Polysynthetic nature of stage-one graphite-metal intercalation compounds prepared from graphite single crystals

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In this paper we address the mechanism of intercalation of commensurate metal-graphite intercalation compounds and its consequences on the structural properties of the synthesized materials. Using the case of KC_8 which crystallizes in the orthorhombic system (*Fddd* space group) and consequently does not possess any hexagonal or rhombohedral symmetries, it has been possible to show that a KC_8 sample prepared from a natural graphite single crystal however exhibits experimentally an hexagonal symmetry. This apparent irrational observation is fully explained in this paper by the intercalation process itself so that after intercalation the compound is no more a single crystal. This result is extended to the cases of all the first stage metal-graphite intercalation compounds.

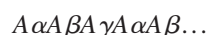PACS number(s): 71.20.Tx, 74.70.Ad, 74.70.Wz, 61.66.−f

I. INTRODUCTION

Graphite intercalation compounds (GICs) were studied from about 80 years.[1] The first ones were metal-graphite intercalation compounds obtained by reaction of potassium, rubidium, and cesium with graphite powder. Very rapidly, it has been shown that during this reaction, the alkali-metal atoms intercalate between the graphene sheets.[2] Indeed, the latter are not destroyed but only spread apart and the intercalated atoms form mono-atomic layers between them.

If enough alkali-metal amount is employed, all the graphitic intervals (van der Waals's gaps) are occupied, so that the compound belongs to the "stage-one" family: a systematic graphene/intercalant/graphene/intercalant... *c*-axis stacking is observed[3] and alkali atoms accommodate the graphitic host. Furthermore, the graphene sheets give up the *ABAB*... hexagonal stacking which is characteristic of graphite and adopt a new *AAA*... stacking. This sequence implies the existence of prismatic hexagonal sites between the successive graphene layers which are partially occupied by the alkali-metal atoms.

With K, Rb, and Cs, one prismatic hexagonal site out of four only is occupied by an alkali atom (octal occupation), so that the chemical formula of the corresponding compounds can be written MC_8. In the case of smaller metallic atoms (which are also a little less electropositive) as Li, Ca, Sr, Ba, Eu, and Yb, it is possible to intercalate an atom in one hexagonal site out of three, in order to respect the formula MC_6.

Of course, when the formula is MC_8, the intercalated atoms can occupy four different positions denoted α, β, γ, and δ. Consequently, it is possible to consider four different *c*-axis stacking for a MC_8 compound,

$$A\alpha A\alpha A\alpha A\alpha A\alpha...$$

$$A\alpha A\beta A\alpha A\beta A\alpha...$$

$$A\alpha A\beta A\gamma A\alpha A\beta...$$

$$A\alpha A\beta A\gamma A\delta A\alpha...$$

On the contrary, concerning the MC_6 compounds, only three different positions (α, β, and γ) can be occupied (hexal occupation), so that only three different **c**-axis stacking have to be considered,

$$A\alpha A\alpha A\alpha A\alpha...$$

$$A\alpha A\beta A\alpha A\beta...$$

$$A\alpha A\beta A\gamma A\alpha...$$

Six stackings out of these seven ones have been experimentally observed for the nine first stage intercalation compounds previously quoted. In each case, the space group of the crystal structure was established as presented in Table I.

The discovery of superconductivity in two binary graphite intercalation compounds as YbC_6 (Ref. 13) and CaC_6 (Refs. 13 and 14) with surprisingly high critical temperatures, 6.5 K

TABLE I. Crystal structures of the binary metal GICs.

