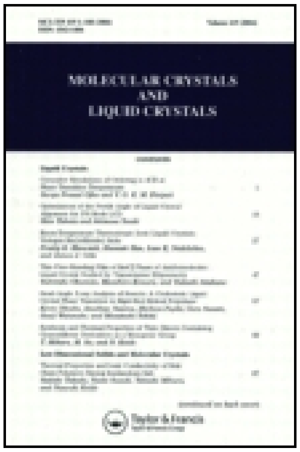

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Why Mono- or Poly-Layered Intercalated Sheets in Graphite-Electron Donors Systems?

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Why mono- or poly-layered intercalated sheets in graphite-electron donors systems ?

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Intercalation into graphite of electron donors is discussed, regarding the nature of the chemical species to be intercalated. In the binary compounds, the intercalated sheets are always mono-layered, while, in the ternaries, they are poly-layered, as soon as the electronegativities of both intercalated elements exhibit a sizeable difference. In the case of the ternary compounds, the intercalated sheets can be regarded as 2D slices of the corresponding bulk binary compounds. These slices are subjected to various distortions, that are caused by the presence of the adjacent graphene planes.

Keywords : graphite, intercalated sheets, electron donors, crystal structure

INTERCALATION INTO GRAPHITE AS 2D HOST STRUCTURE

By its strong heterodesmic character, graphite appears as a remarkable material for the chemist anxious to build atomic or molecular twodimensional constructions in the plane and infinite Van der Waals's gaps[1]. The intercalation reactions into graphite, that are very numerous, lead to push back the graphene planes, without them undergoing marked deterioration, and to put the foreign species between these planes. They are systematically accompanied with an electronic transfer between graphene planes and intercalated sheets consequently, they appear always as oxido-reduction reactions. This charge transfer, that creates electrostatic interactions between graphene and intercalated planes, allows the system to collect energy, that, furthermore, it is necessary to spend in order to push back the carbon layers[2]. Now oxidizing, now reducing, the graphene plane, because of its amphoteric character, is able to exchange negative charges with electron donors as well as electron acceptors. Consequently, graphite appears as a 2D host structure for very numerous chemical species.

INTERCALATION INTO GRAPHITE OF PURE METALS

In order to be able to intercalate into graphite, the electron donor elements have to be strongly electropositive. The heavy alkali metals intercalate very easily into graphite[3, 4, 5]. Lithium and especially sodium intercalate with more difficulty[6, 7]. The alkaline earth metals and several lanthanids (europium, ytterbium, etc...) are also able to intercalate[8, 9]. In all cases, the metallic atoms release electrons in the graphene planes, which become negative : they appear as graphitide macroanions.

In the bulk metals, the delocalized electrons cloud leads the cations to join together in the three directions of the space. On the contrary, in the graphite intercalation compound, this cloud is absorbed by the graphene planes and the metallic cations are not immersed any more in the cloud, so that these ions are compelled to be combined with anions. These latter, that are flat macroanions, compel consequently the cations to form 2D intercalated sheets. And these sheets are obviously mono-layered, because the system has to reduce as far as possible the repulsions between the positive charges. Poly-layered intercalated sheets, that are outlines of 3D stacking, cannot be observed, because the delocalized electrons cloud, that is essential for such a building, is missing.

Let us consider at first the stage one binary compounds. In these materials, the bond, that is ionic, is obtained by the electrostatic interactions, which appear between the metallic cations and the flat graphitide macroanions, whose stacking is regularly alternated along the **c**-axis. Each graphitide macroanion is made of a graphene plane, whose carbon atoms are strongly joined by covalent bonds, and that contains moreover a large excess of electrons. These latter are entirely delocalized in the graphene plane, so that these compounds exhibit a 2D metallic conductivity. Its value is high, as for a classical metal, and its behaviour with temperature is quite similar. For this reason, it is usual to regard their behaviour as that of a « covalent metal ».

It is also possible to consider these lamellar compounds as ionic salts (metallic graphitides). Indeed, the alternated stacking of positive and negative mono-layers along the **c**-axis is practically identical to the one of the fcc rocksalt along the [111] direction : alkali metal cations and graphitide macroanions on one hand, and alkali metal cations and halide anions on the other hand. It is interesting to underline also that the hexagonal symmetry of negative and positive layers is similar for both metallic graphitides and rocksalt.

Furthermore, both intercalated layer and graphene plane exhibit 2D unit cells, which are commensurate, so that it is easy to put a 3D unit cell down to these binary compounds[4, 10, 11]. In the case of alkali metals, whose 3D structure is bcc, the intercalated mono-layer exhibits a 2D hexagonal symmetry. This « hexagonalization » is due to the very strong influence of graphite towards the intercalated atoms.

For the intercalation compounds, whose stage is higher than one, only a part of the Van der Waals's gaps is occupied by intercalated sheets. In this case, two types of bond are observed along the **c**-axis : ionic (or electrostatic), when a metallic cations layer and a graphene plane are adjacent, and Van der Waals, when two graphene planes are side by side.

