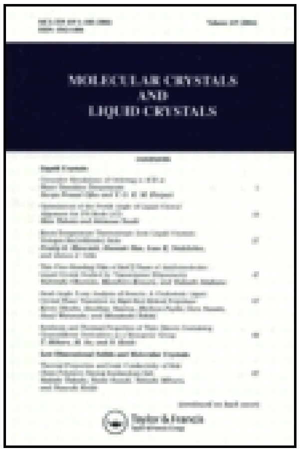

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Graphite Intercalation Compound with Cesium Superoxide: XPS, UPS and STM Study

H. Estrade-szwarckopf [a] , B. Rousseau [a] & V. Z. Mordkovich [b]

[a] CRMD, UMR 6619 CNRS-Université, 45071, Orléans Cédex 2, France

[b] ICMR, East 601, KSP, Sakado 3-2-1, Takatsu-ku, Kawasaki, 213, Japan

Version of record first published: 04 Oct 2006

To cite this article: H. Estrade-szwarckopf, B. Rousseau & V. Z. Mordkovich (1998): Graphite Intercalation Compound with Cesium Superoxide: XPS, UPS and STM Study, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 310:1, 237-242

To link to this article: http://dx.doi.org/10.1080/10587259808045342

*Mol. Cryst. Liq. Cryst.*, 1998, Vol. 310, pp. 237–242
Reprints available directly from the publisher
Photocopying permitted by license only

# GRAPHITE INTERCALATION COMPOUND WITH CESIUM SUPEROXIDE : XPS, UPS and STM STUDY.

H. ESTRADE - SZWARCKOPF[a], B. ROUSSEAU[a], V.Z. MORDKOVICH[b]
[a] CRMD, UMR 6619 CNRS-Université, 45071 Orléans Cédex 2, France.
[b] ICMR, East 601, KSP, Sakado 3-2-1, Takatsu-ku, Kawasaki 213, Japan.

XPS, UPS and STM are used to characterize a first stage $CsO_xC_y$ compound. The charge distribution and the cleavage localization are discussed.

Keywords : XPS, UPS, STM, Graphite-Intercalation-Compound, Cs-Oxide.

## INTRODUCTION

A lot of XPS and UPS studies have been devoted to binary alkaline Metal-Graphite Intercalation Compounds (M-GICs)[1-2] giving informations about the charge distribution in both host and guest lattices. Concerning the oxygen-alkaline GICs, a first XPS and STM study has been yet performed[3,4] but it seemed interesting to reproduce such study on the Cs-O compound and to extend it to UPS observation in order to compare the new sample to clean and slightly oxidized binary Cs-GICs (called $CsC_8$ or $CsC_{24}$ for stage 1 and 2 respectively)[2,5]. Moreover, we had thus, the opportunity to compare this Cs-Oxygen GIC (called $CsO_xC_y$) with a quite similar Na-O-GIC[6].

## PREPARATION AND EXPERIMENTS

A HOPG pellet ($\Phi$ = 7 mm, h = 0.5 mm) was treated with $Cs_3O$ as earlier described[3,4] in order to obtain a stage 1 blue sample, with an identity period of 9.84 Å and the intercalated layer composed of 4 layers Cs-O-O-Cs. The corresponding NaO-GIC was composed of 5 layers, i.e. Na-O-Na-O-Na but with a smaller repeat distance[6].

The intercalated pellet was fixed, in air, on our sample holder and introduced into the photoemission spectrometer analysis chamber. While the pressure was about 6. 10 $^{-11}$ Torr before introduction, it increases to 2. 10$^{-9}$ Torr unless the sample was cooled at 100 K, temperature for which the pressure decreases to about 10$^{-10}$ Torr. The sample being at 300 K, for instance for STM experiments, the pressure remained at its high value during several days after which, it decreased again to its normal value limited by pumping. Thus, it is sure that the sample lost part of its content, probably the outermost layers and this instability under vacuo made the observations a bit unreliable.

In order to limit this instability (without stopping it completely), XPS and UPS experiments were done at 100 K after in-situ cleavage performed on the cooled sample. This procedure is different from what we used in our previous work[4] where the XPS experiments were run at 300 K and at substantially higher pressure of 1. 10 $^{-9}$ Torr. In these conditions, a kind of instability was detected in [4] by the O/Cs ratio drift from 1, immediately after a cleavage, to 2.5 after 24 hours under vacuo.

No pressure increase was detected in presence of the $NaO_xC_y$ sample.

## EXPERIMENTAL RESULTS

### X - Photoemission Spectroscopy

The whole XP-spectra (Mg source 1253.6 eV) did not show any other peaks than those expected from the sample composition: carbon, oxygen and cesium.

