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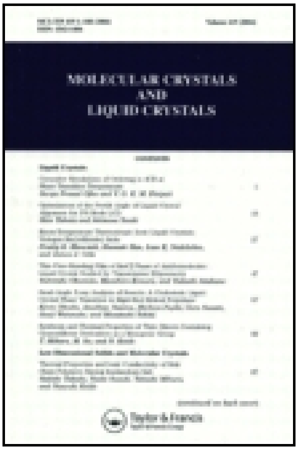

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Low Temperature Structures of Stage 2 Cesium Graphitides with Various Compositions

L. Duclaux [a] [b] , I. Rannou [a] [c] & F. Béguin [a] [b]
[a] CRMD, UMR CNRS-Université d'Orléans.
[b] 1 B rue de la Férollerie, 45071, Orléans Cedex 02, France
[c] rue de Chartres, BP 6759, 45067, Orléans Cedex 02, France

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LOW TEMPERATURE STRUCTURES OF STAGE 2 CESIUM GRAPHITIDES WITH VARIOUS COMPOSITIONS

L.Duclaux °, I.Rannou * and F.Béguin °
CRMD, UMR CNRS-Université d'Orléans.
° 1 B rue de la Férollerie, 45071 Orléans Cedex 02, France.
*** rue de Chartres, BP 6759, 45067 Orléans Cedex 02, France.**

Abstract : Compounds with the compositions CsC_{22}, CsC_{24}, and CsC_{28} were synthesized from H.O.P.G platelets and characterized by X-ray diffraction. All the specimens are basically 2nd stage phases. CsC_{24} appears as an almost pure phase, whereas CsC_{22} and CsC_{28} contain respectively a trace of 1st stage CsC_8, and a relatively large amount of 3rd stage phase. Fourier analysis of the 00ℓ reflexions shows that the composition range for the 2nd stage compound seems to be very limited, and close to CsC_{24}. From the 00ℓ scans realized in the range 300 K-77 K, a first order transition was observed for the 2nd stage phase at about 155 K, giving two new 2nd stage phases, respectively with Ic=9.33 Å (main phase), and Ic =9.58 Å. This transition is attributed to the freezing of the cesium film leading to a 2D segregation inside a unique grain. The domains could be separated by pleats distributed along a canted front.

INTRODUCTION :

The cristallo-chemistry of graphite intercalation compounds with alkali metals has been first studied by Rüdorff and Schultze [1], who found an ideal composition MC_{24} for the stage 2 compounds. Parry et al. [2,3] and Clarke et al. [4,5] followed the structural evolution of the 2nd stage cesium derivative, as a function of temperature, by X-ray diffraction. Cesium forms a 2D liquid at room temperature, as confirmed by the theoretical model of Plischke [6]. A 2D ordered structure with a 3D correlation was observed around 160 K. The low temperature 2D structure is composed of respectively commensurate (2x2, R0°) and non registered phases [5].

Applying the two-bulb intercalation method to the graphite-cesium system [7], Oufkir determined one isobar [9] on which the plateau representing the 2nd stage phase is limited by the compositions CsC_{23} and CsC_{27}. The purpose of our work is to study the influence of the stoichiometry on the structure of 2nd stage CsC_x compounds. In this first paper, we analyze the evolution of the 00ℓ

diffraction lines in the range 77 K- 300 K for three compositions CsC_{22}, CsC_{24} and CsC_{28}.

EXPERIMENTAL :

First stage CsC_8 specimens were synthesized from HOPG platelets (12x4x0.4 mm^3) by the two-bulb method [7]. The compounds were then diluted with an appropriate amount of graphite powder and annealed at 370°C in order to obtain the exact compositions CsC_{22}, CsC_{24} and CsC_{28}.

The compounds were characterized for their 00ℓ lines, using the MoKα1 radiation and a curve position sensitive detector (INEL CPS 120). For each composition, a part of the sample was transfered under helium atmosphere inside a diffraction cell, which part exposed to X-rays is a Lindemann glass capillary (diameter 2 mm).

The diffraction cell was placed on a goniometer head in a continuous flow cryostat (working in the range 77 K to 300 K) which is fixed to a step by step motor for a θ rotation of the sample. The 00ℓ scans were obtained in the reflection mode, with the c-axis in the plane of the incident and diffracted beams, by slowly rotating the sample (900s/°).

RESULTS :

Figure 1 shows the 00ℓ plots at room temperature, respectively for CsC_{22}, CsC_{24}, and CsC_{28}. Even if these diagrams indicate mainly 2nd stage compounds, the last are not single phases. CsC_{22} includes a very small amount of first stage compound and can be considered as a pure phase. On the other hand CsC_{28} is a mixture of second and third stage compounds.

