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Electrical Resistivity of Ternary Compounds, Graphite-Aluminum Bromide-Bromine

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The formation of graphite lamellar compounds is believed to be accompanied with a transfer of electrons between graphite and reactant molecules. Electronic properties of various graphite lamellar compounds have been studied for investigating the nature of the chemical bonding and degree of charge-transfer between reactants and graphite layers.[1] It was found that the charge-transfer did not proceed to the complete ionization of reactant molecules in graphite layer interstices in many cases, and that the ratio of the number of transferred electrons to that of reactant molecules remained fractional. Hennig,[1] and Dzurus and Hennig[2] introduced a model in which only a part of the reactant molecules is completely ionized, making an ionic bonding between graphite layers, while the other molecules remain neutral and stabilize the ions by acting as spacers between them. The case of ternary compounds such as graphite–$AlCl_3$–Cl_2[2] was interpreted as follows: All the chlorine atoms in the compound are completely ionized while $AlCl_3$ molecules remain neutral and act as spacers of Cl^- ions. The mole ratio of $AlCl_3$ to Cl is found to be three for all the reactant concentrations, the chemical formula of the ternary compound being given as $C_n^+\cdot Cl^-\cdot 3AlCl_3$ or $C_n^+\cdot AlCl_4^-\cdot 2AlCl_3$.[2]

A mixture of $AlBr_3$ and Br_2 also formed a ternary lamellar compound with graphite, the ratio of $AlBr_3$ to Br in the compound being nearly three up to the bromine content of Br/C=0.014.[3,4] We measured the electrical resistivity of the ternary compound by changing the amount of reactants. The charge-transfer between the reactants and graphite is discussed.

Experimental

Pyrolytic graphite deposited at 1700°C and heat-treated at 2100°C was used as the sample. *C*-spacing and specific resistivity of the graphite were 3.417 Å and 6.0×10^{-4} Ω·cm, respectively. The graphite sample was cut into $1.5\times20\times0.2$ mm specimens. Platinum wires 0.2 mm in diameter were fixed tightly into small holes drilled on the specimen to make good electrical contacts.

The ternary lamellar compound, graphite–$AlBr_3$–Br_2, was prepared as follows: A controlled amount of bromine was doped in each graphite specimen resulting in the formation of a bromine residue compound. The bromine-doped graphite specimen was then allowed to react with $AlBr_3$ at 120°C in an evacuated reaction tube. After the reaction, the electrical resistivity of the specimen along the direction perpendicular to *c*-axis was measured *in situ* at room temperature by the four contact potentiometric method. Temperature dependence of the resistivity of the compound was found to be very small as compared with that of original graphite.

Results and Discussion

The electrical resistivity of graphite–$AlBr_3$–Br_2 is shown in Fig. 1 by a solid line (open circles). That of the graphite–bromine residue compound with different bromine concentrations measured prior to the reaction with $AlBr_3$ is shown by a dashed line (open triangles). The horizontal axis represents the concentration of free bromine in the ternary compound, in which Br in $AlBr_3$ is not included. The point shown by arrow II is the concentration at which a compound of the second stage structure (compound II, Ref. 4) is formed. The composition of the ternary compounds below this point is represented by $C_n3AlBr_3\cdot Br$.[3,4] The resistivity of the saturation compound of the ternary system (compound I, Ref. 4, with the first stage structure and the composition $C_9AlBr_3\cdot Br_2$) prepared from the same graphite sample was also measured. Although the value of the ratio Br/C of this compound is far beyond the scale, the electrical resistivity indicated by arrow I is nearly the same as that of compound II.

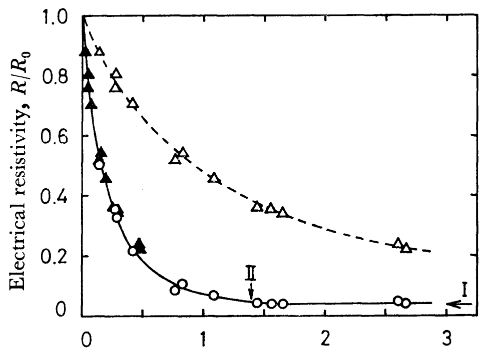

Fig. 1. Electrical resistivity of the graphite compound.
△: graphite bromine residue compound
○: graphite–$AlBr_3$–Br_2 ternary lamellar compound
▲: relation between the electrical resistivity and the assumed concentration of transferred electrons

The electrical resistivity of the bromine residue compound is lower than that of the original graphite. The absorption of $AlBr_3$ by the residue compound led to further decrease of resistivity. Thus it is considered that the addition of $AlBr_3$ in the interstices of graphite layers caused further transfer of electrons from graphite to reactants. With an increase of reactant concentra-

1) G. R. Hennig, "Progress in Inorganic Chemistry," Vol. 1, Interscience Publishers, New York, N. Y. (1959), p. 125.
2) M. L. Dzurus and G. R. Hennig, *J. Amer. Chem. Soc.*, **79**, 1051 (1957).
3) T. Sasa, Y. Takahashi, and T. Mukaibo, This Bulletin, **45**, 937 (1972).
4) T. Sasa, Y. Takahashi, and T. Mukaibo, *ibid.*, **45**, 2250 (1972).

tion in the ternary compound, the electrical resistivity decreased sharply down to the value of compound II. On the contrary, at concentrations beyond that for compound II up to that for compound I, the resistivity showed little change while the reactant contents increased greatly. Thus the fraction of the charge-transferred molecules in the intercalated reactant is considered to decrease considerably when the composition approaches that of compound I.

Hennig[1] reported that the ratio of the number of transferred electrons to that of bromine atoms was 1:5.5 in a graphite-bromine residue compound. A modified plotting of the electrical resistivity of the compound based on this assumption is also given in Fig. 1. Solid triangles show the relation of the electrical resistivity of bromine residue compound *vs.* Br/C$\times$1/5.5, which represents the assumed concentration of transferred electrons. These plots agree quite well with the solid line representing the relation between he electrical resistivity and the bromine concentration in the ternary compound.

This agreement suggests that all the bromine molecules in the ternary compound are ionized. However, it should be pointed out that there is also a possibility of partial donation of electrons from graphite layers to $AlBr_3$ molecules. In the case of graphite–$FeCl_3$ compound,[5,6] the measurements of Mössbauer spectra suggest that all the intercalated $FeCl_3$ molecules equally take an active part in the charge-transfer.

It is difficult at present to determine whether the chemical formula of the compound is $C_n^{+}\cdot Br^{-}\cdot 3AlBr_3$, or $C_n^{+}(Br)^{-\delta}\ (3AlBr_3)^{-\delta'}$. However, from our results it is concluded that bromine assumes a substantially large part in the charge-transfer between the reactants and graphite layers in the ternary compound, graphite–$AlBr_3$–Br_2.

5) B. V. Liengme, M. W. Bartlett, J. G. Hooley, and J. R. Sams, *Phys. Lett.*, **A25**, 127 (1967); *Carbon*, **6**, 681 (1968).
6) A. G. Freeman, *Chem. Commun.*, **1968**, 193.