Structural Study of Novel Graphite−Lithium−Calcium Intercalation Compounds

Sébastien Pruvost,[a,b] Claire Hérold,*[a] Albert Hérold,[a] and Philippe Lagrange[a,b]

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Three new layered compounds were synthesised by immersing a pyrographite platelet in a molten Ca–Li alloy creating a new graphite intercalation compound family. The samples were studied by X-ray and neutron diffraction, revealing that the intercalated sheets are polylayered. The study of the 00*l* reflections allowed us to establish the *c*-axis stacking of these three phases. The α-phase exhibits a five-layered intercalated sheet which has something in common with a Li–Ca–Li–Ca–Li slice cut in the $CaLi_2$ structure ($ThMn_2$ Laves phase type). The β-phase, which is richer in metallic elements and with a greater repeat distance, possesses seven-layered intercalated sheets due to the splitting of the middle lithium plane in three. The third phase is a pseudo-binary compound, containing monolayered sheets and with a formula close to CaC_6. Electron microdiffraction allowed us to determine the 2D unit cell for each compound, all of which were commensurate with that of graphite. Charge transfer from the intercalate to the host lattice was evaluated for the three phases from *hk*0 data, leading to high values.

Introduction

Graphite exhibits a lamellar structure containing two-dimensional Van der Waals gaps, and it therefore acts as a host lattice for numerous reagents. It turns out that the alkali metals are excellent electron donors in order to intercalate into graphite. The intercalation of the pure alkali metal was reported a long time ago;[1] it leads to binary compounds whose stage varies with metal content. Indeed, when potassium, rubidium and caesium react with graphite, it is very easy to prepare the pure first-stage MC_8 (M = K, Rb, Cs) compounds, which contain a monoatomic metal layer in each interlayer space. On the other hand, the behaviour of graphite changes radically when a less electropositive element is added to the reactive alkali metal. For example, when a graphite sample is immersed in liquid potassium containing a small amount of sulfur, a ternary compound is formed whose intercalated sheets are poly-layered with potassium atoms in contact with graphene planes.[2] Moreover, these potassium-rich compounds are very stable in air.

In the case of lithium, the binary first-stage compound is rather different from the previous ones:[3] its metal content is higher, since its chemical formula is LiC_6. This compound is of great interest, due to its widespread use as the negative electrode material in Li-ion batteries.[4] One way to improve the batteries' capacity could be to increase the lithium content of the negative electrode, although the co-intercalation of lithium with another element seems to be very difficult. The data concerning the structure and the properties of the LiC_6 compound, in comparison with those of the heavy alkali metal compounds, are unfavourable to this co-intercalation because the repeat distance would be increased and part of the strong Li−Li interactions along the *c*-axis would be destroyed. Moreover, the synthesis of a ternary alkali metal compound requires the melting of the M−E mixture (M = alkali metal, E = co-intercalated element) or the partial solubility of M−E in the liquid metal. The melting points of most M−E mixtures are very high and the attack of graphite by lithium is very fast above 600 °C, with formation of lithium acetylide (Li_2C_2) and, of course, destruction of the graphene planes. Numerous experiments have been carried out associating lithium with various elements but generally only binary compounds are obtained.[5] Consequently, we tried to co-intercalate lithium with some elements that are able to intercalate into graphite by themselves. We chose the alkaline earth metals because their intercalation into graphite leads to first-stage MC_6 compounds (M = Ca, Sr, Ba)[6] rather close to LiC_6, despite the fact that the reaction is markedly more difficult, especially with calcium. These experiments led to the isolation of the first ternary graphite−lithium−third-element compounds, that were obtained associating lithium and calcium.[7] We report three new intercalation compounds, called α, β and γ, and their description is given below.