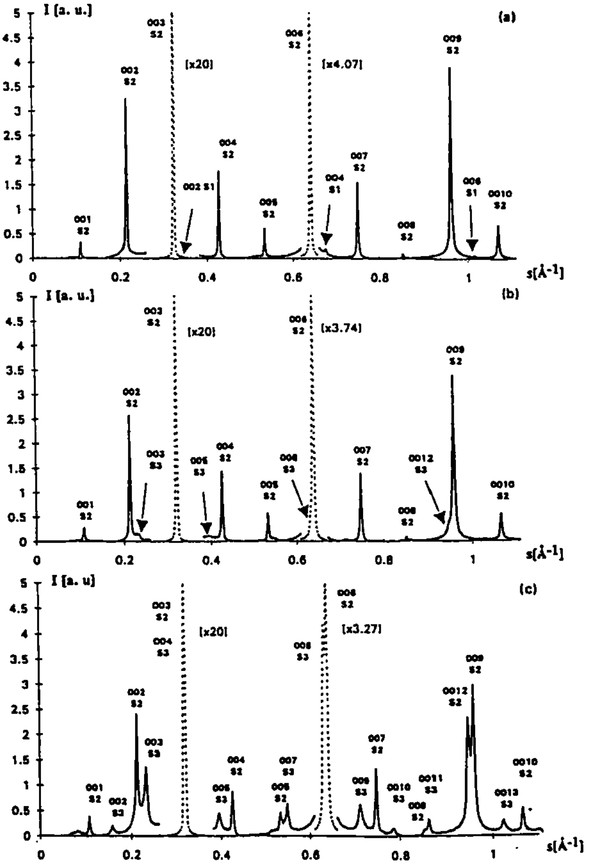

Figure 1 : 00ℓ reflections at room temperature.
S1 : stage 1; S2 : stage 2; S3 : stage 3.
(I: intensity in arbitrary units versus s = 2sin θ/λ in $Å^{-1}$)
(a) : CsC_{22} (b) : CsC_{24} (c) : CsC_{28}

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Third stage is also present in the CsC_{24} compound as a trace. From the 00ℓ reflections analysis we determined the identity period I_c along the c-axis for each compound : I_c=9.38 Å, 9.39 Å, and 9.39 Å respectively for the compositions CsC_{22}, CsC_{24}, and CsC_{28}. The first stage compound in CsC_{22} has an identity period I_c=5.93 Å whereas the parameter of the third stage is I_c=12.71 Å in CsC_{28}.

The 00ℓ reflections were recorded in the range 77 K-300 K for each sample. As expected, upon cooling the I_c parameters decrease slowly for all the phases. Close to 155 K, a reversible first order phase transition was observed for the 2nd stage phase, which segregates into two separated stage 2 phases. At the transition, the identity period sharply reduces from 9.37 Å to 9.33 Å, as a second minor phase of larger I_c appears (respectively 9.56 Å, 9.60 Å, and 9.58 Å for the compositions CsC_{22}, CsC_{24}, and CsC_{28}). Taking the sample CsC_{24} as an example, the evolution of the 009 reflection is represented in figure 2 at 145 K, 150 K, and 155 K. Upon heating, the two low temperature phases disappear simultaneously,

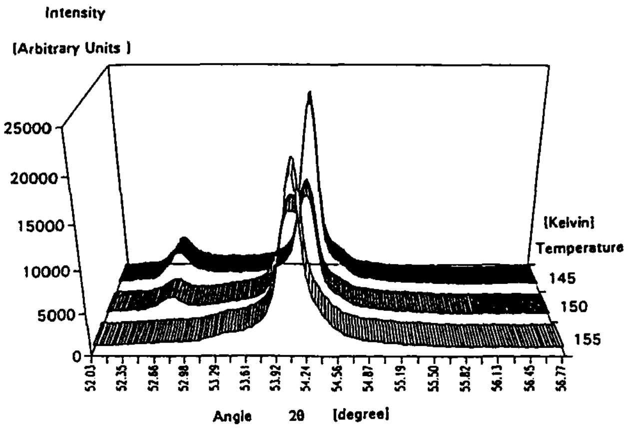

Figure 2 : Profiles of the 009 reflection of CsC_{24} at T = 155 K, 150 K, and 145 K.
MoKα1 radiation : λ=0.70926 Å.

