The Microstructure, Molecular Constituents, and Stability of the Graphite–Antimony Pentachloride Intercalate

William Jones, Peter Korgul, Robert Schlögl, and John M. Thomas

Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, U.K.

Reaction of $SbCl_5$ with graphite at room temperature results in the formation of a dilute first-stage intercalate consisting of several species, including $SbCl_3$, $SbCl_5^{2-}$, $SbCl_6^-$, and $SbCl_6^{3-}$; the occurrence of an unusual low-temperature phase transition is also discussed.

A variety of techniques has been used to investigate the nature and stability of graphite–metal halide acceptor intercalates.[1,2] In particular, the synthesis and properties of antimony halide intercalates have attracted much attention,[3–5] not least because of their interesting electronic and potential catalytic properties.

We have developed[6] several methods for the intercalation of $SbCl_5$ into graphite: these differ one from the other according as to whether insertion of the guest takes place from the vapour or in photoassisted fashion from a solution in CCl_4 either at room temperature or at elevated temperatures, with or without a surrounding atmosphere of chlorine gas.

Using the room temperature–vapour phase procedure and a Kropfmühl (Bavaria) powdered natural graphite (AF) as starting material, we have prepared a compound of stoicheiometry $C_{32}SbCl_{4\cdot7}$, which means that *ca.* 40 wt % of the intercalation compound consists of the antimony halide guest. The intercalate is 'phase pure' since no sign of the original (002) graphite peak (at 2θ 26.66° for Cu-K_α) is seen in the diffractogram, and all observed reflections may be indexed on the basis of a first-stage material,[7] *i.e.*, there are guest species between each graphite sheet, the repeat distance along the c-axis being 9.48 ± 0.02 Å. This indicates that upon intercalation the graphite sheets which initially are 3.36 Å apart are separated by an extra 6.12 Å.

Whereas X-ray diffractometry is a useful technique for identifying the phase and stage of graphite intercalates, it is rather restricted so far as identifying the microstructural details of these poorly ordered materials is concerned. (No single-crystal intercalates of graphite of adequate quality can be formed: conventional X-ray crystallography is, therefore, inapplicable.) Accordingly we have employed several alternative approaches: variable temperature (100—300 K) electron diffraction and electron-induced X-ray emission microanalysis (using specially modified microscopes[7,8]), low temperature differential scanning calorimetry,[6] and Raman spectroscopy.

Recognising that the limiting composition for a densely packed, first-stage intercalate of $SbCl_5$ is $C_{14}SbCl_5$,[9] we conclude that our prepared compound is a *dilute* first-stage intercalate. The interlamellar spaces are not saturated with guest species, presumably as a result of rather limited diffusion of the intercalant into the graphite, an effect which will be of importance for larger particle size graphite (highly oriented pyrolytic graphite) samples, despite the higher temperatures generally used for the intercalation of such graphites.

Raman spectroscopy provides evidence for the occurrence, within the interlamellar regions, of several distinct species produced from $SbCl_5$: $SbCl_3$, $SbCl_5^{2-}$, $SbCl_6^-$, and $SbCl_6^{3-}$ There were no peaks (for example at 170 and 370 cm^{-1}) which would have signified[10] the existence of $SbCl_5$ as such.[6]

In addition, evidence (peaks around 200 cm^{-1}) for the occurrence of bridged chlorine atoms[6] may well suggest that the so-called $SbCl_5$–graphite consists of oligonuclear complexes involving both Sb^{III} and Sb^V oxidation states in a similar way to that known to exist in complex antimony halide salts[11] (compare refs. 11b and c, and also the crystalline III phase of PCl_5 *i.e.*, $2PCl_4^+{\cdot}PCl_6^-{\cdot}Cl^-$). There is no evidence for phase separation of $SbCl_6^-$ and $SbCl_3$. The guest is probably one single extended macroanion.[6]

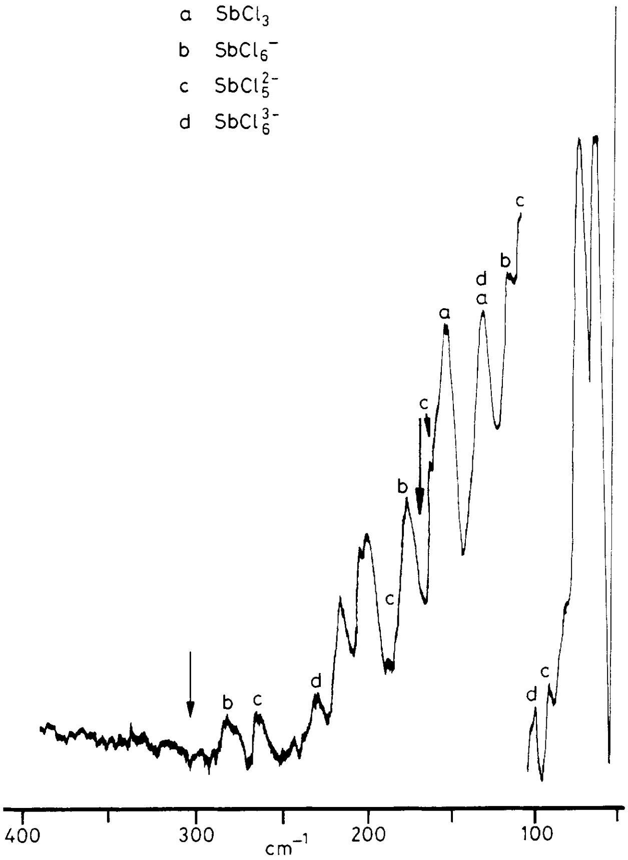

Figure 1. Room temperature Raman spectrum (argon laser, 25 mW) for a dilute $SbCl_5$–graphite intercalate. The two arrows (which are unlabelled) indicate the position expected for two of the non-polarized fundamental vibrations for $SbCl_5$.

