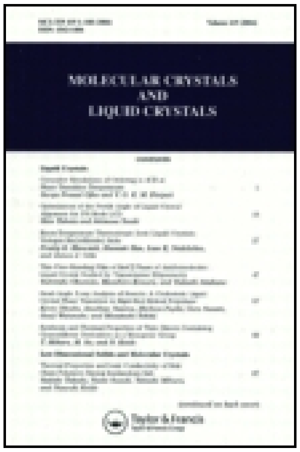

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Neutron Diffraction Study of the N_2-CsC_{24} System

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Neutron diffraction study of the N_2-CsC_{24} system

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Abstract : *Physisorption of molecular N_2 in the 2nd stage CsC_{24} was studied as a function of temperature and pressure using neutron diffraction The new structures resulting from reaction were determined from the analysis of the 00l lines and they were related to the intercalation rate of N_2*

Keywords : graphite, intercalation, CsC_{24}, Nitrogen, physisorption, neutron diffraction, staging effect.

INTRODUCTION

Non polar molecules such as nitrogen are known to be physisorbed into the 2nd stage MC_{24} intercalation compounds at low temperature (M=K, Rb, and Cs) [1]. As reported by Moreh [2], the physisorption of N_2 in KC_{24} and RbC_{24} induces the formation of new 2nd stage structures (in which the intercalates species are N_2 and Cs) which reversibly segregate from the stage 2 host structure at low temperature. In order to study the new structures resulting from the physisorption of molecular N_2 into CsC_{24} we performed in situ powder neutron diffraction as a function of pressure and temperature.

EXPERIMENTAL

CsC_8 powder was first prepared by the conventional two bulb method with graphite at T_G=250°C, and cesium at T_{Cs}=200°C. A stoichiometric amount of graphite powder (Ceylan, 40 to 60 μm) was added to CsC_8 and the mixture was annealed at 370°C during one week so as to obtain the exact composition CsC_{24}.

The CsC_{24} powder was transferred under helium atmosphere into a vanadium container and fixed on a hollow stick. The hollow stick was separated by a valve from a calibrated reservoir connected to a pressure gauge [0-2000 mbar] and a high purity nitrogen bottle allowing the direct measurement of the pressure and the supply with N_2. The stick was placed in a cryostat working in the range of temperature [300K-10K].

Neutron diffraction patterns were "in situ" recorded at a rate of one data set/five minutes on the D1B diffractometer at λ=2.52 Å (ILL, high flux reactor in Grenoble) as a function of pressure and temperature.

Pristine CsC_{24} was firstly analyzed under vacuum from 300 K to 10 K and as expected, with neutron diffraction method, no change in the *00l* diffraction lines intensities was observed confirming the purity of the sample.

In a conventional experiment, the initial pressure was set to almost 2 bar at room temperature, and the temperature was progressively lowered to 10 K while the pressure was measured at equilibrium at each temperature. The rate of nitrogen intercalation could be estimated from the pressure measurements using the relation PV=nRT (where T is the room temperature) with a good approximation at temperature higher than 77 K [3].

In a last experiment, CsC_{24} was saturated with liquid nitrogen at a pressure>2.7 bar and at 70 K. The structural evolution of the sample on high pressure of nitrogen was studied in the temperature range [10 K-300 K].

Some of the *00l* diffraction lines were fitted using ab-initio calculations and adjusting parameters such as the rate of N_2 and Cs in the different structures, the atomic Debye Waller factors (C, Cs, N_2), the coherence length along the c axis, and the proportion and probabilities of occurrence of each layered structures, following a procedure previously used [4], adapted for neutron diffraction.

RESULT AND DISCUSSION

The intensities of the *00l* lines at room temperature before sorption could not be reproduced without taking into account the partial orientation of the GIC crystallites (Fig. 1).

N_2 Intercalation at low pressure ($P \leq 2$ bar)

When the system was submitted to a pressure close to 2 bar, intercalation started at room temperature. As the temperature decreased, the rate of N_2 intercalation increased continuously and finally reached the value of 1.5 mole of N_2/CsC_{24} at 100 K (Fig. 2), which is slightly higher than N_2/CsC_{24}=1.3 at saturation found by Watanabe et al [1] with an initial pressure of 1 bar.

The intercalation occurs at first randomly in the 2nd stage cesium layers resulting in a great change of *00l* lines and a continuous shift of the identity period from 9.35 Å to the maximum value of 9.58 Å at 100 K (Fig. 3).