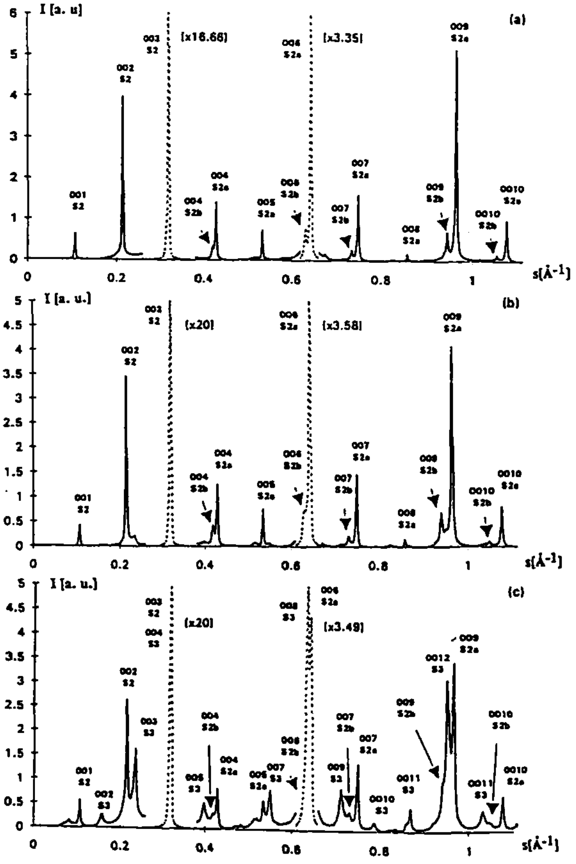

Figure 3 : 00ℓ reflections at T = 145 K. S1 : stage 1; S2 stage 2; S2a : stage 2 main phase; S2b : stage 2 minor phase, S3 : Stage 3 (I: intensity in arbitrary units versus s = 2sin θ/λ in $Å^{-1}$)
(a) : CsC_{22} (b): CsC_{24} (c): CsC_{28}

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whereas the high temperature phase is formed. Figures 3 represents the low temperature (T=145 K) diffractograms for the stoichiometries CsC_{22}, CsC_{24}, and CsC_{28}. The proportion of the minor phase could be roughly estimated to about 10 % for all the samples.

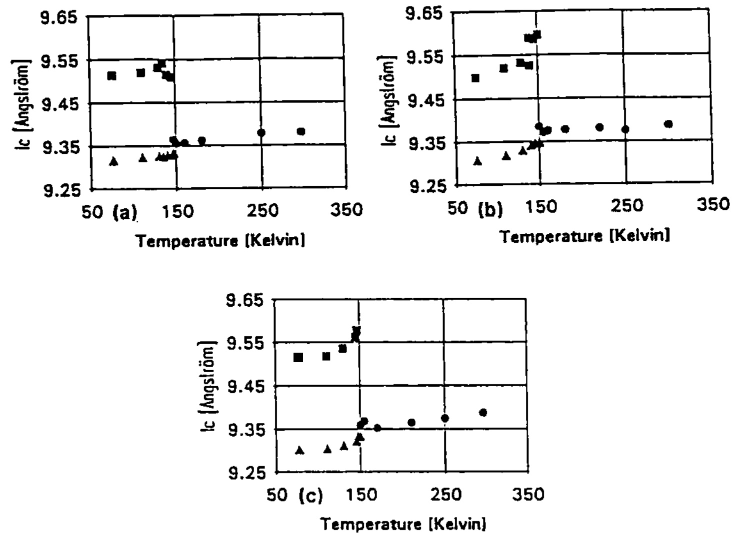

Figure 4 : Thermal evolution of the identity period I_c for the second stage phase.
(a) : CsC_{22} (b) : CsC_{24} (c) : CsC_{28} • : Stage 2 high temperature phase.
▲ : Stage 2 low temperature main phase.
■ : Stage 2 low temperature minor phase.

The thermal evolution of the identity period is represented on figure 4 for the second stage phase. Increasing the temperature, the I_c parameter of the main phase increases very slowly with an abrupt step of several hundredths of Å at transition.The minor phase presents an almost parallel evolution. The relative intensities of the well resolved 0010 reflections of the two stage 2 phases remain constant in the range 300 to 77 K, so that the relative proportions can be considered as almost stable with temperature. The line width of the main phase is independant of temperature whereas it broadens regularly with decreasing the temperature for the minor phase.