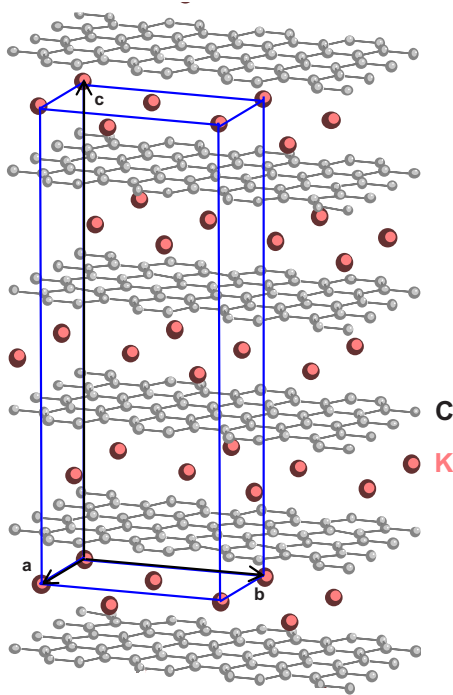| Graphite intercalation compound	Stacking sequence	Space group	Reference
KC_8	$A\alpha A\beta A\gamma A\delta...$	*Fddd*	4
KC_8	$A\alpha A\beta A\alpha A\beta...$	*Fmmm*	5, this work
RbC_8	$A\alpha A\beta A\gamma A\delta...$	*Fddd*	6
CsC_8	$A\alpha A\beta A\gamma A\alpha...$	$P6_422$	7
LiC_6	$A\alpha A\alpha A\alpha...$	$P6/mmm$	8
CaC_6	$A\alpha A\beta A\gamma...$	$R\bar{3}m$	9
SrC_6	$A\alpha A\beta A\alpha...$	$P6_3/mmc$	10
BaC_6	$A\alpha A\beta A\alpha...$	$P6_3/mmc$	10
EuC_6	$A\alpha A\beta A\alpha...$	$P6_3/mmc$	11 and 12
YbC_6	$A\alpha A\beta A\alpha...$	$P6_3/mmc$	11

FIG. 1. (Color online) Unit cell of the KC_8 compound crystallized in the orthorhombic *Fddd* space group with $a=492$ pm; $b=852$ pm; and $c=2140$ pm.

and 11.5 K, respectively, has renewed the interest in this family of lamellar materials.

The aim of this paper consists in showing how the intercalation of metallic atoms into a graphite single crystal occurs and if the synthesized intercalation compound is a single crystal or not. To this aim we will consider the case of both KC_8 and RbC_8 which have orthorhombic unit cells and possess, at the same time, a symmetry which is neither hexagonal nor rhombohedral[4,6] and consequently very different from pristine graphite (see Fig. 1).

II. TRUE AND APPARENT SYMMETRIES OF KC_8 (OR RbC_8)

KC_8 is obtained by the conventional two-bulb method where potassium in the vapor phase reacts with graphite single crystal at $T=250$ °C, leading to a potassium vapor pressure equal to $P=11.4$ Pa. The temperature gradient between potassium and graphite sample is quite low, equal to $10°$. As we have seen, KC_8 belongs to the *Fddd* space group.[4] The unit cell (Fig. 1) possesses the following parameters: $a=492$ pm; $b=852$ pm; $c=2140$ pm. The potassium atoms occupy the 8a position (origin of the cell) and the carbon atoms the 32h one (with $x=1/4$, $y=1/12$, $z=1/8$ and $x=1/4$, $y=1/12$, $z=5/8$).

The unit cell is of course orthorhombic, but a and b parameters are not completely independent, because they are both parallel to the graphene planes that exhibits a hexagonal symmetry. For this reason, $b=a\sqrt{3}$, and it is usual to describe this cell as "ortho-hexagonal." Consequently in the reciprocal lattice (Fig. 2), some nodes with different Miller's indices

correspond to the same reticular distance (for instance, 040 and 220 with $d_{hkl}=213$ pm or 400 and 260 with $d_{hkl}=123$ pm).

Figure 2 represents the reciprocal lattice of the KC_8 compound. On one hand, hkl (with $l=0-4$) strata are drawn in Fig. 2(a): only the nodes for which no extinction exists (that is, to say for which the structure factor is not exactly nil) are indicated. On the other hand in Fig. 2(b), the projection of each stratum is shown individually, and the summation of three equivalent strata rotated from each other by 120° is also represented, leading to a "more symmetric" result (the justification of this summation is given in the text here below).

The zero and fourth strata exhibit a hexagonal symmetry while the second and sixth ones lead to binary and quaternary symmetries; the first, third, fifth, and seventh ones exhibit exclusively a quaternary symmetry. The reflection conditions generated by the symmetries of the *Fddd* orthorhombic unit cell[15] are given in Table II.

Using an original homemade goniometric device,[16] the multiplicity factor and intensity have been measured for each $hk0$ and hkl reflection. These measurements have been obtained from a KC_8 sample, synthesized at low temperature by reaction between potassium vapor and a natural graphite single crystal[17] (extracted from Norway's subsoil).