[a] Laboratoire de Chimie du Solide Minéral, UMR 7555, Université Henri Poincaré Nancy I
B. P. 239, 54506 Vandœuvre-lès-Nancy Cedex, France
E-mail: Claire.Herold@lcsm.uhp-nancy.fr
[b] Ecole Européenne d'Ingénieurs en Génie des Matériaux, Institut National Polytechnique de Lorraine,
6, rue Bastien-Lepage, B. P. 630, 54010 Nancy Cedex, France

Results and Discussion

Structure of the α Compound

The 00*l* diffraction diagram of this compound (Figure 1) gives a *c*-axis repeat distance of 776 pm. According to the dilatometric measurements, which give values of around 157%, it belongs to the first stage thus confirming the crystallographic data (the theoretical calculation leads to 132%). This difference is almost certainly due to the non-uniformity of the sample's faces. The repeat distance is quite characteristic of a poly-layered intercalated sheet. Indeed, the repeat distances are only 370 pm and 455 pm for both the binary compounds LiC_6 and CaC_6, respectively.[3,6]

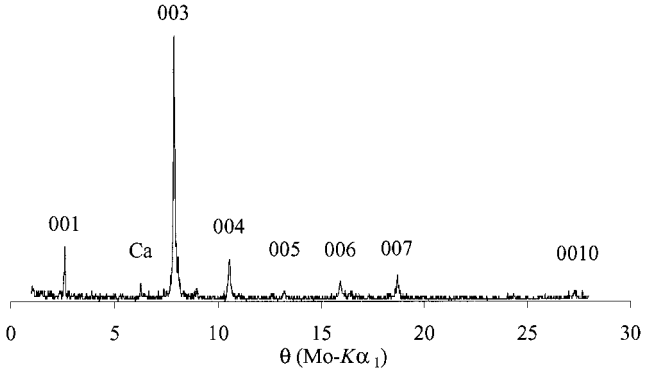

Figure 1. 00*l* X-ray diagram of the α compound

The study of lithium by X-ray diffraction is particularly difficult due to the presence of very few electrons in these atoms, therefore neutron diffraction experiments are often necessary in order to complete the data and allow us to calculate the *c*-axis atomic stacking.

Firstly, however, we will consider only the results obtained from the X-ray experiments. The Fourier transform of the 00*l* structure factors allowed us to produce the *c*-axis electronic density profile in the direct space. From a *c*-axis atomic stacking model, without taking the lithium atoms into account, we then plotted a second electronic density profile, which was compared to the previous one. When the best agreement had been obtained between both profiles (Figure 2), the atomic stacking model was considered to be a good description of the carbon and calcium positions along the *c*-axis. This model presents two superimposed symmetrical calcium layers in the graphitic interval, with a graphene—calcium layer distance of 238 pm, such that the calcium layer—calcium layer distance in the same graphitic interval reaches 300 pm. Moreover, the C/Ca ratio is equal to 2.3, in accordance with the results of the analyses.

Secondly, we used the neutron-diffraction data in order to take the lithium atoms into account. Using the same method, we obtained a final model with three additional lithium layers: one of them is placed at the centre of the

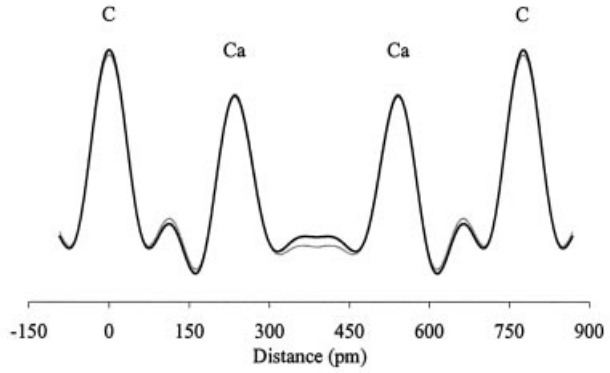

Figure 2. Electronic density profiles along the **c** axis of the α compound; black line: experimental data; grey line: calculated data; seven reflections are taken into account (residual factor R_{F00l} = 8.35%)

graphitic interval with two symmetrical layers between the graphene plane and the calcium layer. The graphite—lithium layer distance is estimated to be 160 pm. This result, nevertheless, remains qualitative, because it has been shown by nuclear microprobe analysis[8] that lithium distribution inside the compound is not really homogeneous. Consequently, it is not possible to attribute a well-defined metal content for each lithium layer. The lithium content is, however, higher in both of the symmetrical external layers.

