

The electrical conductivity of graphite intercalated with superacid fluorides: experiments with antimony pentafluoride

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The electrical conductivity in graphite measured normal to the crystallographic *c*-axis is observed to increase after intercalation with acid molecules which act as acceptors. This behaviour is regarded as the result of ionization of the acid molecule which, in turn, increases the positive current carriers in the host graphite. Since the carrier density depends on the degree of ionization of the acid, it follows that the stronger the acid the greater the increase in carrier concentration, and assuming no adverse mobility effects, the greater the electrical conductivity. The hydrogen fluoride-antimony pentafluoride system produces some of the strongest acid substances known. The experiments described here represent the initial examination of the electrical conductivity resulting from intercalation of this material into graphite. The experiments consisted of intercalating graphite powder with antimony pentafluoride in a copper tube and swaging the sheathed compound into wire. The measured conductivity of the graphite intercalation compound, when the copper conductivity is subtracted out and allowance is made for departure from ideal density, is about $1 \times 10^6 \Omega^{-1} \text{cm}^{-1}$. This is approximately 40 times the conductivity of pristine graphite and more than one and a half times the conductivity of pure copper.

1. Introduction

At present, it is a well established generality that the intercalation of solute species into graphite increases its electrical conductivity measured normal to the crystallographic *c*-axis [1]. The intercalants themselves can be separated into two types, donors or acceptors depending on whether the major carrier increase is of the electron or hole type respectively. Another generality that appears to be emerging from a large amount of experimental work concerns the relative effects on the conductivity increase of the two types of intercalants. The donors, typically alkali metals, but to a lesser degree the alkaline earths [2-4], are observed to increase the perpendicular *c*-axis conductivity from its usual crystal value of $25\,000 \Omega^{-1} \text{cm}^{-1}$ by a factor of 4 to 6 times [5, 6]. On the other hand, the acceptor species such as Br_2 , H_2SO_4 and

HNO_3 , which have been intercalated into graphite produce an increase in perpendicular *c* conductivity of 10 to 12 times that of the pristine graphite measured in the same crystallographic direction [7-9]. Likewise, the aluminium halides, Lewis acids, induce conductivity increases of the same magnitude and much larger than that experienced with the donor elements. This difference in conductivity of donor compounds and acceptor compounds is in accord with a model proposed by Fischer [11]. He noted that the intercalated ionic radii of the donors is greater than the normal ionic radii and the intercalated ionic radii of the acceptors is less than their normal ionic radii. The smaller ionic radius results in less electron bonding and a greater availability of carriers for the conduction process. Thus, as a class the acceptor compounds are seen to exhibit generally higher

electrical conductivities than the donor compounds.

The accepted model for the electrical conductivity increases on intercalation with an acid molecules requires an electron transfer from the hexagonal graphite net to the acid. In the case of intercalation with a protonic acid such as HNO_3 the transfer is to the acid radical creating an anion [9] whereas in the case of a Lewis acid such as the metal halides, a compound of the type MX_3 is converted to MX_4 . Consequently, electron charge transfer increases the density of electron holes in the graphite network thereby increasing the p-type conductivity in the a direction. For a given concentration or stage of intercalation, it is the degree of ionization of the acid which determines the electron hole density increase. A measure of this ionization capability or electron affinity of strong acid substances, be they protonic acids, Lewis acids or mixtures of the two sometimes designated as superacids is given by the Hammett acidity function, H_0 [12] which can be defined by the equation:

$$H_0 = \text{p}K_{\text{BH}^+} - \log \frac{[\text{BH}^+]}{[\text{B}]}$$

where $\text{p}K_{\text{BH}^+}$ is the acid dissociation constant of the conjugate acid of base B and $[\text{BH}^+]/[\text{B}]$ is the ionization ratio.

The precise value of H_0 depends upon the identity of the base and the same acidity function value does not always result from the use of different bases. However, although the absolute values of H_0 cannot be regarded as having significance they are useful in giving a semi-quantitative measure of the acidities or electron affinities of highly acid substances, and these indications are applicable to the solid as well as the liquid state.

