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RECENT DATA CONCERNING THE INTERCALATION OF THALLIUM ALLOYS INTO GRAPHITE

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Abstract The ternary graphite-potassium-thallium and graphite-rubidium-thallium systems were systematically studied. New compounds were observed, and the **c**-axis and 2D structures of all the ternary phases were determined and compared.

INTRODUCTION

The potassium-thallium and rubidium-thallium alloys intercalate very easily into graphite. The ternary phases, which are obtained in most cases, contain very thick intercalated metallic sheets, whose structure was considered, in a first time, as completely disordered. It is now well established that the intercalated alloy, in these compounds, is well organized : it is constituted by five superimposed atomic layers. On the other hand, we have recently prepared new ternary phases, whose intercalated sheets are thiner and present a lower thallium amount (only three superimposed atomic layers in each intercalated sheet). In this paper, we describe all the ternary compounds belonging to both ternary systems.

GRAPHITE-POTASSIUM-THALLIUM SYSTEM

In this system, two stage 1 phases are known. The first one, denoted α, can be isolated very easily : it is obtained by action of the liquid $K_{0.33}Tl_{0.67}$ alloy on graphite, at 400°C during 3 or 4 days. Its chemical formula is written $KTl_{1.5}C_4$, and its interplanar distance is 1210 pm. Its intercalated metallic sheets are of course very thick, and, in a first time, we believed that their structure was entirely disordered[1], because the X-ray examination did not show any hk0 reflection. In fact, the absence of these reflections was due only to the strong absorption of the radiation by the heavy thallium atoms. Some more refined measurements exhibited now the presence of numerous hk0 reflections, and we have to consider that the intercalated alloy is very well crystallized : its 2D arrangement can be described by a square unit cell, not commensurate with that of graphene planes, and whose parameter is equal to 1095.5 pm (Figure 1). Along the **c**-axis, the stacking of the

metallic atoms corresponds to a "five-layered" intercalated sheet, according to the sequence / K Tl Tl Tl K /. We compare, in Figure 1, this model with the entirely disordered metallic sheet. The electronic density profiles are obtained by Fourier transform of nine 00l structure factors.

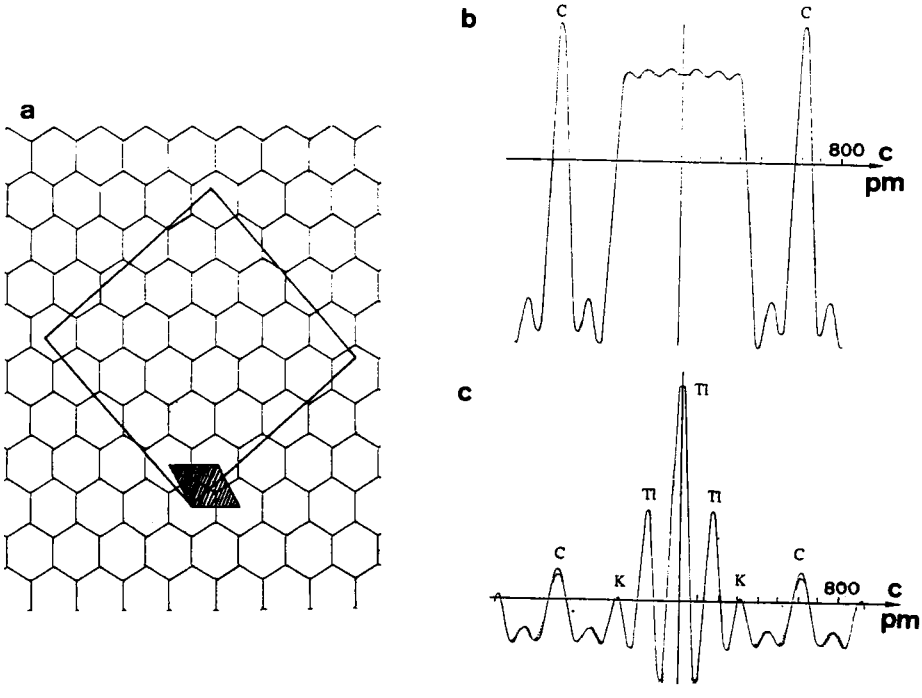

FIGURE 1 2D and **c**-axis structures of first stage α-$KTl_{1.5}C_4$ compound.
a) 2D unit cell (in black : graphene unit cell).
b) **c**-axis structure : disordered metallic sheet.
c) **c**-axis structure : five-layered metallic sheet.
(solid line : experimental ; dashed line : model).