Finally, the intercalated sheet appears as a five-layer, according to the Li−Ca−Li−Ca−Li sequence and we can clearly see that there are lithium atoms in contact with the graphene planes. Indeed, as is usual in these ternary compounds, the more electropositive element is localised close to the more electronegative one, in this case the carbon atoms.

The intercalation reaction into graphite is always an oxido-reduction. With electron donor species, graphite is reduced and the electron concentration of the graphene planes increases; the carbon−carbon distance simultaneously increases. The *hk*0 X-ray diagram allows us to determine this charge transfer between the intercalated species and the graphene layers, since measuring the angular position of the 110 reflection generated by the graphene planes very precisely is enough to be able to calculate this distance. Its value was compared to that of pristine graphite, and the increase of the carbon−carbon distance was deduced. For these measurements, diamond was used as an internal standard (the 220 reflection of the CFC diamond for our calculations). The d-spacing of the 110 reflection is equal to 125.2 pm for the ternary compound, whereas it only reaches 123 pm in pristine graphite. The corresponding increase of the C−C distance is of the order of 1.8%. Pietronero and Strässler[10] have established the following equation between this parameter and the charge transfer (f_c):

$$\Delta d_{C\text{-}C} = 0.157 f_c + 0.146 f_c^{3/2} + 0.236 f_c^2$$

According to this relation, the electronic transfer reaches 0.111 electrons per carbon atom for the compound. In comparison, the corresponding value is only 0.07 electrons per carbon atom in the LiC_6 compound. In spite of the very large amount of intercalated metal, the charge transfer remains moderate, so that it is probable that there are metallic bonds within the intercalated sheets. These bonds could explain the unusual hardness of the samples.

The 2D organisation of the compound was observed by several techniques, including TEM (transmission electron microscopy) and XRD (*hk*0 reflections). The TEM study was carried out in a single-crystalline area of the sample. In order to be sure that this area is well representative of the compound, it was systematically observed by EDS (electron dispersive spectroscopy) measurements. The electron microdiffraction images gave the symmetry and the parameters of the 2D unit cell: it is rectangular with $a = 2000$ pm and $b = 430$ pm, and it is commensurate with the graphitic one after taking the charge transfer into account. The 110 graphitic reflection becomes the 830 one in this unit cell. Furthermore, the a and b parameters can be respectively written as $8a_G$ and $\sqrt{3}{\cdot}a_G$. Of course, in these expressions the value of a_G is not that corresponding to pristine graphite, but that obtained from the expanded graphene planes present in the ternary compound. The particular values of these parameters lead to a 2D unit cell that contains exactly 32 carbon atoms (Figure 3).

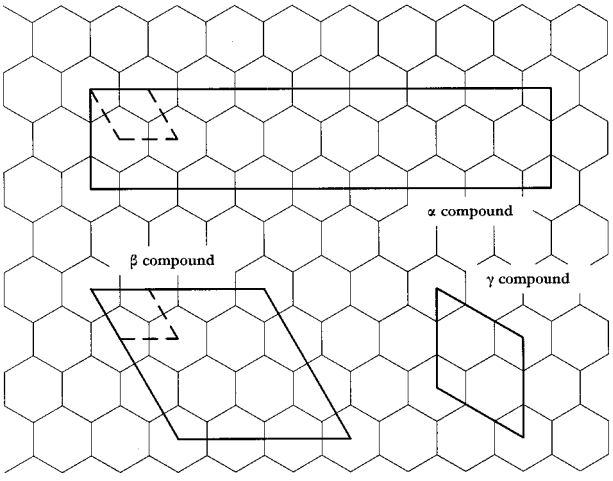

Figure 3. 2D unit cells of the α, β and γ compounds; dotted lines represent the 2D graphite unit cell

A rotating crystal image (Figure 4) allowed us to determine the value of the third parameter, which is twice the repeat distance, that is to say: $c = 1552$ pm. Consequently, the 3D unit cell of the compound is orthorhombic with the three previous parameters.