The Hammett acidity function for HNO_3 is approximately -6.0 [13]; Red fuming nitric acid when intercalated into graphite to stage II or I changes the conductivity by a factor of 10 times [8]. This corresponds to a change in hole concentration by approximately the same amount. A number of acid fluoride compounds have Hammett acidity functions which are considerably higher (see Table I) and therefore represent the possibility of greater conductivity. This possibility was first indicated experimentally by the higher plasma frequency observed for the SbF_5 and the $\text{SbF}_5 + \text{HF}$ compounds in graphite [14].

TABLE I Hammett acidity function for several strong acid fluorides

Acid fluoride	Hammett acidity function	Reference
$\text{HF} + \text{BF}_3$	- 11	[15]
HSO_3F	- 15	[12]
$\text{HF} + \text{SbF}_5$	- 15	[16]
$\text{HSO}_3\text{F} + \text{SbF}_5$	- 18	[12]

This paper will describe experiments which were designed to examine the possibility of higher a -axis electrical conductivity of graphite as a result of intercalation with antimony pentafluoride.

2. Experimental work

A major problem affecting electrical measurements of graphite intercalation compounds, especially the acid acceptor compounds is the difficulty in maintaining low resistance contacts. This difficulty arises out of the corrosive nature of the acid intercalants and the rather considerable expansion that takes place on intercalation. A further problem to be avoided is the change in composition that can occur on removing the intercalating medium and substituting an atmosphere that may be reactive, such as ordinary air. These objectionable factors were vitiated by using a method that has been employed to form brittle superconductors into a ductile composite namely by sealing the material in a copper ampoule under inert atmosphere and then swaging or drawing to wire. Under these conditions the copper sheath protects the graphite intercalation compound core and provides an easily contacted surface on the composite material so formed. To determine the conductivity of the graphite intercalation compound core the conductivity of the copper sheath is subtracted from the composite conductivity. For purposes of comparison and control, a sample was prepared having a core formed high purity copper powder which reproduces the conductivity of copper ($\sigma = 5.8 \times 10^5 \Omega^{-1} \text{cm}^{-1}$) on achieving ideal density.

3. Materials

The copper sheaths used in this series of experiments were of two separate kinds: phosphorus deoxidized copper tubing (resistivity $\rho = 2 \times 10^{-6} \Omega\text{cm}$) and conductor grade oxygen free copper (resistivity $\rho = 1.7 \times 10^{-6} \Omega\text{cm}$). The phosphorus deoxidized copper was used because of initial difficulties in machining the purer oxygen-free high conductivity copper.

For the high conductivity copper a cavity 0.38 cm diameter, 5 cm deep was drilled into a rod and provided with a tightly fitting end plug. On subsequent swaging, the end plug cold welded to the copper sheath forming a reasonably tight end seal, although some difficulty was experienced with breakage at this point.

The graphite powder used was Fischer Laboratory grade graphite flake — a high quality natural graphite having an approximate 10 μm particle size. Prior to use it was annealed overnight at 600° C vacuum (10^{-6} Torr) in the manner described by Lalancette and Lafontaine [17]. Subsequent to this treatment, the graphite powder was retained in a closed container under dry nitrogen.

For the control experiment, the copper tubes were filled with high purity copper powder designated as "LO" which is available from AMAX. This powder when reduced to near ideal density yields a resistivity which is substantially equal to solid conductivity grade copper ($\rho = 1.7 \times 10^{-6} \Omega\text{cm}$). The intention here is to give a direct comparison between the resistivity of copper and the resistivity of the graphite intercalation compound taking account of the fact that densified powders are used in both cases.

The antimony pentafluoride used was obtained commercially from Ozark Mahoning Co. This material is difficult to prepare and handle because of its extreme tendency to react particularly with atmospheric moisture by hydrolysis. The grade obtained was described as "distilled and colourless" but no special information related to purity was supplied. Experiments subsequent to this investigation [18] revealed that very special care must be taken to exclude atmospheric moisture to maintain the purity of the antimony pentafluoride. Otherwise, the generation of HF as an impurity is likely.

4. Methods

To form the compound, weighed amounts of the graphite powder and SbF_5 were loaded separately into the copper tubes. These were then sealed and heated overnight at 150° C in a muffle furnace. At this point then, presumably one has a randomly oriented undensified graphite intercalation compound sealed in a copper ampoule. The ampoules were then reduced to wire 0.040 in. (1 mm) diameter by swaging at room temperature in eleven steps. The wires were then cut to approximately 50 cm lengths and annealed for 1 h at 500° C in air.