Curiously, the **carbon 1s core level** peak (fig. 1) is very similar to that of the binary second stage $CsC_{24}$ and also to that of the $NaO_xC_y$ sample studied in [6]: one unique peak, at binding energy equal to 285.0 eV, dissymmetrically shaped. As for the $CsC_{24}$ [2], it was not possible to fit it with an unique component, even with a dissymmetrical shape due to an electron-hole pair creation process[7]. Another component (about 15% of the total C1s peak area), eventually double, had to be introduced, located at about +1 eV from the main peak maximum, we attributed both to carbon atoms located in crumpled domains created during the intercalation and to an intra-band plasmon specific of GIC and not present in pure graphite.

From the position and the shape of the main one, in $CsO_xC_y$, we conclude that the carbon atoms are bearing the same charge as in $CsC_{24}$ , and that this charge located in the $\Pi$ functions and/or in the interlayer orbital, contributes to the conduction band.

The only feature which differenciates the C1s line of the $CsO_xC_y$ from the $CsC_{24}$ one, is the inter-band plasmon located at 5.5 eV from the main component (to be compared with 5.1 eV in $NaO_xC_y$ and 6.8 eV in $CsC_{24}$ ).

The 3 **cesium core level** doublets could all be fitted with broad symmetrical lines in which a 10% small component had to be added, 2 eV high binding energy shifted. The main peaks 5p3/2, 4d5/2 and 3d5/2 (fig. 2) have respective

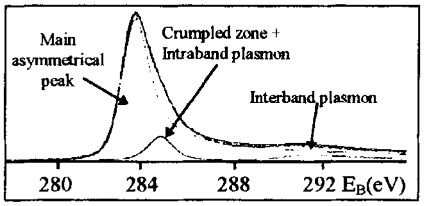

***Fig.1 CsOxCy XPS C1s spectrum.***
(See Color Plate IX).

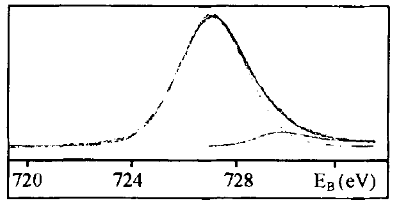

***Fig.2 CsOxCy XPS Cs3d 5/2 peak fitted as a main broad peak.***
(See Color Plate X).

$E_B$ = 12.1, 77.3 and 726.8 eV, very close to the respective peaks in $CsC_{24}$ but quite different from the oxide ones which are all low energy shifted from the metal (≈ -1 eV for the Cs3d). The position of the Cs peaks are difficult to compare with pure metal[8] or compounds even in an energy scheme which takes into account the shifts relative to the vacuo level[9]. Indeed, except for the case of sodium, in oxides, the alkaline core levels are low energy shifted contrarily to the classical electrostatic rule. In the binary M-GICs, relatively to vacuo, the metal appears partly discharged compared to the free metal, and when their surfaces are slightly oxidized the alkali lines shift abruptly to the oxide position below the pure metal one[5]. In $NaO_xC_y$[6], the situation is simpler and the sodium atoms are surely completely discharged. In $CsO_xC_y$, from the sole binding energy no conclusion could be deduced but, as in $NaO_xC_y$[6], the Cs line shapes, broad and symmetrical, surely prove that no charge remains on the Cs atoms, contrarily to $CsC_{24}$, in which the lines are much narrower and asymmetrical, signature of remaining conducting charge on the alkaline atoms.

The **oxygen 1s core level** spectra depend on the cleavage. When cleaved in air and immediately introduced in the vacuum chamber, the spectrum shows an unique peak at $E_B$ = 533.1 eV. If the cleavage is performed in situ, the oxygen spectrum intensity is a lot weaker (see below the stoichiometry) and may be decomposed into two peaks (fig. 3), the main one, A, at $E_B$ = 533.7 eV and a smaller one, B, ( 25% of the total) at $E_B$ = 531.1 eV.

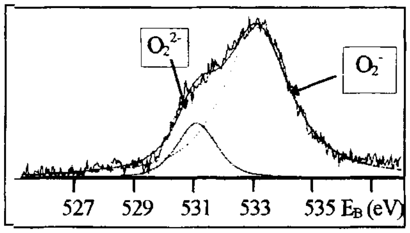

***Fig.3 In situ cleaved $CsO_xC_y$ XPS O1s spectrum.*** (See Color Plate XI).

The first peak is due to an $O_2^-$ superoxo-species and the smaller peak to an $O_2^{2-}$ peroxo-species. This last species represents 90% of the oxygen present on in situ cleaved $NaO_xC_y$[6] with 10% of $O^{--}$ oxo-species.