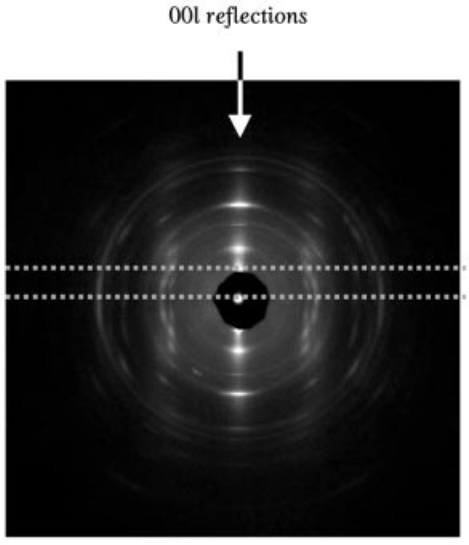

Figure 4. Rotating crystal image of the α compound; both dotted lines symbolise the equatorial stratum and stratum 2

It is interesting to compare the *c*-axis atomic stacking of the α ternary compound with the structure of the $CaLi_2$ binary solid alloy. $CaLi_2$ appears in the Ca−Li phase diagram[11,12] as the only definite compound. Its structure, first studied by Hellner and Laves[13] and later by Carfagno,[11] is hexagonal and isomorphic with the Laves's $ThMn_2$ phase with the following parameters: $a = 631.3$ pm and $c = 1028$ pm. Its space group is $P6_{3/m}mc$, with calcium atoms occupying the 4f sites and lithium atoms the 2a and 6h ones, such that each unit cell contains four $CaLi_2$ units. Along the *c*-axis, the structural arrangement of $CaLi_2$ can be described by a perfectly alternating sequence of calcium and lithium layers, in accordance with a Li−Ca−Li−Ca−Li five-layered intercalated sheet. As is shown in Figure 5, two possibilities exist in order to allow the formation of a *c*-axis five-layered sequence in the $CaLi_2$ solid alloy. The first slice (denoted A) seems to be more likely than the second one (denoted B) for two reasons. Firstly, in the A-slice the out-

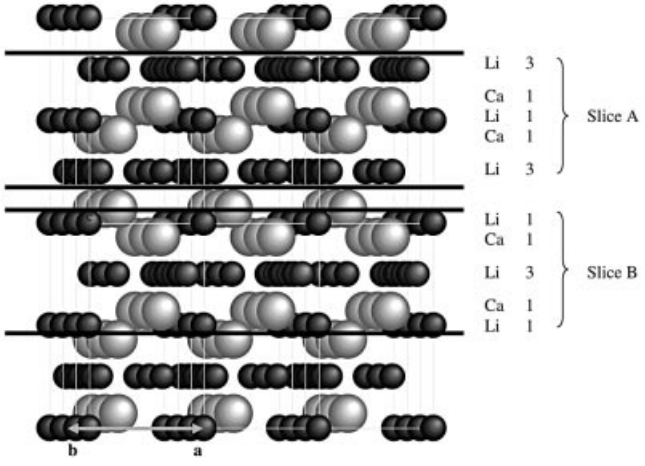

Figure 5. $CaLi_2$ structure and both possible slices

side lithium layers contain a larger number of atoms than the internal lithium plane — an identical distribution was observed in the intercalated sheet, according to the neutron-diffraction data — whereas in the B-slice the metal content of the internal lithium layer is particularly high. Secondly, the calcium atoms are exactly superimposed in the B-slice, while they are shifted in the A-slice, therefore it is likely that this second arrangement is more stable for a 2D slice intercalated between graphene planes.

These comments present a great interest because we can observe that the intercalation into graphite of binary species often allows a comparison between the sequence of the intercalated sheets and the structure of the free binary species. In spite of the stress applied by the graphene planes, the atomic stacking in the intercalation compound could be identical to a slice judiciously cut off in the structure. Similar results were previously observed in several cases, for example potassium sulfide,[14] potassium amalgam[15] and sodium peroxide.[16,17]

A mixture containing the second stage compound (α type) and CaC_6 was also obtained but it was not possible to isolate this ternary phase. The value of its repeat distance is 1100 pm, that is to say approximately (776 + 335) pm. Therefore, this compound exhibits alternating occupied graphitic intervals (with the same atomic stacking as in the first stage α phase) and empty ones along the *c*-axis.