The $hk0$ and hkl reflections which were observed and indexed (see Fig. 2) in the orthorhombic unit cell are gathered in Table III. In each case, we compare the theoretical multiplicity factor and the observed one. Surprisingly, we note that the latter is systematically higher than the one predicted for the orthorhombic cell, as if it was more symmetrical. Indeed, it appears that the observed symmetry is in fact hexagonal and not orthorhombic, contrarily to what expected. Hence, there is a large contradiction between the symmetry of the unit cell and the observed one. The *Fddd* orthorhombic cell is nevertheless confirmed by the diffraction pattern, which was obtained from the rotating crystal method.[4] Consequently, we have to reconcile the apparent hexagonal symmetry with the true orthorhombic one.

Let us consider several perfect hexagonal graphene planes exactly superimposed according to the $AAA\dots$ stacking (Fig. 3). In the first van der Waals's gap, we arrange the potassium atoms in the α position. In the second one, the choice between three equivalent possibilities appears: β, γ, and δ. In accordance with the chosen position, we can thus consider three stackings: $A\alpha A\beta A$, $A\alpha A\gamma A$, and $A\alpha A\delta A$. Since they are equivalent, it is possible that three zones coexist in the same crystal. During the filling up of the third and fourth gaps, each zone divides again into two domains, so that, when the four successive gaps are filled, we obtain six different domains in the same single crystal (Fig. 3): $A\alpha A\beta A\gamma A\delta A$, $A\alpha A\beta A\delta A\gamma A$, $A\alpha A\gamma A\beta A\delta A$, $A\alpha A\gamma A\delta A\beta A$, $A\alpha A\delta A\beta A\gamma A$, and $A\alpha A\delta A\gamma A\beta A$.

Each domain is of course characterized by an orthorhombic *Fddd* cell and we can see on Fig. 3 that these six cells are not parallel but rotated one from another by 60°. However, it should be noted that the unit cells corresponding to both $A\alpha A\beta A\gamma A\delta A$ and $A\alpha A\delta A\gamma A\beta A$ domains are strictly identical, because the second one is obtained from the first one by a simple translation characterized by the following vector:
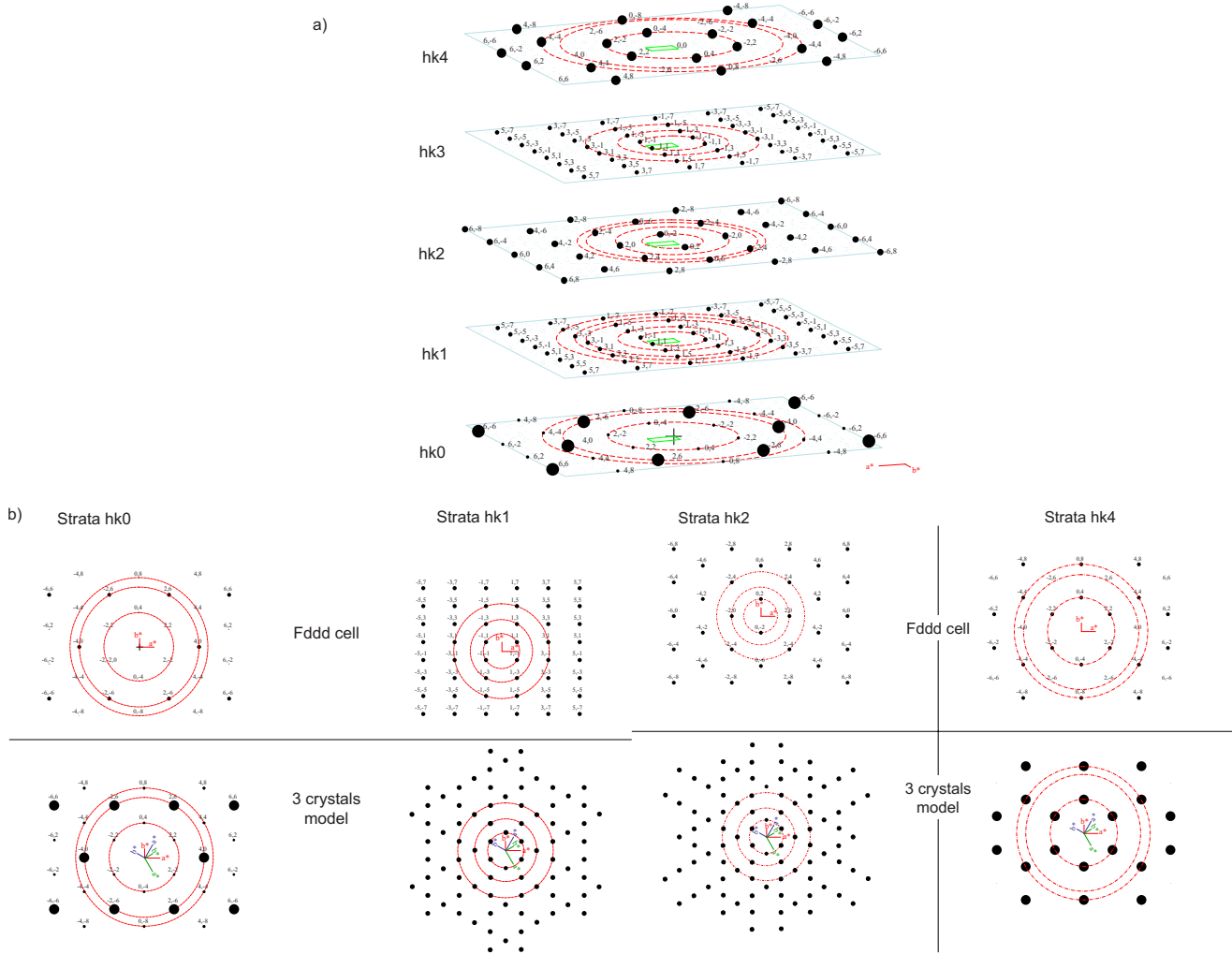
FIG. 2. (Color online) Reciprocal lattice of the KC_8 *Fddd* GICs. (a) Representation of the $hk0$ to $hk4$ strata. Circles drawn with dotted lines indicate a same inter-reticular distance. $hk1$ strata is equivalent to $hk3$, $hk5$, $hk7$; $hk2$ to $hk6$; (b) planar projection of strata. The upper part corresponds to individual contribution in the *Fddd* space group. The lower part reveals the superimposition of the three rotated domains (three crystals model). Larger dark spots indicate the superimposition of diffraction spots. The three a^*b^* axis couples represent the three reciprocal axis orientations taken into account.