The second phase, denoted x, is always obtained as a mixture with α compound. It is prepared using the $K_{0.44}Tl_{0.56}$ liquid alloy, at 350°C during 3 days. This compound possesses an interplanar distance of 1076 pm only. By Fourier transform of its 00l structure factors (six reflections are used), it was possible to determine (1) its chemical formula and (2) the **c**-axis atomic stacking of its intercalated sheets. In this phase, the thallium amount is weak, so that the thallium central three-layer, in the intercalated sheet, is reduced to a simple thallium mono-layer. The formula of the compound is $KTl_{0.67}C_4$, and it possesses three-layered metallic sheets : / K Tl K / (Figure 2).

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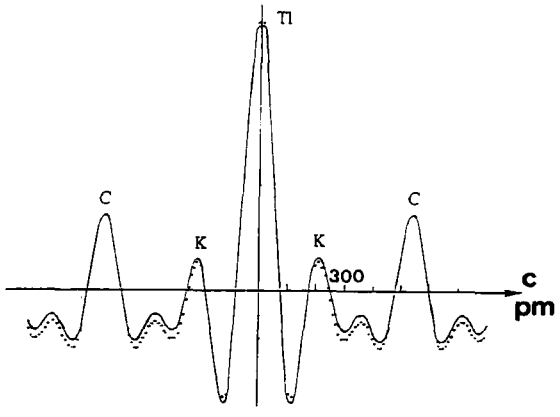

FIGURE 2 c-axis structure of first stage x-$KTl_{0.67}C_4$ compound.
(solid line : experimental ; dashed line : model).

Two stage 2 phases are also known. The first one, denoted α, corresponds exactly to the first stage α compound : it exhibits the same interplanar distance, the same five-layered intercalated sheets and the same 2D square structure ; its chemical formula is of course $KTl_{1.5}C_8$. This compound is obtained by action on graphite of the $K_{0.30}Tl_{0.70}$ alloy during 3 or 4 days at 400°C.

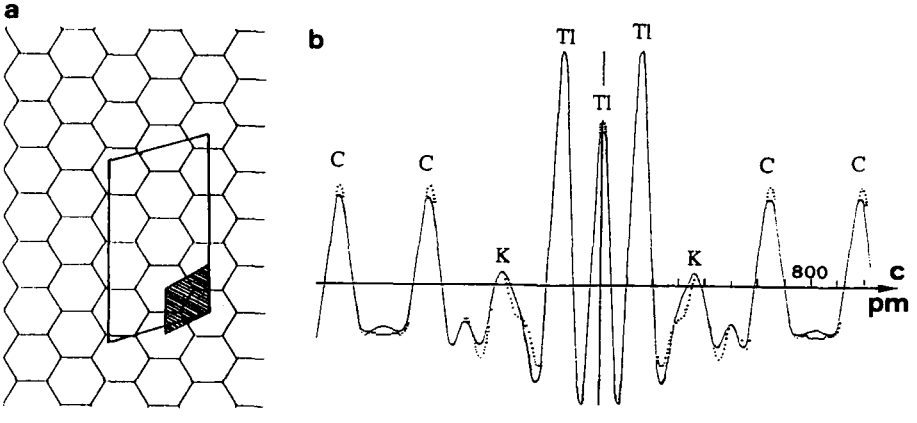

FIGURE 3 2D and c-axis structures of second stage β-$KTlC_8$ compound.
a) 2D unit cell (in black : graphene unit cell).
b) c-axis structure (solid line : experimental ; dashed line : model).

The second stage 2 compound is denoted β. It is obtained in the following manner : the second stage α compound is submitted to an annealing under vacuum and without free alloy, between 200 and 300°C for 5 or 6 days ; the result is the β compound, which

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contains however some inclusions of pure hexagonal thallium. Its chemical formula ($KTlC_8$) is of course determined by Fourier transform of its 00l structure factors ; it shows clearly that its thallium amount is smaller than that of α phase. During the annealing, the thallium excess remains as inclusions in the sample, because this metal presents a very small volatility. The interplanar distance of this β compound is very high (1291 pm), so that its intercalated metallic sheets are also five-layered according to the sequence / K Tl Tl Tl K /, but the central thallium plane is here particularly little dense (the Fourier transform exhibited in Figure 3 was obtained using thirteen 00l reflections). On the other hand, the study of its hk0 reflections allowed to determine its basal plane structure. It is described by means of a 2D oblique unit cell, with the following parameters : a = 516 pm, b = 890 pm and γ = 107° (Figure 3).

In Table I, are collected and compared the **c**-axis structural data concerning the intercalated sheets of x, α and β ternary graphite-potassium-thallium compounds.