Structure of the β Compound

As described above, the 00*l* X-ray diffraction diagram (Figure 6) gives the repeat distance of this first-stage compound. It is much higher for this phase, since it reaches 970 pm (instead of 776 pm for α compound). There is an obvious connection between this high value and the very large lithium content of the phase, which possesses a C/Li ratio slightly lower than 2.

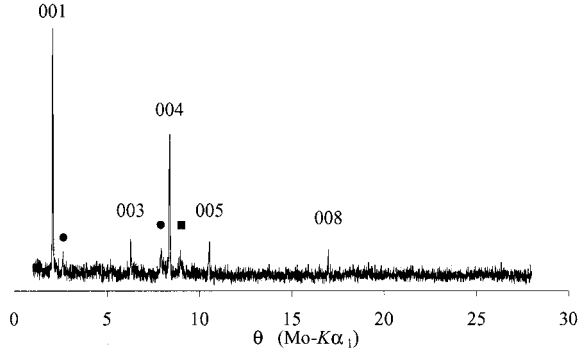

Figure 6. 00*l* X-ray diagram of the β compound; • α phase, ■ CaC_6

Using the previous method, it is possible to draw the experimental *c*-axis electronic density profile. This model then allows us to draw a second profile, and the comparison between both profiles leads to an improvement of this model until a better agreement was obtained. However, since this compound contains a lot of lithium, it is necessary in this case to take the lithium atoms into account. Indeed, their presence is clearly evident in Figure 7. The *c*-axis atomic stacking model contains seven layers, according to the Li−Ca−Li−Li−Li−Ca−Li sequence. The central lithium layer is very rich in metal (1.5 lithium atoms for every six carbon atoms), whereas the outer lithium planes (130 pm above and below) contain only 0.6 lithium atoms for every six carbon atoms. For this reason it is not easy to confirm the presence of these latter lithium layers by XRD, although the inter-calcium layer distance of 510 pm means that the calcium layers cannot surround only one lithium plane. This large value therefore confirms the presence of three central lithium layers. Both calcium planes contain 2.1 calcium atoms for every six carbons. Moreover, this very thick sheet is sandwiched between two lithium layers 650 pm away from one another, which contain one lithium atom for every six carbon atoms.

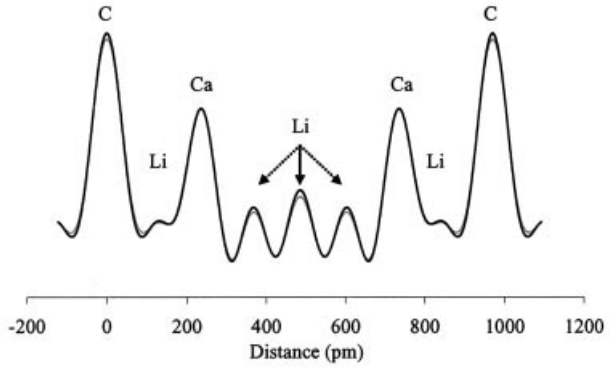

Figure 7. Electron-density profiles along the *c* axis of the β compound; black line: experimental data; grey line: calculated data; eight reflections are taken into account (residual factor R_{F00l} = 6.6%)

This intercalated sheet is extremely rich in metal and is consequently very thick. A similar phenomenon was observed previously in another system when we carried out the intercalation reaction of potassium−thallium alloys into graphite.[18] The amount of intercalated metal was also very high, as was the repeat distance, and the core of the intercalated sheet was also constituted by three metal layers, although with Tl−Tl−Tl stacking instead of Li−Li−Li stacking. In these cases it is generally not possible to establish a connection between the structure of the binary alloy and that of the poly-layered intercalated sheet.

The charge transfer between the graphene layers and intercalated species can also be measured by XRD using the positions of the *hk*0 reflections. In the graphene plane, the internal C−C distance reaches in this case 143.5 pm, instead of 142 pm in pristine graphite, meaning that the charge transfer is close to 0.07 electrons per carbon atom, which is about the same value as in LiC_6. This β ternary compound contains approximately five times as much metal as the binary compound, but nevertheless the electron transfer remains essentially unaltered. As above, this interesting result clearly emphasises the difficulty in correlating

both phenomena: a high metal content does not inevitably lead to a sizeable charge transfer, because there are automatically metallic bonds in the intercalated sheet in order to maintain its cohesion. These latter, of course, strongly reduce this transfer.

