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Reduction of $MoCl_5$ Graphite Intercalation Compounds by Heavy Alkali Metal Vapour

Véronique Krebs, Claire Hérold, Jean-François Marêché and Guy Furdin

Laboratoire de Chimie du Solide Minéral, UA CNRS n°158, Université H. Poincaré, BP 239,
54506 Vandoeuvre-les-Nancy Cedex, France

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Résumé. — La réduction des composés d'insertion du graphite avec le chlorure de molybdène V par les métaux alcalins lourds (potassium, rubidium et césium) en phase vapeur conduit à la formation de produits complexes. L'étude de ces produits réduits par Microscopie Électronique à Transmission montre en effet qu'ils contiennent des inclusions de chlorures alcalins mais également des phases du métal de transition présentant plusieurs organisations bidimensionnelles et tridimensionnelles selon la nature du réducteur.

Abstract. — The reduction of $MoCl_5$ graphite intercalation compounds by heavy alkali metal vapour (potassium, rubidium and cesium) leads to the formation of complex products. The analysis of these reduced compounds indeed shows that they contain alkali metal halide inclusions and also transition metal in several two-dimensional and three-dimensional phases depending on the reducing agent.

1. Introduction

Direct intercalation of transition metals into graphite has never been obtained due to their high ionisation energies and vaporization enthalpies [1]. Several studies have therefore been carried out which consist in making an indirect intercalation of these elements. The most often used method consists in reducing a metal halide graphite intercalation compound. Intercalated transition metal chlorides have a low mobility between graphene layers and are therefore usually used; alkali metals are interesting reducing agents which intercalate spontaneously into graphite, favouring the *in-situ* reduction of the metal chlorides and then the formation of inclusions or intercalation products. This type of reaction usually leads to products containing several phases. Vol'pin *et al.* [2, 3] tried for the first time in 1970 to reduce graphite intercalation compounds with transition metal chlorides using various reducing agents. In the case of molybdenum chloride compounds, they obtained a transition metal GIC characterized by an interplanar distance of 370 pm. Later, Hérold *et al.* [4-6], reducing $FeCl_3$, $CoCl_2$ and $CuCl_2$ graphite intercalation compounds by heavy alkali metal vapour obtained complex products containing alkali metal halide inclusions, transition metal inclusions and two-dimensional intercalated transition metal. Both the structure and the abundance of these two-dimensional phases depend strongly on the nature of the reducing agent. Moreover, the authors observed that the change from potassium to cesium provokes an increase in the abundance of the two-dimensional metal phases and a simultaneous decrease in that of the three-dimensional phases.

In 1981, Novikov and Vol'pin [7] observed that transition metal graphite intercalation compounds develop interesting catalytic activities on various organic reactions such as oxidation of organic compounds, polymerization, hydrogenation and isomerization. In view of these properties and of the results obtained by Hérold *et al.*, the aim of this investigation was to study the reduction of $MoCl_5$ graphite intercalation compounds by strong reducing agents such as heavy alkali metals potassium, rubidium and cesium.

2. Experimental Data

2.1 SYNTHESIS OF $MoCl_5$ GRAPHITE INTERCALATION COMPOUNDS. — The graphite used to prepare the GIC is constituted of Madagascar natural single crystals characterized by an average diameter of 10 μm and a thickness of 0.1 μm [8]. This starting material is outgassed at 850 °C for two days while molybdenum chloride is distilled under vacuum then under a chlorine atmosphere. Intercalation reaction is carried out for 15 days in a "two bulb" reactor, the temperature of graphite and molybdenum chloride being respectively 250 °C and 245 °C.

2.2 REDUCTION OF $MoCl_5$ GRAPHITE INTERCALATION COMPOUNDS. — The obtained $MoCl_5$ graphite intercalation compound is transferred under argon in one part of a "two bulb" Pyrex glass reactor. The alkali metal is then distilled under vacuum in the second reactor bulb. The evacuated and sealed reactor is then put in a furnace and a small temperature gradient is imposed between the two bulbs so as to allow vapour phase reaction. Reduction reaction is carried out for 15 days at 75 °C for potassium and 100 °C for rubidium and cesium. The reduced product is left overnight in an argon atmosphere containing a few ppm of oxygen in order to permit diffusion and slow oxidation of the excess of alkali metal at the crystal edges.