TABLE I **c**-axis structural data for x, α and β potassium-thallium sheets.

	x	α	β
Interplanar distance	1076 pm	1210 pm	1291 pm
Central thallium layer			
Tl / 4C	0.67	0.82	0.24
Second thallium layer			
Tl / 4C	-	0.35	0.38
Distance from central layer	-	167 pm	149 pm
Potassium layer			
K / 4C	0.5	0.5	0.5
Distance from central layer	236 pm	312 pm	362 pm

GRAPHITE-RUBIDIUM-THALLIUM SYSTEM

In this system, two stage 1 phases are observed. They are denoted α and β, and their interplanar distances are respectively : 1265 and 1340 pm. The intercalated metallic sheets correspond exactly to their potassium homologous.

The α compound is obtained using the $Rb_{0.40}Tl_{0.60}$ liquid alloy at 400°C for 2 days. When the reaction time is higher, one obtains a mixture containing both α and β compounds. In order to prepare the β compound, it is necessary to carry out the

annealing of α compound (or α and β mixture) at 200-300°C during 2-3 days, without free alloy. As in potassium case, this β phase contains also some hexagonal thallium inclusions, because the α and β phases do not possess the same thallium compositions. Indeed, their chemical formulas are respectively $RbTl_{1.5}C_4$ and $RbTlC_4$. Their electronic density profiles are exhibited in Figure 4 (nine and ten reflections are respectively used for α and β compounds) : they show clearly that the intercalated sheets are five-layered in both cases, according to the **c**-axis sequence / Rb Tl Tl Tl Rb /. As in potassium compounds, the central thallium layer contains particularly few atoms in β phase, which paradoxically possesses the largest interplanar distance.

Structural data concerning the intercalated metallic sheets of α and β graphite-rubidium-thallium compounds are gathered in Table II.

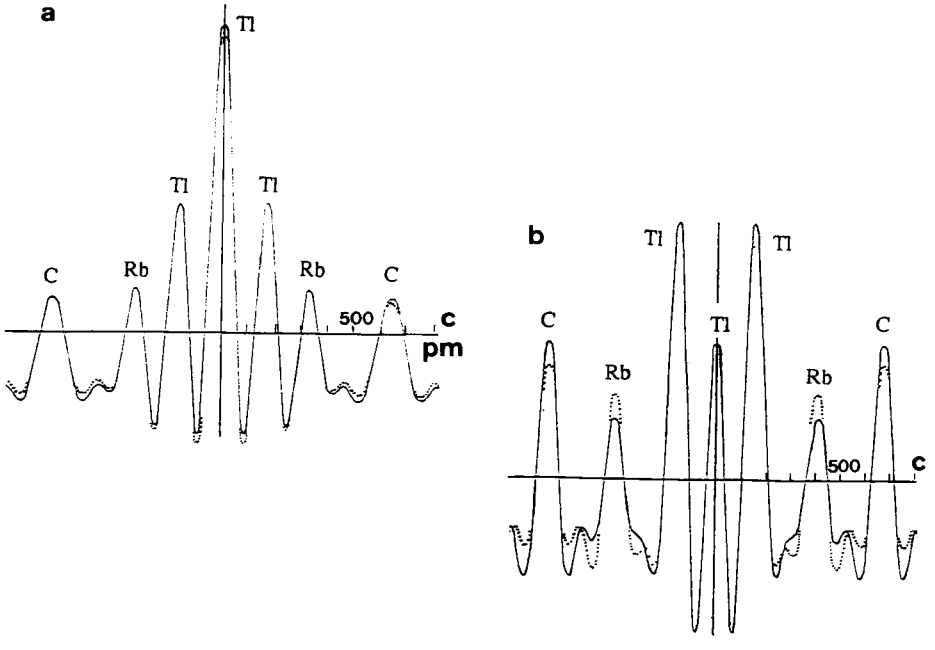

FIGURE 4 **c**-axis structures of first stage α-$RbTl_{1.5}C_4$ and β-$RbTlC_4$.
(solid line : experimental ; dashed line : model).
a) α compound.
b) β compound.

On the other hand, the study of the hk0 reflections of these compounds allowed to conclude that they possess the same 2D structures to those, which are described in Figures 1 and 3, for α and β potassium compounds.

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Table II c-axis structural data for α and β rubidium-thallium sheets.

	α	β
Interplanar distance	1265 pm	1340 pm
Central thallium layer		
Tl / 4C	0.82	0.18
Second thallium layer		
Tl / 4C	0.34	0.41
Distance from central layer	165 pm	158 pm
Rubidium layer		
Rb / 4C	0.5	0.5
Distance from central layer	338 pm	403 pm

CONCLUSION

The intercalation into graphite of potassium-thallium and rubidium-thallium alloys leads to numerous ternary phases, whose intercalated sheets can be three- or five-layered. These five-layered sheets are the most stable. On the other hand, these compounds are very little sensitive to air and water. Finally, we have also to underline that both α-$KTl_{1.5}C_4$ and α-$KTl_{1.5}C_8$ become superconducting[2] respectively below 2.70 and 2.45 K.

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