The 2D unit cell of the compound was obtained by TEM and XRD (*hk*0 reflections) techniques. Both methods give the same results: Figure 8 shows the *hk*0 diffraction diagram, for which all the reflections can be easily indexed in a hexagonal two-dimensional unit cell identical to the graphitic one. Indeed, the value of its parameter is 745 pm, that is to say $3a_G$. From this value, one can see that this unit cell contains 18 carbon atoms (Figure 3).

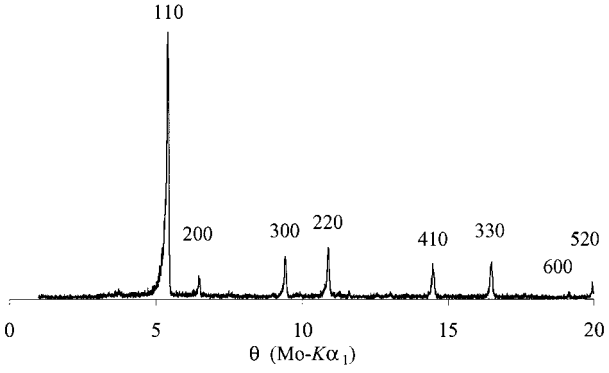

Figure 8. *hk*0 X-ray diagram of the β compound

Structure of the γ Compound

This first-stage compound exhibits a repeat distance that is much smaller than that of the previous ones (Figure 9). It has a value of only 454 pm, which is exactly the same as that of the CaC_6 binary intercalation compound. As expected, the study of the 00*l* reflections intensities (Fourier transform) shows unambiguously the presence of mono-layered intercalated sheets (Figure 10). This intercalated layer contains calcium atoms and its metal content corresponds accurately to a C/Ca ratio of six. It is basically the same compound as the CaC_6 binary, although it nevertheless contains a very small amount of lithium (1 atom-% of lithium), as was shown by nuclear microprobe measurements. This lithium amount is, of course, strictly invisible by XRD measurements. It is possible to consider this compound as a quasi-binary CaC_6 phase.

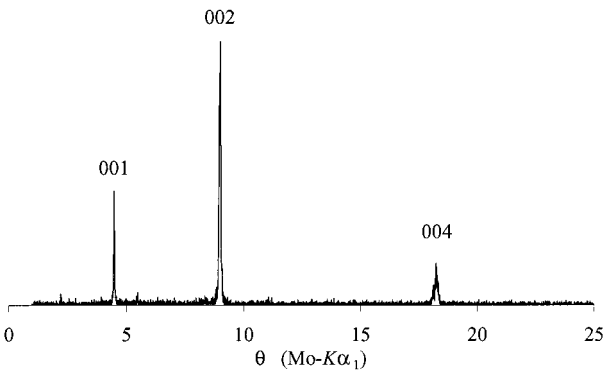

Figure 9. 00*l* X-ray diagram of the γ compound

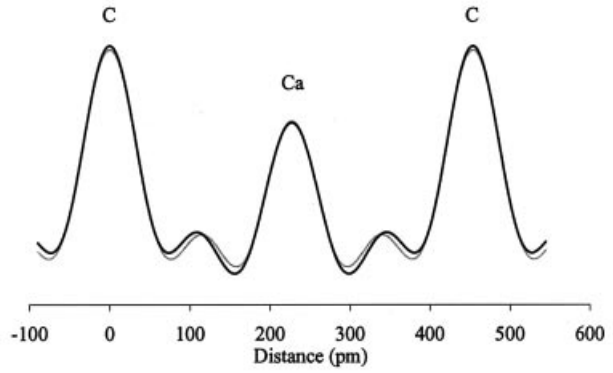

Figure 10. Electron-density profiles along the *c* axis of the γ compound; black line: experimental data; grey line: calculated data; five reflections are taken into account (residual factor R_{F00l} = 7.5%)