$[-\frac{1}{4} \ \frac{1}{4} \ \frac{1}{4}]$. In the same manner, the $A\alpha A\beta A\delta A\gamma A$ and $A\alpha A\gamma A\delta A\beta A$ domains are exactly equivalent and both $A\alpha A\delta A\beta A\gamma A$ and $A\alpha A\gamma A\beta A\delta A$ domains are also identical. Finally, only three domains are really different and cannot be considered as equivalent by translation: it is the case of the $A\alpha A\beta A\gamma A\delta A$, $A\alpha A\gamma A\delta A\beta A$, and $A\alpha A\delta A\beta A\gamma A$ domains. Their unit cells are so rotated one from another by 120°, as seen in Fig. 3.

TABLE II. Reflection conditions for the *Fddd* orthorhombic unit cell.

hkl	$h+k, h+l, k+l=2n$
$0kl$	$k+l=4n, k, l=2n$
$h0l$	$h+l=4n, h, l=2n$
$hk0$	$h+k=4n, h, k=2n$
$h00$	$h=4n$
$0k0$	$k=4n$
$00l$	$l=4n$

Although initially the graphite sample was a single crystal, after intercalation of potassium, three different KC_8 crystals coexist in the sample: it is a matter of three "twinning crystals" with angles of 120° and 240° (model of three crystals). The Fig. 2 shows the result of the superimposition of the three twinning crystals in the reciprocal space for each stratum (0–7). In Fig. 4 the superimposition of the reflections of each of three crystals in several cases is shown.

As validation of this model, it can be noted that the measurements obtained by the previously described goniometric method show the superimposition of the three diagrams, respectively, generated by the three crystals (Fig. 4). For each reflection, it is possible to specify the theoretical multiplicity factor which results from this superimposition, in order to compare it with the observed one. These results are gathered in Table IV, and show that the agreement is quite perfect. The hexagonality, which is lacking in the orthorhombic symmetry, was artificially restored by the presence of three crystals well arranged in the van der Waals's gaps of the graphite single crystal. Consequently, we can say that the KC_8 binary

TABLE III. Comparison between observed and calculated multiplicity factors for different *hkl* reflections. The Miller's indices are given in italic, the experimental multiplicity factors are noted in bold, and the theoretical ones are in regular.