Direct current resistivity measurements of the composite wire were made using a four point method. A jig was constructed having outer or current contacts about 15 cm apart and inner or voltage contacts 10.1 ± 0.05 cm apart. These four contacts were connected directly to the four terminals of a Shallcross Milliohmmeter which read the resistance directly. The measurements were cross-checked by separate determinations of current from a d.c. supply and voltage drop in the inner contacts. Also, satisfactory checks were made against a copper wire of known resistivity.

It became apparent that the swaging and annealing treatment was not producing ideal density of the material in the core of the composite wire. Therefore, density measurements of the graphite core composites were made by dissolving the copper sheath in dilute nitric acid and subtracting that amount of copper determined as the nitrate from the weighted average of the total.

From this information the electrical resistivity or conductivity of the core material can be calculated using the Law of Mixtures relationship:

$$\sigma_{\text{total}} = V_{\text{Cu}} \cdot \sigma_{\text{Cu}} + V_{\text{G}} \cdot \sigma_{\text{G}}$$

where σ is the electrical conductivity in $\Omega^{-1}\text{cm}^{-1}$, V the volume fraction, subscripts Cu and G refer to the copper sheath and graphite intercalation compound core respectively. Since the powdered core material did not densify to its ideal, zero void value for either the copper or the graphite intercalation compound case, an adjustment is made to V_{G} by multiplying it by the ratio of the apparent measured density to the ideal density.

5. Results

Tables II and III give the results of the experiments with the phosphorus copper and high conductivity copper sheaths, respectively.

TABLE II Antimony pentafluoride intercalated graphite in phosphorus copper sheath

	Control sample	Experimental sample
Composite resistance (Ω)	0.00262	0.00215
Composite resistivity (Ωcm)	2.2×10^{-6}	1.77×10^{-6}
Apparent density of core, % of ideal	75	85
Resistivity of sheath (Ωcm)	2.1×10^{-6}	2.1×10^{-6}
Resistivity of core at ideal density (Ωcm)	1.7×10^{-6}	0.9×10^{-6}

TABLE III Antimony pentafluoride intercalated graphite in conductivity grade copper sheath

	Control sample	Experimental sample
Composite resistance (Ω)	0.00220	0.00205
Composite resistivity (Ωcm)	1.81×10^{-6}	1.68×10^{-6}
Apparent density of core, % of ideal	73	80
Resistivity of sheath (Ωcm)	1.7×10^{-6}	1.7×10^{-6}
Resistivity of core at 1. ideal density (Ωcm)	1.7×10^{-6}	1.0×10^{-6}

6. Discussion

The implications of an electrical conductivity greater than that of copper are considerable and raise the question of the unique features that bring it about. The following discussion is an attempt to resolve some of these questions and indicate a direction for further experiments.

The nominal intercalant of this experiment, antimony pentafluoride is, by reason of its impurities considerably more complex. Incidental exposure of this highly reactive material to even small amounts of atmospheric moisture results in a reaction that produces visible amounts of SbF_3 — a waxy white solid — and therefore probably HF as well. Thus, one of the intercalating species is the superacid $\text{HF} + \text{SbF}_5$. Since any departure from the pure SbF_5 composition increases the Hammett acidity function [15] it follows that the HF impurity is beneficial in increasing the electrical conductivity after intercalation in the graphite. Obviously, further effort is required to clarify the question of precise chemical composition.

An important element in producing the elevated electrical conductivity reported here is the reorientation of the graphite which occurs during the swaging deformation. The electrical resistivity in graphite crystals is highly anisotropic, i.e. $\rho_a = 4 \times 10^{-5} \Omega\text{cm}$ and $\rho_c = 10^{-1} \Omega\text{cm}$ [19] for a resistivity ratio of 4000. Thus in a single crystal, the direction of measurement has a pronounced effect on the electrical conductivity. There is evidence that this anisotropy increases on intercalation by acid acceptor molecules [20] although this is in disagreement with an earlier report [21]. Deformation occurs by motion of dislocations having Burger's vectors in the crystallographic a direction and moving in the c plane. Thus in the case of swaging, reorientation that occurs places the a

direction parallel to the longitudinal tensile stress, and the c direction parallel to the radial compression stress. This type of preferred orientation is usual for hexagonal materials [22] and has been observed experimentally in the case of intercalated graphite samples [23] but the results are not presented here since they will be subject of a future paper.