All its characteristics are exactly identical to that of the real binary.[6] The internal C−C distance of the graphene planes is equal to 125 pm, so that the charge transfer between the graphene and intercalated layers is close to 0.102 electrons per carbon atom. One can explain this high value for a binary compound as follows. Firstly, contrary to the alkali metals, calcium is divalent so that it is more easily able to release two electrons instead of one. Secondly, in a binary compound the intercalated sheet is mono-layered. Consequently the delocalised electrons, which are partially used in the ternaries in order to supply the internal cohesion of the poly-layered intercalated sheet by the means of metallic bonds, can in this case be wholly "absorbed" by the graphene layers. Indeed, the intercalated mono-layer does not need any internal cohesion, since it appears as a cation plane sandwiched between two macro-anionic planes: this situation is exactly the same as that observed in ionic salts, such as NaCl.

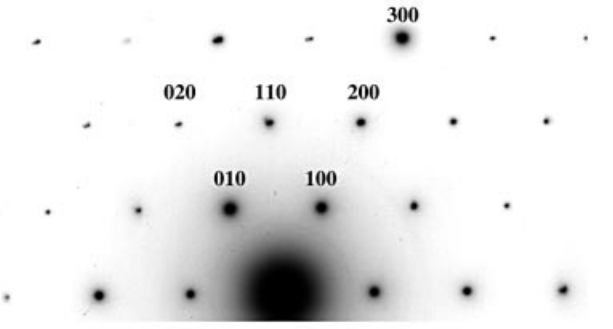

Figure 11. Electron-microdiffraction pattern of the γ compound; hexale lattice: *a* = 431 pm; the 110 reflection corresponds to the 100 reflection of graphite; the 300 reflection corresponds to the 110 reflection of graphite

Figure 11 shows the reciprocal lattice observed using a TEM technique. The two-dimensional unit cell of the compound is hexagonal with a parameter of 431 pm (Figure 3). It is the same as the graphitic one, since $a = 3d_{C-C} = \sqrt{3}\cdot a_G$. This classic 2D arrangement is known as the "hexal structure".[3]

As has been mentioned above, this compound is essentially the CaC_6 binary compound, since the lithium content is exceedingly low. However, this is the first time that the binary has been isolated. Its synthesis makes use of the reaction between graphite and calcium vapour at high temperature, so that the vapour pressure is sufficient, but nevertheless not so high as to allow the attack of the metal on graphite, leading to acetylides. The reaction is strongly limited by this range of temperatures, so that the formation of CaC_6 in that case is just superficial. But using a calcium-lithium liquid alloy, we have prepared this compound in the bulk of the sample.

Two hypotheses can explain this phenomenon. Firstly, the interstitial lithium (even though its content is extremely low) is necessary in order to carry out the intercalation right through to the core, so that thermodynamically its role is very significant. Secondly, this novel method is able to give a bulk CaC_6 sample and makes use of a liquid, and not a vapour, as reagent, so that the reaction can be undertaken at low temperatures (350 °C) with a very concentrated reagent. In these conditions, the carburisation by lithium or calcium is completely avoided and the intercalation reaction becomes total. The interstitial lithium is dragged towards the graphitic intervals by calcium during its intercalation, and after reaction it is trapped inside the intercalated sheet, but it does not play a role in the stability of the compound. This second explanation is probably the most likely.

This interesting synthesis technique has been used previously with another binary system: the reaction between graphite and lithium−sodium liquid alloys leads to the quasi-pure LiC_6 compound.[19] This latter, however, was isolated using the vapour method, although its preparation is much easier by this second method. On the contrary, for CaC_6, the liquid method is absolutely essential in order to isolate this compound.

Conclusion

It has been shown that the co-intercalation of lithium and another element into graphite is very difficult since the thermodynamic parameters are not favourable for such a reaction. However, the first ternary graphite intercalation compounds containing lithium and a second metal were prepared from lithium−calcium alloys.