d_{hk0} (pm)	Stratum 0	Stratum 1	Stratum 2	Stratum 3	Stratum 4	Stratum 5	Stratum 6	Stratum 7
		111	*022*	*113*		*115*		
428		**12**	**12**	**12**		**12**		
		8	4	8		8		
		131	*202*	*133*		*135*	*206*	*137*
246		**12**	**12**	**12**		**12**	**12**	**12**
		8	4	8		8	4	8
	040 *220*				*044* *224*			
213	**6**				**12**			
	2 4				4 8			
		151 *311*	*242*	*153* *313*		*155* *315*	*246*	
162		**24**	**24**	**24**		**24**	**24**	
		8 8	8	8 8		8 8	8	
		331	*062*	*333*		*335*	*006*	*337*
142		**12**	**12**	**12**		**12**	**12**	**12**
		8	4	8		8	4	8
	400 *260*				*404* *264*			
123	**6**				**12**			
	2 4				4 8			

compound prepared from true graphite single crystal is no more a single crystal. Thus, the expected geometry and the observed one are reconciled.

III. PHYSICAL JUSTIFICATION OF THE PREVIOUS MODEL

When the graphite single crystal is brought to react with potassium vapor, the metallic atoms enter in the graphitic intervals by all edges simultaneously. Since the size of the

FIG. 3. Projection in the *ab* plane of the potassium and graphite sublattices in the orthorhombic KC$_8$ crystal (*Fddd* space group). This leads to a pseudohexagonality corresponding to the three crystals model.

graphite single crystal is large (it can be considered as infinite), one can consider these edges as independent. Consequently, the growth of the KC$_8$ compound occurs independently from one edge to another, so that the three possibilities for this growth take place with exactly the same probability. Finally, considering the whole sample, it is easy to understand that the three crystals will coexist at the end of the reaction in statistically identical amounts in KC$_8$ compound. For this reason, KC$_8$ binary compound prepared from a graphite single crystal is thus a mixture of three crystallographic phases. It is worth to note that each of them is probably broken up in numerous domains, whose joins appear probably as crystal defects.
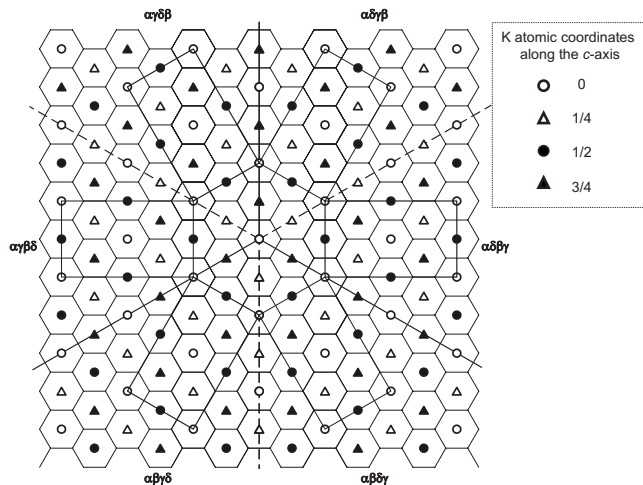
IV. CASE OF THE OTHER STAGE-ONE GRAPHITE-METAL INTERCALATION COMPOUNDS