The **stoichiometry** was deduced from photoemission X spectra. The calculated chemical formula for the in situ cleaved surface is $CsO_{0.5\pm0.2}C_{14\pm3}$. This is in relative good agreement with the results of chemical analysis and electron probe microanalysis[3,4]. Cleavage in air resulted in the increase of the O and Cs contents by some 30% with corresponding chemical formula $CsO_{0.8\pm0.1}C_{10\pm1}$. It is necessary to note that in the XPS experiments carried out at 300 K[4], we observed much higher values of O/Cs ratio (1/1 to 2.5). However, the difference in O/Cs ratio may result from the temperature difference and corresponding strong departure of outermost layers, resulting in general instability of XPS intensities (see discussion in the experimental part).

## UV Photoemission Spectroscopy

The UV spectrum is given in fig. 4 and, similarly to what was done in [6], following conclusions may be deduced from it :

1/ The $CsO_xC_y$ compound is of donor type with a Fermi energy shift relatively to graphite of +1 eV[9,10], a noticeable Fermi level peak and a work function of 2.85 eV (4.4 in graphite and 2 eV in $CsC_{24}$ or 3.4 after strong superficial oxidation[5]).

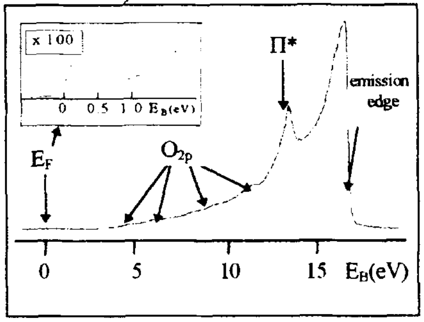

***Fig.4 In situ cleaved $CsO_xC_y$ UPS spectrum.*** (See Color Plate XII).

2/ Weak and broad spectral features due to O2p levels are located at 4.0, 5.7, 9.7 and 12.1 eV from the Fermi level. They might be attributed to the super oxo-species $O_2^-$ in agreement with the presence of the main 533.7 eV peak in the O1s spectrum[5,11]. However, as for XPS, a reliable UPS characterization of the outermost layer seen by UPS remains questionable due to the departure of superficial oxide vacuo. In $NaO_xC_y$ , the O2p peaks attributed to peroxo-species, are slightly different from the usual ones.

## Scanning Tunnelling Microscope

The STM observations have been performed in a vacuo chamber connected to the photoemission spectroscope and the surface could thus be studied without exposure to air.

Observed some days after an in air cleavage or after an in situ cleavage, the surface is rather flat and a small h.c.p. atomic lattice with an interatomic distance of 2.5 Å is observed, which can be attributed without greater risk to a graphene plane. However, when the sample was cleaved in situ, the graphitic lattice was 1D modulated (period 14 Å, about 0.1 Å deepness) (fig. 5). This modulation was observed during several hours and at different places on the surface, and then it disappears, the graphitic lattice completely flat and stable being restored.

lattice was 1D modulated (period 14 Å, about 0.1 Å deepness) (fig. 5). This modulation was observed during several hours and at different places on the surface, and then it disappears, the graphitic lattice, completely flat and stable, being restored.