2.3 TRANSMISSION ELECTRON MICROSCOPY EXAMINATIONS. — Microscopy grids were prepared by dispersing reduced particles in alcohol, depositing them on a Nuclepore membrane between two amorphous carbon layers and finally dissolving the membrane with chloroform. This method permits obtaining an orientation of graphene layers parallel to the grid plane, due to the particular morphology of the graphite particles. Direct imaging, microdiffraction, microanalysis and electron energy loss spectroscopy were performed on a CM 20 Philips TEM. For the indexation of diffraction patterns, graphite reflexions were used as an internal standard. The distances were measured manually on the original microscope plates with an accuracy of ±0.1 mm.

3. Results

The diffusion of heavy alkali metals between graphene layers as well as the small size of graphite particles lead to complete reduction reactions. Reduced products are very complex. Whatever the nature of the reducing agent, they are all constituted of three types of zones. The first type of zone corresponds to pure graphite areas. The second type contains three-dimensional inclusions of alkali metal chlorides which are more or less oriented with respect to the graphite. The third type contains the transition metal in the form of either two-dimensional species or three-dimensional clusters, the abundance of each form depending on the nature of the reducing agent.

Table I. — *Measured and calculated d-spacings of a G-$MoCl_5$ compound reduced by Cs at 100 °C (corresponding to Fig. 1a): 2Ds2: two-dimensional square lattice a = 350 pm; 2Ds3: two-dimensional square lattice a = 325 pm.*

Diagram distance (mm)	d_{hkl} measured (pm)	Indexation	d_{hkl} calculated (pm)
13.9	410.6	(100) CsCl	412.0
16.5	345.9	*(10) 2Ds2 Mo*	345.9
17.3	329.9	*(10) 2Ds3 Mo*	329.9
19.7	289.7	(110) CsCl	291.7
23.3	244.9	*(11) 2Ds2 Mo*	244.6
24.0	237.8	*(11) 2Ds3 Mo*	233.3
26.8	213.0	(100) Graphite	213.0
27.7	206.0	(200) CsCl	206.2
30.9	184.7	(210) CsCl	184.4
32.7	174.5	*(20) 2Ds2 Mo*	172.9
33.9	168.4	*(20) 2Ds3 Mo*	164.9
36.6	155.9	*(21) 2Ds2 Mo*	154.7
39.0	146.3	(220) CsCl	145.7
41.3	138.2	(300) CsCl	137.4
43.6	130.9	(310) CsCl	130.4
46.3	123.2	(110) Graphite	123.0
49.6	115.1	(320) CsCl	114.3
51.9	109.9	*(30) 2Ds3 Mo*	109.9

Study of the reduced products was mainly carried out using electron microdiffraction. The incident electron beam is perpendicular to the (001) graphite planes, which allows only ($hk0$) reflexion observation. The ($hk0$) reflexions of graphite were present in all diagrams and were used as internal standards for diagram indexation.

3.1 REDUCTION OF $MoCl_5$-GIC BY CESIUM. — Figure 1 presents diffraction diagrams of a $MoCl_5$ graphite intercalation compound reduced by cesium at 100 °C. Tables I and II show the corresponding measured and calculated d-spacings. The strong ($hk0$) reflexions with hexagonal symmetry are characteristic of the graphite network.

The presence of cesium chloride is characterized by the observation of a series of continuous ($hk0$) rings. Twelve reinforcements separated each other by an angle of 30° can however be observed on each of these rings: the twelve spots on the ($h00$) CsCl rings are in the same directions as those of (100) and (110) graphite reflexions whereas spots on (110) and (220) CsCl rings are rotated at ±15° to the previous. The presence of these reinforcements is characteristic of the existence of three cubic domains rotated at 120° to each other and having their basal planes parallel to the graphene layers.

Table II. — *Measured and calculated d-spacings of a G-*$MoCl_5$ *compound reduced by Cs at 100 °C (corresponding to Fig. 1b): 2Ds1: two-dimensional square lattice a = 812 pm; 2Ds2: two-dimensional square lattice a = 350 pm; 2Ds3: two-dimensional square lattice a = 325 pm.*