Selected area electron diffraction (room temp.) showed that the freshly prepared, dilute first-stage compound consisted of two co-existent superlattices.[7,12] The spots in the complicated diffraction pattern could be indexed on the basis of the occurrence of the following interpenetrating two-dimensional superlattices: $\pm 16.1° \sqrt{39}.\sqrt{39}$ and $\pm 19.1° \sqrt{7}.\sqrt{7}$. As the freshly prepared sample is exposed to air the diffraction pattern grows simpler and, after an hour or so at room temperature, only the $\pm 19.1° \sqrt{7}.\sqrt{7}$ superlattice remains. When the Sb:Cl atom ratio is monitored (by electron-induced X-ray emission) as a function of time of exposure to air, the results can be rationalized on the basis of a facile process of de-intercalation followed by, rate-determining, hydrolysis of the halide released on to the exterior surfaces of the graphite.[6,7]

Furthermore, when the symmetry of the electron diffraction pattern is monitored as a function of temperature down to *ca.* 100 K a dramatic change is observed at *ca.* 210 K. The pattern simplifies greatly and, at first sight, appears indistinguishable from that of pure graphite. On warming the specimen, however, both sets of superlattice spots reappear, so that loss of guest, which in any case would have been unlikely, may be ruled out. Closer examination of the low-temperature diffraction pattern shows it to consist of faint diffuse rings close to the position of the primary beam. Clearly a rather unusual glass transition takes place *on cooling*, an effect which the solid $SbCl_5$, which is known not to exist as unimolecular units[13] at the transition temperature, also exhibits, as evidenced by our differential scanning calorimetric measurements.[6] The occurrence of this glass transition has been independently reported by other investigations.[14] Its nature is enigmatic. Its occurrence may well be linked to the degree of dilution (or undersaturation, see above) of the intercalate. Preliminary indications are that in the more concentrated first-stage 'graphite–$SbCl_5$' intercalates, where compositions closer to the ideal are found, no glass transition sets in on cooling presumably because there is now inadequate physical space available to accommodate the disordered state.[6]

We thank the S.E.R.C. and N.C.B. for support. The assistance of Prof. Breitinger and Mr. G. Petrikovski in obtaining the Raman data is appreciated.

Received, 21st February 1983; Com. 233

References

1 M. S. Dresselhaus and G. Dresselhaus, *Adv. Phys.*, 1981, **30**, 139.

2 J. M. Thomas, G. R. Millward, and L. A. Bursill, *Philos. Trans. R. Soc. London, Ser. A*, 1981, **300**, 43; R. Schlögl, H. P. Boehm, P. Bowen, W. Jones, and G. R. Millward, *J. Chem. Soc., Faraday Trans.*, 1983, in the press.

3 J. Mélin and A. Hérold, *Carbon*, 1975, **13**, 357.

4 V. R. K. Murthy, D. S. Smith, and P. C. Eklund, *Mater. Sci. Eng.*, 1980, **45**, 77.

5 R. Clarke, M. Elzinga, J. M. Gray, H. Homma, D. T. Morelli, M. J. Winokur, and C. Uher, *Phys. Rev. Sect. B.*, 1982, **26**, 2323.

6 R. Schlögl, W. Jones, P. Korgul, and J. M. Thomas, in preparation.

7 J. M. Thomas, R. Schlögl, W. Jones, and P. Korgul, *Carbon*, 1983, in the press.

8 G. M. Parkinson, W. Jones, and J. M. Thomas, 'Electron Microscopy at Molecular Dimensions: State of the Art & Strategies for the Future,' eds. W. Baumeister and W. Vogell, Springer–Verlag, Berlin, Heidelberg, and New York, 1980, pp. 208—225 (Proc. of Internal Workshop, Burg Gemen, Munsterland, June 1979); R. Eiermann, G. M. Parkinson, H. Bässler, and J. M. Thomas, *J. Phys. Chem.*, 1982, 313.

9 A. Hérold in 'Intercalated Materials,' ed. F. Levy, vol. 6, D. Reidel, Holland, 1979, p. 323

10 R. Savoie and A. Anderson, *J. Opt. Soc. Am.*, 1965, **55**, 133.

11 (a) J. D. Donaldson, M. J. Tricker, and B. W. Dale, *J. Chem. Soc., Dalton Trans.*, 1972, 893; (b) A. Finch, P. N. Gates, F. J. Ryan, and F. F. Bentley, *J. Chem. Soc., Dalton Trans.*, 1973, 1863; (c) H. D. B. Jenkins, K. Prasad Thakur, A. Finch, and P. N. Gates, *Inorg. Chem.*, 1982, **21**, 423.

12 Tian Jie-mo, Wange Shui-ju, Cuo Cui-ju, Zhang Hong-pu, Zhang Bao-ging, and Lo Wen-gun, Extended Abstracts, Carbon '82 International Carbon Conf., London, 1982, p. 82.

13 K. Olie, C. C. Smitshamp, and H. Gerding, *Inorg. Nucl. Chem. Lett.*, 1968, **4**, 129.

14 G. Timp, L. Salamanca-Riba, L. W. Hobbs, G. Dresselhaus, and M. S. Dresselhaus, Proc. Fortieth Annual EMSA Meeting, Washington, D.C., Claitor's Publishing Division, Barton Range, 1982, p. 544.