All the other known binary graphite-metal compounds possess unit cells whose symmetries are hexagonal or rhombohedral ($P6_422$, $P6/mmm$, $R\bar{3}m$, $P6_3/mmc$). Nevertheless, the intercalation process stays identical whatever is the geometry of the crystal structure, i.e., intercalation of metallic atoms from all graphite edges simultaneously. As a result, the "hexagonalization" phenomenon would occur in the same manner. Consequently, in each case the reciprocal lattice exhibits systematically a hexagonal symmetry. As previously, the goniometric device is able to measure the multiplicity of the reflections leads of course to a hexagonal symmetry for these phases. In conclusion, the "hexagonalization" of a hexagonal crystal remains of course invisible whereas it can be put in evidence in the case of KC$_8$.
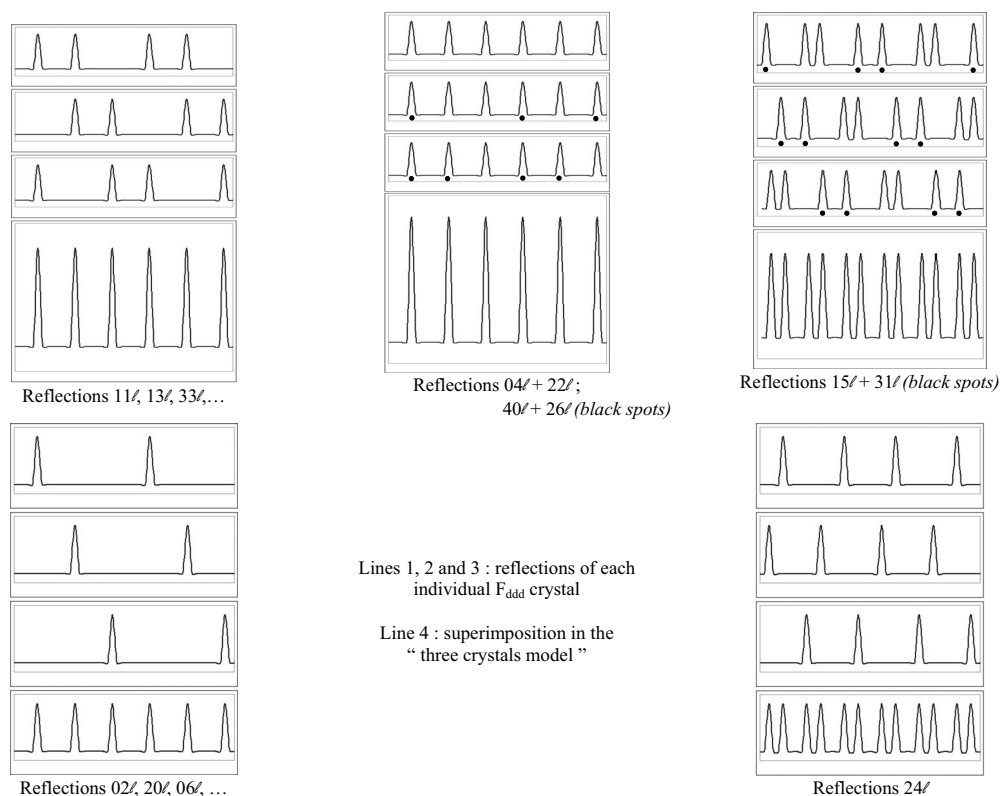
Reflections 11ℓ, 13ℓ, 33ℓ,…

Reflections 04ℓ + 22ℓ; 40ℓ + 26ℓ *(black spots)*

Reflections 15ℓ + 31ℓ *(black spots)*

Lines 1, 2 and 3 : reflections of each individual F$_{ddd}$ crystal

Line 4 : superimposition in the " three crystals model "

Reflections 02ℓ, 20ℓ, 06ℓ, …

Reflections 24ℓ

FIG. 4. Determination of the intensities for *hk*0 *and hkl* reflection lines for KC$_8$ on the 360° angular domain.

Thus, the mechanism previously proposed should be universal, so that it is reasonable to think that, as KC$_8$ or RbC$_8$, CsC$_8$ and the MC$_6$ compounds are not expected to be single crystals when they are synthesized from graphite single crystals. For this reason it his highly improbable that graphite single crystals intercalated by using the molten alloy

TABLE IV. Comparison between observed multiplicity factors for different *hkl* reflections with those retrieved from the "three crystals model," showing perfect agreement. The Miller's indices are given in italic, the experimental multiplicity factors are noted in bold, and the theoretical ones are in regular.

d_{hk0} (pm)	Stratum 0		Stratum 1		Stratum 2	Stratum 3		Stratum 4		Stratum 5		Stratum 6	Stratum 7
			111		*022*	*113*				*115*			
428			**12**		**12**	**12**				**12**			
			12		12	12				12			
			131		*202*	*133*				*135*		*206*	*137*
246			**12**		**12**	**12**				**12**		**12**	**12**
			12		12	12				12		12	12
	040	*220*						*044*	*224*				
213	**6**							**12**					
	6							12					
			151	*311*	*242*	*153*	*313*			*155*	*315*	*246*	
162			**24**		**24**	**24**				**24**		**24**	
			24		24	24				24		24	
			331		*062*	*333*				*335*		*006*	*337*
142			**12**		**12**	**12**				**12**		**12**	**12**
			12		12	12				12		12	12
	400	*260*						*404*	*264*				
123	**6**							**12**					
	6							12					

method[14] can give as final product a single crystal as it has been claimed in Refs. 18 and 19.

V. CONCLUSION

Even if the used graphite sample is a single crystal, after intercalation of metallic atoms the stage-one binary synthe-sized compound is no more a single crystal. This phenom-enon is due to the process of intercalation itself. The final sample contains in fact numerous domains, which are distrib-uted in three crystallographic phases, which are rotated one from another by 120° and 240°. It is very important to take this phenomenon into account in the course of some physical measurements and also of their interpretation.

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