Diagram distance (mm)	d_{hkl} measured (pm)	Indexation	d_{hkl} calculated (pm)
10.0	575.1	*(11) 2Ds1 Mo*	575.1
13.8	416.7	(100) CsCl	412.0
15.8	363.9	*(21) 2Ds1 Mo*	363.7
16.5	348.5	*(10) 2Ds2 Mo*	348.5
17.5	328.6	*(10) 2Ds3 Mo*	328.6
19.3	297.9	(110) CsCl	291.7
20.3	283.3	*(22) 2Ds1 Mo*	287.5
23.1	248.9	*(11) 2Ds2 Mo*	246.4
24.2	237.6	*(11) 2Ds3 Mo*	232.3
27.0	213.0	(100) Graphite	213.0
27.4	209.9	(200) CsCl	206.2
30.7	187.3	(210) CsCl	184.4
32.8	175.3	*(20) 2Ds2 Mo*	174.2
35.0	164.3	*(20) 2Ds3 Mo*	164.3
36.7	156.7	*(21) 2Ds2 Mo*	155.8
39.0	147.4	(220) CsCl	145.7
41.2	139.6	(300) CsCl	137.4
43.5	132.2	(310) CsCl	130.4
46.3	124.2	(110) Graphite	123.0
49.5	116.2	(320) CsCl	114.3
53.6	107.3	(200) Graphite	106.5
55.0	104.5	(400) CsCl	103.1

The reflexions (spots and rings) which belong neither to the graphite nor to the cesium chloride have been attributed to molybdenum intercalated between graphene layers and can be indexed in three distinct square lattices. Several series of twelve spots have been attributed to a square lattice characterized by a parameter of 812 pm. The first visible set of twelve spots has been indexed as (11) reflexions and is in the same directions as the (100) and (110) graphite spots. A series of continuous rings presenting twelve reinforcements belong to another square lattice charaterized by a parameter of 350 pm. The first ring, the reinforcements of which are rotated at ±15° to the (100) and (110) graphite spots, has been attributed to (10) reflexions. The second one corresponds to (11) reflexions (reinforcements in the same directions as (100) and (110) graphite spots). The last series of continuous rings finally corresponds to a third square lattice with a parameter of 327 pm.

