layers through the intercalation of potassium atoms.

We tried to introduce the third component, H_2 molecules$^{4)}$ in the present work, into these vacancies to observe its effect on the basal-plane electrical conductivity of the alkali-graphite compounds.

The potassium and cesium graphites were synthesized by vapor phase reaction between grafoil (Union Carbide Co.) and vacuum-distilled K, or Cs in vacuum-sealed pyrex glass tubes which were placed in a dual furnace. The applied temperature scheme for the furnace was the same as in the literatures.$^{3,5)}$
A specimen, 30 x 2.5 mm^2 in area and 0.13 mm in thickness (in the c-axis direction) on a quartz plate was clipped with four electrodes of platinum contacts,

and their leads were crimp-sealed into one end of the tube before the vapor phase reaction. The other end of the tube was equipped with a breakable seal for an introduction of hydrogen gas.

The electrical resistivity of a specimen was measured by a four-point technique. The resistive voltage which appeared between the 10 mm separated voltage contacts for a constant current flow of 10 mA along the length of the specimen was read with the aid of a Keithley 174 digital multimeter. A whole assembly was immersed into alumina powder in a glass vessel and cooled with liquid nitrogen from outside. A small electric heater, surrounding the tube, was used for controlling the temperature of the specimen. After the resistivity was measured for the alkali-graphite, hydrogen gas which was purified by passing through a 450 °C heated Pd-Ag thimble was admitted onto the cooled specimen up to the pressure of 250 Torr at 80 K.

The basal-plane resistivity of a grafoil specimen increased with decreasing temperature from 700×10^{-6} at 300 K to 1440×10^{-6} Ωcm at 80 K. This resistivity change is opposite to that of a graphite single crystal. The grafoil intercalated with either potassium or cesium, however, was found to show a significantly reduced basal-plane resistivity, in the range of $23 \sim 26 \times 10^{-6}$ Ωcm for C_8K and C_8Cs (the 1st stage reddish gold compounds) and in the range of $31 \sim 36 \times 10^{-6}$ Ωcm for $C_{24}K$ and $C_{24}Cs$ (the 2nd stage deep blue compounds) at 300 K. In addition, these 1st and 2nd stage compounds were found to be metallic in character, showing a decrease in resistivity with decreasing temperature. No difference in resistivity value was found between the potassium and the cesium intercalated compounds.

Figure 1a shows the plots of the resistive voltage against temperature for a C_8K specimen. The plots are found on a slightly concave curve. The admission of hydrogen gas onto the C_8K specimen at 80 K caused a slight increase in the resistive voltage. The resistive voltage was found to change in nearly proportional to temperature up to at least 200 K (Fig. 1b). The effect of hydrogen on the resistive voltage was reversible, as the resistive voltage returned to the value on the concave curve on pumping out the hydrogen in this temperature region.

The C_8K specimen which was kept in hydrogen at room temperature, however, showed a gradual increase in resistive voltage, though no color change was noticed at least for a day. After a week, it was found that its color turned blue, and the specific resistivity reached the constant value of 40×10^{-6} Ωcm at 300 K.

The resistivity did not change on pumping out the hydrogen and increased in proportional to temperature from 80 to 400 K (Fig. 1c). A $C_{24}K$ specimen showed the similar tendency in the resistive voltage change, and its resistivity reached the constant value of 41×10^{-6} in hydrogen from the original value of 31×10^{-6} Ωcm in vacuo at 300 K.

In contrast to these potassium intercalated compounds, the cesium intercalated compounds, both the 1st and the 2nd stage compounds, received no influence of hydrogen on their resistivities and no color change occurred, even if they were kept in hydrogen at room temperature more than a week.

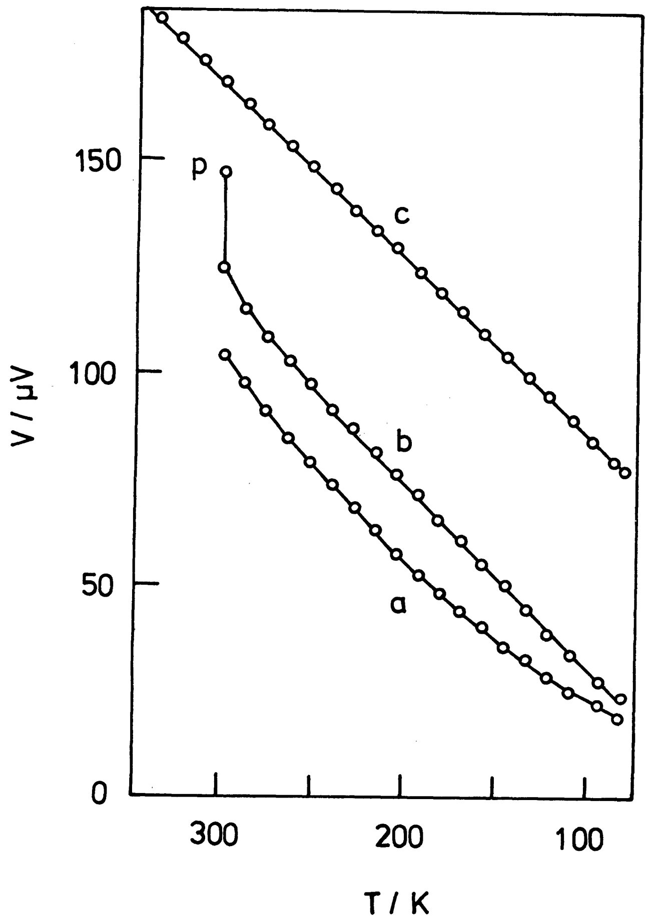

Fig. 1. The temperature dependence of resistive voltage for a) C_8K, b) C_8K in hydrogen (p: the value 4 h after H_2-admission), and c) C_8K-hydride.

The great decrease in basal-plane resistivity for graphite through the intercalation of alkali metals has been explained in terms of the electron transfer from the alkali metals to graphite. The electron transfer leads to an increase of charge carrier density in the carbon network of graphite.$^{2,6)}$ Therefore, the increase in resistivity observed for the admission of hydrogen onto the potassium intercalated compounds can be explained in terms of the electron transfer from the compounds to the hydrogen, which causes a decrease of charge carrier density in the carbon network.

The reversible change in resistivity observed below 200 K indicates the occurrence of a weak charge transfer interaction between the compounds and hydrogen molecules. The similar result has been reported for a perylene-cesium-hydrogen system.$^{7)}$ The irreversible increase in resistivity observed at room temperature is explained in terms of the formation of a stable hydride. The formation of the hydride of C_8K has been confirmed by the x-ray diffraction method, but no formation of hydride has been reported for C_8Cs.8)

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