DISCUSSION :

The compositions CsC_{22} and CsC_{28} are not strictly in the range determined for the stage 2 phase by Oufkir [9], which is bounded by the compositions CsC_{23} and CsC_{27}. This could be the reason for the presence of stage 1, and stage 3 phases, respectively, in CsC_{22} and CsC_{28}. However, the difference in

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composition between CsC_{28} and CsC_{27} cannot explain a so large amount of stage 3 in CsC_{28} (see Fig. 1c). The presence of stage 1 or stage 3 together with the stage 2 are better to be attributed to the particular conditions used for the synthesis. Our samples were not obtained at the equilibrium and it is likely that the temperature has also a strong influence on the nature of the metal layer. An inclined plateau, as observed on the isobars [9], is the signature that the intercalated metal might be in the form of a bidimensional gas [8]. Therefore one could imagine that at the temperature used for the synthesis (370 °C), the CsC_{28} derivative is a pure stage 2. At room temperature, the layer becomes a "bidimensional" liquid and a mixture of stage 2 and 3 is more stable than a single stage 2. Indeed a dense stage 3 with $C/Cs=12$ is more stable than a stage 2 with $C/Cs=14$, because of lower repulsive and spacing energies [12].

The identity period of the stage 2 is nearly the same for the three compounds. By least-squares structure refinement of the first fifteen 00ℓ reflexions of the compounds CsC_{24} and CsC_{22} at room temperature, we found respectively the compositions $CsC_{23.9}$ and $CsC_{23.6}$ indicating an ideal composition close to CsC_{24} for the 2nd stage. The differences in total stoichiometry are then explained by the presence of the other stages.

Clarke et al. [4,5], and Parry et al. [2,3] studied the hk0 and $hk\ell$ reflexions for graphite monocristals intercalated with cesium. They observed a transition at 160 K where cesium becomes 2 D ordered with a 3 D correlation. Mixed phases were detected in which the cesium atoms are registered to the graphite hexagons [10]. At the transition, the cesium atoms are locked with the sequence...$A\alpha AB\beta BC\gamma CA$... [3]. Following the thermal evolution of the 007 line for a CsC_x stage 2 compound, Oufkir observed 007 line of low temperature phase identified as a stage 2 together with another reflexion of an unknown phase [9].

In our samples, the stage 2 segregates into two second stage phases at about 155 K. For the main phase, the distance between the layers is reduced from 9.38 Å to 9.33 Å. The decrease of the interlayer distance can be explained by the locking of the cesium atoms by the graphite lattice, as reported by Clarke [10] and Parry [2,3]. Though the stoichiometry of the three samples differs, the low temperature main phase has always the same identity period : 9.33 Å. As discussed previously for the high temperature phase, the low temperature main phase can be considered identical in all the samples.

For the minor phase, the mean value of the identity period is $I_c=9.58$ Å, which is quite large for a stage 2 compound. In this case, the cesium positions are probably not registered with the graphite planes. Moreover the broadening of the 00ℓ reflexions, as the temperature decreases, reveals a disordered phase.

The coexistence of the two low temperature phases in the same grain and their constant proportions may indicate that their formations are linked. The similarity of the low temperature main phase in the three sample suggests that this phase is the most stable, with well defined structure and stoichiometry. As two phases are formed at the transition, it is likely that the main phase has a stoichiometry different from CsC_{24}, and the proportion or the composition of the minor disordered phase would equilibrate the global stoichiometry of the sample.

These two phases are undoubtedly due to the 2 D segregation of the cesium in separated domains which accompanies the freezing of the layer. Such a reversible first order transition can occur in the favour of the flexibility of the graphite planes. As already proposed by other authors, one could imagine that the elastic energy is minimized by distributing the pleats along a canted front [11]. More information, particularly about the compositions of these two phases would be obtained by modelisation of the 00ℓ row spectrum, and analysis of the $hk\ell$ reflexions.

CONCLUSION :

The average composition of the 2nd stage cesium graphitide seems to be very close to CsC_{24} at room temperature. From the 00ℓ scans performed on this 2nd stage phase in the sample CsC_{22}, CsC_{24}, and CsC_{28}, in the range 77 K to 300 K, a first order phase transition was detected at about 155 K. The transition is attributed to the freezing of the cesium layer inducing a 2D segregation in distinct 2nd stage domains. These domains separated by pleats of graphite layers may differ by their cesium compositions. The difference in the identity period of the two phases suggests important changes in their 2 D structures which are probably registered, and not registered, respectively for the main, and the minor components. To account with the structural data, and with the easy diffusion of cesium at the transition, one could imagine a pleated layers model with the pleats separating the domains distributed along a canted front. The main advantage of such a model is the equivalence of all the intervals.

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