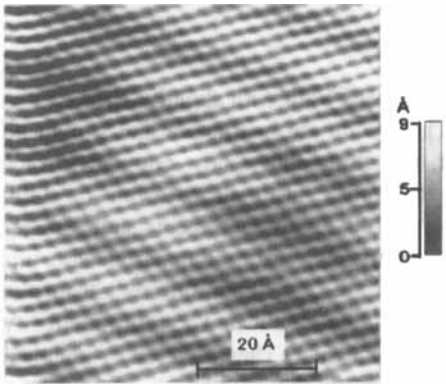

***Fig.5 STM image of an 1D modulated 2.5 Å h.c.p. lattice on $CsO_xC_y$ surface.*** (See Color Plate XIII).

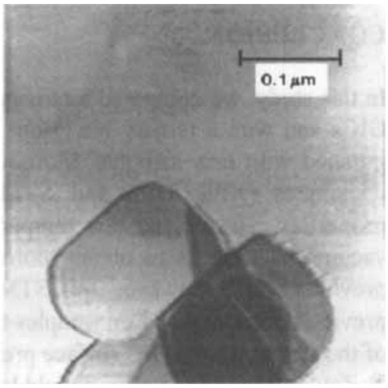

***Fig.6 (0.5x0.5) µm² STM image of a $CsO_xC_y$ surface showing flat bottomed holes.*** (See Color Plate XIV).

In spite of thorough observation of the surface, no other lattice has been detected contrarily to the hexagonal or square atomic lattices observed on $NaO_xC_y$[6] or on $CsO_xC_y$ similar samples[4], and probably due to an oxide layer : if such an oxide was present on the surface after the cleavage, it sublimed under vacuo and this sublimation explains the elevation of the chamber pressure in the presence of the sample. 1D modulation like that described here over, had been yet observed on binary alkali-GICs, after a long stay in an argon atmosphere[12,13] or after an oxidation of a $CsC_8$ surface[14]. The origin of such modulations of the graphitic lattice is not clearly understood and their stability not yet surely established. What is sure, is that they appear on GIC surfaces after the intercalate outermost layer has sublimed away under vacuo or under "inert atmosphere", and several days after cleavage.

Beside the atomic lattices, larger images 0.5 x 0.5 µm², like that given on figure 6, have been obtained. At this scale, we see a mean flat level out of which several flat pellets, about 1000 Å diameter and 5-6 Å thick, seems to have been cut away. No defects of this kind had been observed before, neither on HOPG nor on GIC surfaces, except on $NaO_xC_y$ [6]. It is, of course, tempting to interpret them in a similar manner : contrarily to what occurs during alkaline metal intercalation in HOPG to form binary GICs, the oxide or superoxide intercalation loosens the interconnections between the pristine HOPG cristallites, and some of them may be taken away by a cleavage. It is their prints which appear as flat bottomed holes cut out of the outermost graphene plane, with more or less regular contours. Those STM images reveal thus a specific mechanism of the alkali-oxide intercalation, different from the intercalation of alkaline metals.

## CONCLUSION

In this study, we compared a ternary Cs-O-GIC both with slightly oxidized Cs-GICs and with a ternary Na-O-one. The results are instructive and should be pursued with new samples. Moreover, our study shows how coupled surface techniques (XPS, UPS and STM) may give informations even on bulk properties. The use of low temperature (100 K) measurements and higher vacuum allowed us to obtain more accurate XPS results compared with our previous work. However, our STM results are completely different from the previous ones obtained on samples thought to be identical. The reproductibility of the ternary Cs-O-GIC surface properties which are characterized by identical X-Ray diffraction patterns, should be more thoroughly studied.

### References

[1] see for instance G.K. Wertheim, P.M.Th.M. Attekum and S. Basu, *Solid State Comm.* **33**,1127 (1980) and P. Pfluger, P. Oelhafen, H.U. Kunzi, R. Jeker, E. Hauser, K.P.Ackermann, M. Müller and H.J. Güntherodt, *Physica*, **99B**, 395 (1980).

[2] H. Estrade-Szwarckopf and B. Rousseau, *J. Phys. Chem. Solids*, **53**, 419 (1992).

[3] V.Z. Mordkovich, M. Baxendale, Y. Ohki, S. Yoshimura, T. Yamashita and T. Enoki, *J. Phys. Chem. Solids*, **57**, 6, 821-825, (1996).

[4] V.Z. Mordkovich and S. Yoshimura, *Synthetic Metals*, **85**, 1-3, 1667 (1997)

[5] M. Vayer-Besançon, B. Rousseau and H. Estrade-Szwarckopf, *Surface Science*, **318**, 169 (1994).

[6] H.Estrade-Szwarckopf, B.Rousseau, C. Hérold and P. Lagrange, *this issue.*

[7] G. K. Wertheim and P.H.Citrin, in Photoemission in Solids, Topics in Applied Physics, **26**, 206 (1978)

[8] G.Ebbinghaus and A. Simon, *Chemical Physics*, **43**, 117 (1980).

[9] B. Rousseau and H. Estrade-Szwarckopf, *Solid State Comm.* **85**, 793 (1993).

[10] R.C. Tatar, Dissertation, Univ. of Pennsylvania (1985) and S. Rabii, *private communication.*

[11] J. Jupille, P.Dolle and M. Besançon, *Surface Science*, **260**, 271 (1992).

[12] D. Anselmetti, V. Geiser, D. Brodbeck, G. Overney, R. Wiesendanger and H.J. Güntherodt, *Synthetic Metals*, 38, 157 (1990).

[13] ] S.P. Kelty and C. M. Lieber, *Phys. Rev. B*, 40, 5856 (1989).

[14] B.Rousseau and H. Estrade-Szwarckopf, *to be published.*