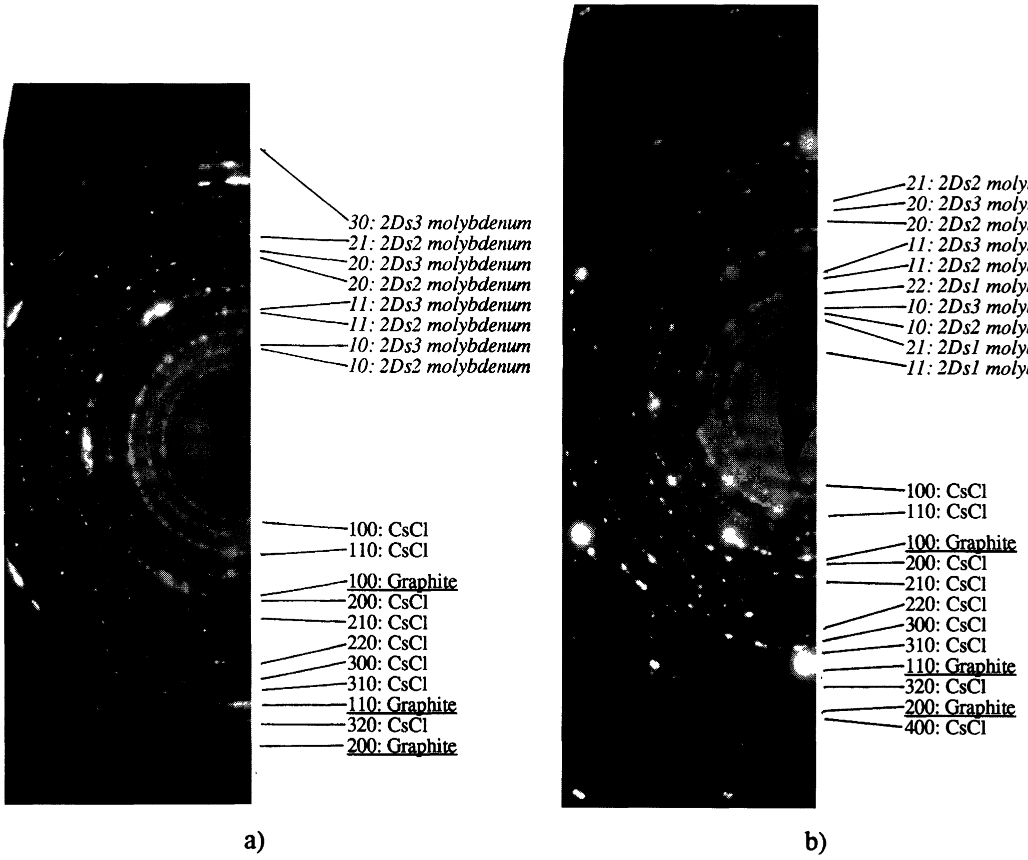


Fig. 1. — Selected area electron diffraction diagrams of G-MoCl$_5$ compounds reduced by Cs at 100 °C: 2Ds1: two-dimensional square lattice $a = 812$ pm; 2Ds2: two-dimensional square lattice $a = 350$ pm; 2Ds3: two-dimensional square lattice $a = 325$ pm.

3.2 REDUCTION OF MoCl$_5$-GIC BY RUBIDIUM. — Figure 2 presents the diffraction diagram of a MoCl$_5$ graphite intercalation compound reduced by rubidium at 100 °C. The strong reflexions characterized by a hexagonal symmetry correspond to the graphite network (Tab. III).

As in the case of cesium chloride, only the $(hk0)$ reflexions characteristic of the rubidium chloride are present in the form of reinforced rings. These rings have twelve reinforcements oriented with respect to the graphite spots: the reinforcements on the (200) ring are rotated at ±15° to (100) and (110) graphite spots whereas those on the (220) ring are oriented in the directions of the (100) and (110) graphite spots. So rubidium chloride is in the form of cubic inclusions but is however rotated at ±15° to cesium chloride inclusions in the (a, b) graphite plane.

Several series of 6 strong and not equidistant spots have been attributed to a two-dimensional rectangular lattice of molybdenum. This phase is characterized by a and b parameters equal to 396 pm and 792 pm respectively.

Three dimensional clusters of metallic molybdenum are also present in small quantities in the reduced product. A series of diffuse spots corresponding to all the (hkl) reflexions of metallic molybdenum with a parameter of 314 pm are indeed observed: the (110) and (200) molybdenum spots are in the directions of the (100) and (110) graphite spots.

Table III. — *Measured and calculated d-spacings of a G-*$MoCl_5$ *compound reduced by Rb at 100 °C (corresponding to Fig. 2): 2Dr: two-dimensional rectangular lattice a = 396 pm, b = 792 pm; 3D molybdenum: three-dimensional inclusions.*

Diagram distance (mm)	d_{hkl} measured (pm)	Indexation	d_{hkl} calculated (pm)
14.4	396.4	*(02) 2Dr Mo*	396.4
16.1	354.5	*(11) 2Dr Mo*	354.5
17.2	331.9	(200) RbCl	329.1
20.5	278.4	*(12) 2Dr Mo*	280.3
24.4	233.9	(220) RbCl	232.7
25.5	223.8	*(110) 3D Mo*	222.5
26.0	219.5	*(13) 2Dr Mo*	219.9
26.8	213.0	(100) Graphite	213.0
28.9	197.5	*(04) 2Dr Mo*	198.2
32.5	175.6	*(22) 2Dr Mo*	177.3
36.0	158.5	*(200) 3D Mo*	157.4
43.4	131.5	*(06) 2Dr Mo*	132.1
48.6	117.4	*(33) 2Dr Mo*	118.2

Table IV. — *Measured and calculated d-spacings of a G-*$MoCl_5$ *compound reduced by K at 75 °C (corresponding to Fig. 3a): 2Ds: two-dimensional square lattice a = 395 pm; 3D molybdenum: three-dimensional inclusions.*

Diagram distance (mm)	d_{hkl} measured (pm)	Indexation	d_{hkl} calculated (pm)
14.6	395.0	*(10) 2Ds Mo*	395.0
18.1	318.9	(200) KCl	314.6
20.6	280.2	*(11) 2Ds Mo*	279.5
25.7	224.0	*(110) 3D Mo*	222.5
27.1	213.0	(100) Graphite	213.0
29.2	197.6	*(20) 2Ds Mo*	197.6
37.1	155.5	*(200) 3D Mo*	157.4
44.4	130.0	*(211) 3D Mo*	128.4
46.6	123.8	(110) Graphite	123.0
51.3	112.5	*(220) 3D Mo*	111.3