In taking the experiments reported here as evidence of electrical conductivities higher than copper in graphite intercalated with strong acid fluorides it is important to note that all of the expected errors argue in favour of the conductivity being higher than the observed one. Specifically, errors that make the true a -axis conductivity of the intercalated graphite higher than the observed one in the experimental one under consideration are:

- (1) contact resistance;
- (2) uneven current spreading or irregular current paths;
- (3) contact resistance between particles of intercalated graphite;
- (4) imperfect orientation of graphite "a" axis in current direction;
- (5) density variation in the intercalated graphite.

Therefore, as long as the resistivities of the experimental samples shown in Tables II and III are significantly lower than the control samples which are prepared by identical means, then there is reasonable assurance that the intercalated graphite core material has a significantly lower resistivity than the control copper. It remains to isolate all of the important factors which contribute to the high conductivity in graphite intercalation compounds and optimize these.

7. Conclusions

Experimental evidence is presented that indicates a incremental change in the a -axis conductivity of graphite when intercalated with antimony pentafluoride superacid. Electrical resistivities of approximately $1 \times 10^{-6} \Omega\text{cm}$ were observed. This represents a 40 times increase in conductivity over pristine graphite and an approximately 70% greater than pure copper.

References

1. A. R. UBBELOHDE, L. C. F. BLACKMAN and J. F. MATTHEWS, *Nature London* **183** (1959) 454.
2. A. HEROLD, *Bull. Soc. Chim. Fr.* (1955) 999.
3. W. RUDORFF and E. SCHULZE, *Z. Anorg. Allgem. Chem.* **279** (1954) 156.

4. D. GUERARD and A. HEROLD, *Compt. Rend.* **280** (1975) 729.
5. L. C. F. BLACKMAN, J. F. MATHEWS and A. R. UBBELOHDE, *Proc. Roy. Soc.* **A258** (1960) 339.
6. J. J. MURRAY and A. R. UBBELOHDE, *ibid* **A312** (1951) 191.
7. F. R. M. McDONNELL, R. C. PINK and A. R. UBBELOHDE, *J. Chem. Soc.* (1951) 191.
8. A. R. UBBELOHDE, *Proc. Roy. Soc.* **A304** (1968) 25.
9. B. BACH and A. R. UBBELOHDE, *ibid* **A325** (1971) 437.
10. T. SASA, Y. TAHASHI and T. MUHAIBO, *Bull. Chem. Soc. Japan* **45** (1972) 2657.
11. J. E. FISCHER, Abstract of APS 1976 March Meeting, Atlanta, *Bull. APS II* **21** (1976) 261.
12. R. J. GILLESPIE and T. E. PEEL, *Adv. Phys. Org. Chem.* **9** (1971) 1.
13. M. A. PAUL and F. A. LONG, *Chem. Rev.* **57** (1957) 1.
14. JOHN E. FISCHER, THOMAS E. THOMPSON and F. LINCOLN VOGEL, A.C.S. Symposium series No. 21, "Petroleum Derived Carbons" (1975) p. 418.
15. H. H. HYMAN and J. J. KATZ, "Non-Aqueous Solvent Systems", edited by T. C. Waddington (Academic Press, New York, 1965) p. 76.
16. H. H. HYMAN, L. A. QUARTERMAN, M. KILPETRICH and J. J. KATZ, *J. Phys. Chem.* **65** (1961) 123.
17. J. M. LALANCETTE and J. LAFONTAINE, *J.C.S. Chem. Commun.* (1973) 815.
18. DANIEL GUERARD, private communication.
19. I. L. SPAIN, *Chem. Phys. Carbon* **8** (1973) 1.
20. A. R. UBBELOHDE, *Proc. Roy. Soc.* **A327** (1972) 289.
21. *Idem*, Proceedings of the 5th Carbon Conference (1961) 1.
22. A. H. COTTRELL, "An Introduction to Metallurgy" (St. Martins Press, New York, 1967) p. 313.
23. JIMY GAN, private communication.

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