Two novel first-stage graphite−lithium−calcium compounds were isolated and a structural study was carried out with samples prepared from pyrolytic graphite platelets. They are very rich in metal and one of them particularly in lithium. Both ternaries possess poly-layered intercalated sheets, with roughly an alternate sequence of lithium and calcium. Lithium, the more electropositive, builds two layers in contact with graphene planes, the more electronegative. Between these lithium layers are sandwiched two monoatomic calcium layers, which surround a central lithium sheet (mono- or three-layered according to the compound). This atomic stacking is typical for such ternary intercalation compounds. The charge transfer caused by the oxido-reducing character of the reaction takes place in the interfaces of the host structure and the intercalated species, that is to say between the graphene planes and adjacent lithium.

The α compound can be considered as a slice of $CaLi_2$ crystal alloy. Indeed, this latter consists of an alternating *c*-axis lithium−calcium stacking, exactly similar to that present inside the intercalated sheet of the ternary compound.

The two-dimensional unit cells of these ternaries were established: they are both identical to the graphitic one, with rectangular or hexagonal symmetry according to the compound. The 3D unit cell of one of them was found.

The third compound contains a very low amount of lithium, such that it appears as a quasi-binary phase, which could be identified as CaC_6. The liquid-solid reaction used for this synthesis appears to be a better method for the preparation and isolation of bulk CaC_6.

Experimental Section

Synthesis: The synthesis of these novel ternary graphite−lithium−calcium intercalation compounds requires a rigorous experimental process, including several successive steps: purification of the reagents, formation of the reactive alloy, reaction and sample recovery. All the steps must be done in a glove box, under a very pure argon atmosphere. The purity of the reagents is one of the main factors influencing the synthesis of the ternary graphite−lithium−calcium compounds. The dendritic calcium used was distilled and exhibited a purity of 99.99%. The lithium, with an initial purity of 99.95%, required a further purification step, which was carried out in the glove box, after melting of the metal. The formation of the alloy is tricky, because its good homogeneity is absolutely essential for the preparation of the ternary compounds. In order to obtain pure ternary phases, we use Ca−Li alloys whose composition is well defined and varies according to the nature of the ternary compound. Both metals were mixed carefully in order to obtain a molten alloy that is as homogeneous as possible (the binary phase diagram shows a complete miscibility in the liquid state). Then, the pyrographite platelet was immersed in this liquid mixture in a tightly closed reactor. Lastly, the temperature of the reagents was raised to the appropriate value for several days: 350 °C for ten days when using an equimolar Ca−Li alloy (α compound); 350 °C for ten days when using a $CaLi_2$ alloy (β compound); and 350 °C for ten days when using an alloy whose composition is included between Ca_3Li and Ca_4Li (γ compound). After reaction, the sample obtained after removal of the alloy was introduced into a Pyrex or a Lindemann capillary tube (according to the size of the sample), which was sealed for characterisation of the sample by X-ray diffraction (XRD). The chemical formulae of these compounds were established by nuclear microprobe measurements,[8] because it is difficult to determine lithium concentration and distribution by classical methods such as Castaing microprobe, SEM and TEM. The formulae, which represent the composition of the bulk samples, are $Li_{0.4}Ca_{2.7}C_6$ for the α compound, $Li_{3.1}Ca_{2.1}C_6$

for the β compound, and $Li_{0.07}CaC_6$ for the γ compound. It should be emphasised that the third compound (γ) has a very low lithium content, and it is so low that it appears to be almost a binary compound, close to the well-known CaC_6 phase.[6] On the other hand, the metal contents of the α and β compounds are much higher. The β compound in particular exhibits a very large lithium content (eight times richer than the α compound). It is probably the most metal-rich phase amongst the graphite intercalation compounds.

Structural Study: The compounds were studied by X-ray diffraction, using a specific technique because the samples are partially oriented. The host graphite sample used for the intercalation reaction is a platelet of highly oriented pyrolytic graphite (HOPG from Union Carbide). The *c*-axes of all elemental graphite crystals are mutually parallel but, within the graphene sheets, their *a* and *b* axes are randomly distributed. This structural particularity confers the properties of a single crystal along the *c* axis and the properties of a powder in the perpendicular plane. Consequently, it is very easy to observe the 00*l*, *hk*0 and *hkl* reflections with a device perfected in our laboratory.[9]

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