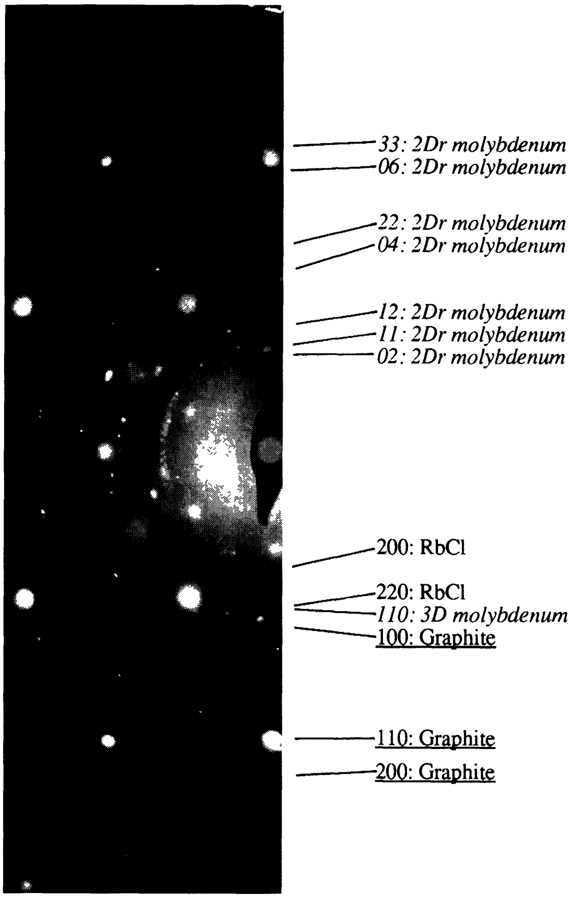
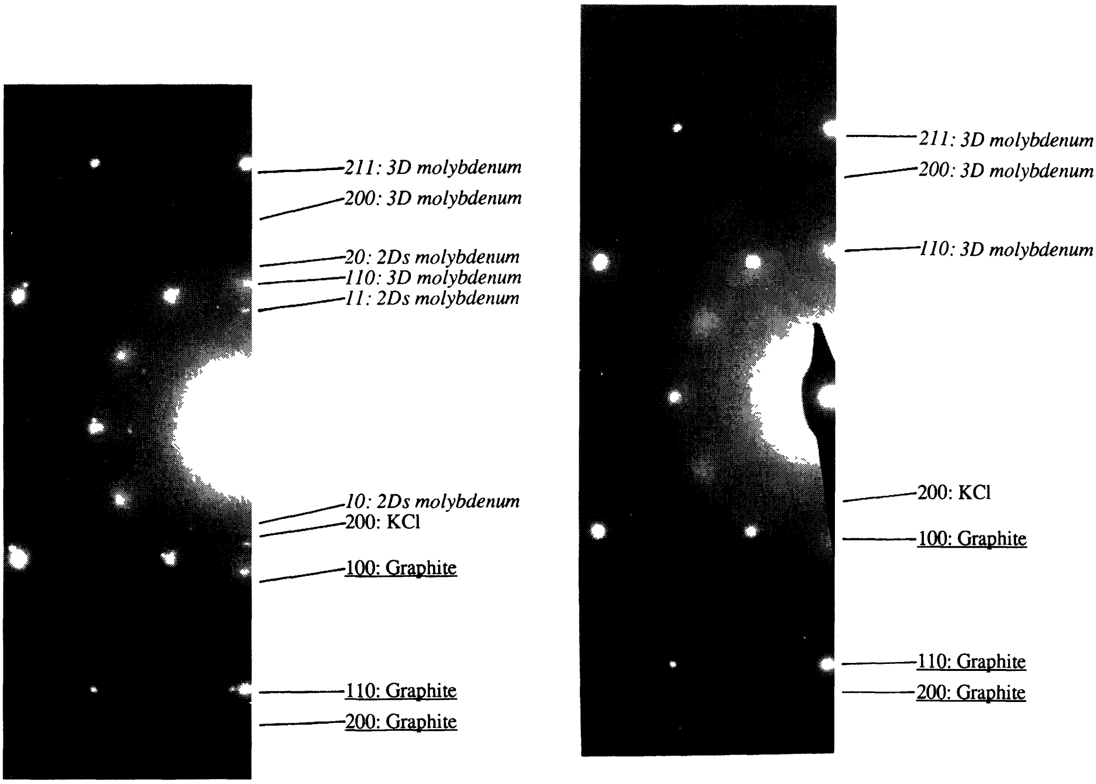


Fig. 2. — Selected area electron diffraction diagram of a G-$MoCl_5$ compound reduced by Rb at 100 °C: 2Dr: two-dimensional rectangular lattice a = 396 pm, b = 792 pm; 3D molybdenum: three-dimensional inclusions.