In brief, one can say that the intercalated sheets of the binary graphite-metal compounds are necessarily mono-layered, because of the electronic transfer between metallic atoms and graphene planes.

Some ternary graphite intercalation compounds containing two heavy alkali metals were synthesized[12, 13]. Because the electronegativities of these metals are of course almost the same, these ternary compounds exhibit intercalated sheets, which are mono-layered too ; but these sheets contain simultaneously both alkali metals. In these ternaries, the cations are randomly distributed in each layer, so that these compounds can be regarded as solid solutions of both corresponding binaries.

INTERCALATION INTO GRAPHITE OF ALKALI METALS WITH A FAIRLY ELECTRONEGATIVE ELEMENT

When we add a more electronegative element to the alkali metal, the intercalation reaction is very strongly altered : indeed, the reaction product is from now on a ternary compound and the intercalated sheets are no more mono-layered, but poly-layered. The noticeable electronegativity difference between the alkali metal and the second element is the cause of the growth of poly-layered intercalated sheets inside the Van der Waals's gaps.

In a first time, we consider the ternaries containing both an alkali metal and a fairly electronegative element as mercury, thallium, bismuth, antimony or arsenic[14]. The intercalation of the binary alloy is obtained by means of a reaction between an HOPG platelet and a large excess of liquid alloy, whose composition is well defined. In this reactive alloy, the alkali metal concentration varies, according to the cases, between 20 and 80 atomic percent. When the alkali metal concentration is too high, only this alkali metal intercalates into graphite and we obtain a binary compound. But, if it is too small, no reaction appears at all, and the graphite remains free.

For the middle alkali metal concentrations, the intercalated species appears as a binary sheet. It is generally made of an intermediate electronegative element layer sandwiched between two superimposed alkali metal layers. If we look at the succession along the **c**-axis of the atomic layers, it appears alternately a positive plane, a negative plane, a positive plane, etc... The existence of negative layers different from graphene planes is the root of the poly-layered nature of the intercalated sheets. Indeed, these mercury, thallium or arsenic layers attract, as the graphene planes, a part of the s electrons, that are released from both adjacent alkali metal planes. Consequently, in these phases, the intercalated sheet has to be naturally three-layered.

A well-known characteristic example is observed with the potassium amalgam[15]: a perfect K-Hg-K sandwich is indeed intercalated between the graphene planes. However, it is reasonable to think that, inside the sandwich, the bond is not ionic but rather metallic. In fact, the intercalated sheet is a slice of alloy, comparable to a free amalgam. We have precisely shown that this three-layered sandwich is quite simply a slice of the monoclinic KHg_2 amalgam. But, after intercalation, this latter becomes flatter and loses its own symmetry in aid of an hexagonal and commensurate symmetry, that is it imposed by the adjacent graphene layers. In this ternary compound, the interactions between the intercalated amalgam slice and the carbon planes are of course very strong.

We know obviously much more complex cases. A classical example is the one of the graphite-potassium-thallium ternary, for which, inside the intercalated sheet, the intermediate thallium layer is splitted into three, so that this sheet is five-layered, according to the K-Tl-Tl-Tl-K atomic stacking[16]. This alloy slice is very thick and possesses consequently a strong internal coherence, so that the interactions between this intercalated slice and the graphene planes are obviously very poor : indeed, in this case, the carbon layers are unable to impose their hexagonal symmetry to the intercalated sheet, that, moreover, does not even become commensurate. In this example, both graphitic and intercalated 2D sublattices are absolutely distinct and quasi-independent.

In other ternary compounds (graphite-potassium-arsenic, for instance), the intercalated sheets are three-layered too. They exhibit of course an inner arsenic plane, but both outer potassium layers contain moreover arsenic, so that these latter are mixed[17].

In these ternary compounds, it is interesting to underline that the intercalated alloy slices are mostly incommensurate in relation to the graphitic 2D sublattice. Consequently, one can say that the graphene planes are able to cut up some slices in the binary alloys, but they are generally unable to impose them their own symmetry.

On the other hand, the intercalated alloy slice exhibits always an overall positive charge, that is compensated for an excess of delocalized electrons in the graphene planes. This charge transfer, that creates again graphitide macroanions, authorizes moreover the building of intercalated poly-layers, thanks to the large difference of the electronegativities of both alloy components.

The intercalation into graphite of the alkali metal hydrides has to be mentioned here[18, 19, 20], because the phenomenon is exactly comparable. In the compound, whose chemical formula is $KH_{0.8}C_4$, a three-layered K-H-K sandwich is indeed intercalated between the graphene planes. But, of course, inside the sheet, the bond is iono-covalent and no more metallic as previously. In fact, these compounds allow the transition with the following ternary phases.

INTERCALATION INTO GRAPHITE OF ALKALI METALS WITH A STRONGLY ELECTRONEGATIVE ELEMENT

If we replace now the fairly electronegative species with a strongly electronegative element, the previous phenomenon is of course largely emphasized.