Table V. — *Measured and calculated d-spacings of a G-$MoCl_5$ compound reduced by K at 75°C (corresponding to Fig. 3b): 3D molybdenum: three-dimensional inclusions.*

Diagram distance (mm)	d_{hkl} measured (pm)	Indexation	d_{hkl} calculated (pm)
18.7	314.3	(200) KCl	314.6
26.5	221.0	*(110) 3D Mo*	222.5
27.6	213.0	(100) Graphite	213.0
37.8	155.5	*(200) 3D Mo*	157.4
46.1	127.5	*(211) 3D Mo*	128.4
47.5	123.7	(110) Graphite	123.0
52.0	113.0	*(220) 3D Mo*	111.3



a) b)

Fig. 3. — Selected area electron diffraction diagrams of G-$MoCl_5$ compounds reduced by K at 75 °C: 2Ds: two-dimensional square lattice $a = 395$ pm; 3D molybdenum: three-dimensional inclusions.

3.3 REDUCTION OF $MoCl_5$-GIC BY POTASSIUM. — Figure 3 shows diffraction diagrams of a $MoCl_5$ graphite intercalation compound reduced by potassium at 75 °C. As in the previous cases, the strong $(hk0)$ reflexions with hexagonal symmetry correspond to the graphite network (Tabs. IV and V).

Moreover, only $(hk0)$ reflexions of potassium chloride are visible. Their intensities are however very weak and only the first (200) reflexion is most often observed. The microanalysis also shows that the reduced product is constituted of about 50% of molybdenum and 50% of potassium; chlorine element is barely present in the sample. Amongst the three types of alkali metal chloride, potassium chloride is the most extractible in alcohol, which explains the very small quantity of this compound in the final reduced product. The significant amount of potassium element can be explained by the formation of KC_8 compound, resulting from the intercalation of potassium into graphite.

The majority of the reduced product is composed of three-dimensional clusters of metallic molybdenum with a parameter of 314 pm as shown by the presence of a series of diffuse spots on the diffraction diagram. All the (hkl) reflexions are indeed observed: (110) and (200) spots are in the directions of (100) and (110) graphite spots. Dark field imaging using one of these (110) beams allows the observation of very small-sized metallic clusters, the diameter of which ranging from 5 to 20 nm. These clusters are homogeneously distributed in the whole sample and are well-oriented with respect to the graphite network. Another experimental evidence of the complete reduction

of molybdenum chloride is given by EELS, the absorption spectra being close to that of metallic molybdenum.
A small proportion of a two-dimensional phase is sometimes also observed. A series of twelve spots have been indexed in a square lattice characterized by a parameter of 395 pm. This lattice is oriented with respect to the graphite network: (10) reflexions are rotated at ±15° to (100) and (110) graphite reflexions whereas (11) reflexions are in the same directions as (100) and (110) graphite reflexions.

4. Concluding Remarks

The nature of the two-dimensional metal phases depends strongly on the nature of the reducing agent. Reduction by cesium leads to three distinct oriented square lattices of intercalated molybdenum with parameters of 327 pm, 350 pm and 812 pm. Reduction by rubidium gives a rectangular lattice with parameters of 396 pm and 792 pm. Reduction by potassium finally leads to a square lattice with a parameter of 395 pm. The existence of several lattices for an intercalant in the same sample is very often encountered for graphite intercalation compounds [9]. In our case, the two-dimensional lattices are not commensurate with that of graphite, there are only preferential orientations.
The nature of the reducing agent has also an effect on the abundance of these two-dimensional phases with respect to that of the three-dimensional phases. The change from potassium to cesium provokes a significant increase in the abundance of the two-dimensional phases and a simultaneous decrease in that of the three-dimensional phases. These results wholly confirm those previously obtained by Hérold *et al.* [4-6] concerning the reduction of $FeCl_3$ and $CoCl_2$ graphite intercalation compounds by heavy alkali metals and are coherent with previous works showing that the use of more or less strong reducing agents gives very different compounds [3, 10, 11]. A hypothesis that can be proposed to explain this evolution is that the bigger the alkali metal, the more separated the graphene layers and consequently the more stabilized the two-dimensional metal phases.

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