The intercalation is obtained by means of a reaction between an HOPG platelet and a large excess of alkali metal, that contains a very little amount of electronegative element, as an halogen (Cl, Br, I) or a chalcogen (O, S, Se) for instance. In this reagent, the halogen or chalcogen concentration reaches often only 1 atomic percent ; but the intercalation of the alkali metal into graphite is accompanied by a very large enrichment in electronegative element, since the intercalated species exhibits frequently a concentration of 5, 10, 20 and even 30 or 50 atomic percent.

This intercalated species is of course a binary sheet, that is generally made of an intermediate electronegative element layer sandwiched between two superimposed alkali metal layers. Along the **c**-axis, it appears again alternately a positive plane, a negative plane, a positive plane, etc...

A first example is observed with the graphite-potassium-oxygen ternaries, that contain, between the graphene planes, classical K-O-K sandwiches[21]. The latter are characterized by a central plane, which contains a remarkably little oxygen amount, since the O/K ratio reaches only 7%. For this reason, these ternaries are sometimes considered as quasi-binary compounds. As second example, we have to report the graphite-potassium-sulphur compound[22]. It exhibits also classical K-S-K intercalated sandwiches, but, in this case, the S/K ratio reaches 25%.

The difference of the electronegativities of both elements is even larger than in the previous cases, so that the formation of intercalated poly-layered sheets is even easier. For this reason, the iono-covalent character of the intercalated sheets is here obviously indisputable.

The intercalated ionic sandwich exhibits an overall positive charge, so that the graphene planes appear again as graphitide macroanions, characterized by an excess of delocalized electrons. The positive charge exhibited by the intercalated ionic sheet is due to the fact that the cations are largely superior in number in relation to the anions. Very often, the intercalated sheet can be regarded as an ionic slice, which is inserted between the graphene planes after cutting up inside the 3D binary ionic (or iono-covalent) compound. Thus, we can describe three various compounds belonging to this category. ■

The graphite-sodium hydroxide compound contains two-layered intercalated sheets[23]. Both layers are constituted by sodium cations and hydroxide anions simultaneously. However, the number of cations is weakly superior, so that the graphene planes carry a negative charge and appear as graphitide macroanions. The structure of the two-layered hydroxide sheet is a slice of the bulk tetragonal sodium hydroxide, that can be described by a 2D square unit cell, which is of course no-commensurate in relation to the graphitic 2D sublattice. In this case, the interactions between graphene planes and intercalated hydroxide slice are obviously weak. ■

The graphite-sodium-oxygen compound contains five-layered intercalated sheets, according to the Na-O-Na-O-Na stacking[24]. They are composed at once of sodium cations (Na^+) and peroxide anions ($^-O\text{-}O^-$). The latter are arranged perpendicularly to the graphene planes and occupy the double octahedral sites, that are created by the Na^+ cations, as in the bulk Na_2O_2 peroxide. The intercalated sheet appears again as a slice of sodium peroxide, that contains an excess of cations, so that the graphene planes are again turned into graphitide macroanions. Although the latter compress strongly the peroxide slices, they do not succeed completely to make commensurate both 2D sublattices.

Other ternary compounds have been synthesized by intercalation of sodium halides[25]. They exhibit three-layered intercalated sheets, according to the Na-halogen-Na stacking. Both intercalated and graphitic 2D sublattices are sometimes commensurate : in the graphite-sodium-chlorine compound, the intercalated sheet is a three-layered slice, cutted up in the bulk fcc sodium chloride in parallel to the (111) plane. Sometimes, both 2D sublattices are incommensurate : it is the case of several types of graphite-sodium-iodine compounds.

CONCLUSION

The pure reducing metals and the binary alloys of strongly electropositive metals are able to intercalate into graphite, with the help of an oxido-reduction reaction, that brings about the ionization of the metallic atoms combined with an electron transfer from all these atoms to the adjacent graphene planes. This charge transfer strips the intercalated metal sheets of its delocalized electrons, so that they are necessarily and exclusively mono-layered.

On the other hand, when these reducing metals are associated with a more electronegative element (metal, semi-metal or non-metal), the same oxido-reduction reaction occurs. But, the electron transfer takes place from reducing metal atoms to the graphene planes and to the associated electronegative atoms simultaneously. For this reason, the intercalated sheets become poly-layered, according to the basic alkali metal - second element - alkali metal stacking, that corresponds to a regular positive-negative-positive alternation. Thus, the presence of anions (or electronegative atoms) allows the stacking of several cations layers.

In the most cases, it is possible to recognize the poly-layered sheet as a slice of the binary ionic compound (or binary alloy), that is intercalated in the Van der Waals's gap. But, this slice is often deformed because of the interactions with the graphitic sublattice, that can be indeed more or less strong, according to the cases. As previously reported, we can observe various distortions for the intercalated sheets as compression, hexagonalization, commensuratization, etc...

Now strongly now more softly, graphite imposes often its structural geometry on the intercalated species. At least, this latter is obliged to adopt a positioning, which is imposed by the adjacent graphene planes. At last, the intercalated sheet is poly- or mono-layered according to whether the electropositive metal can exchange electrons or not inside the intercalated sheet itself.

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