Below 220 K, a pure first stage CsC_8 together with the 2nd stage $Cs(N_2)_xC_n$ (n>24) derivative is formed (Fig 4). Due to the intercalation of molecular N_2, the internal pressure increased and provoked the motion of a part of cesium in more dense CsC_8 binary domains [5].

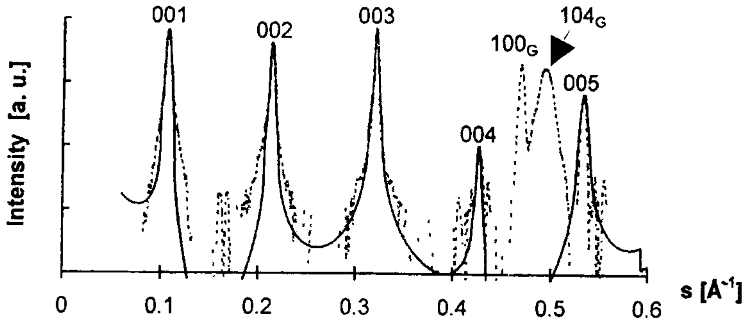

Figure 1 : Logarithmic intensity plot of the experimental scan of pure CsC_{24} at room temperature (dotted line). The continuous line is the result of a model with a partial preferred orientation function [6] : $G_1+(1-G_1)\exp(-G_2*(\theta-\theta_0)^2)$ [$G_1=0.54$, $G_2=0.012$, and $\theta_0=26°$]. 10*l* lines belonging to the graphite network are indexed (100_G and 104_G).

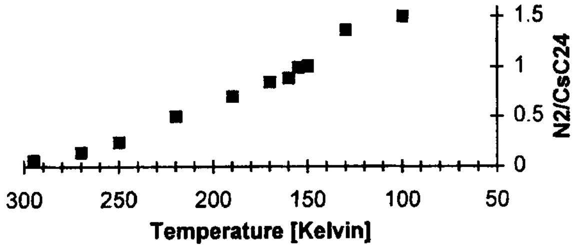

Figure 2 : Ratio of the sorbed molecules at equilibrium to the number of intercalated alkali atoms [N_2/CsC_{24}] as a function of the temperature.

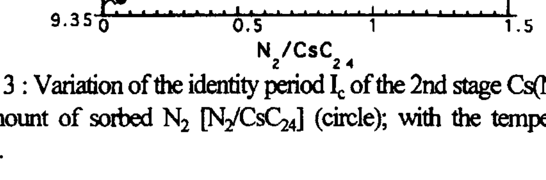

Figure 3 : Variation of the identity period I_c of the 2nd stage $Cs(N_2)_xC_n$ (n>24) with the amount of sorbed N_2 [N_2/CsC_{24}] (circle); with the temperature [in Kelvin] (cross).

The *00l* lines of the 2nd stage $Cs(N_2)_xC_n$ (n>24) were well reproduced at 220 K (Fig. 4) taking $N_2/CsC_{24}=0.5$ and an $I_c=9.51$ Å in agreement with the experimental values of sorbed amount of nitrogen at this temperature (Fig. 2). The proportion of first stage CsC_8 is very weak as compared to the 2nd stage $Cs(N_2)_{0.53}C_{25}$ (Fig. 4).

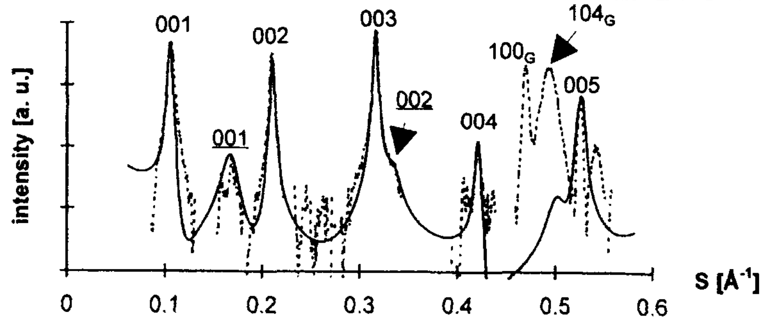

Figure 4 : Logarithmic intensity plot of the experimental scan of CsC_{24} saturated with N_2 ($N_2/CsC_{24}=0.5$) at 220 K (dotted line). The continuous line is the result of a model of the *00l* lines with 93% of 2nd stage $Cs(N_2)_{0.53}C_{25}$ partly interstratified with pure first stage CsC_8 (underlined *00l* indexes).

The identity period I_c of the 2nd stage $Cs(N_2)_xC_n$ (n>24) increases linearly with the N_2 content until 170 K corresponding to a rate of 0.8 N_2/CsC_{24} (Fig 3). At T<170 K, there is a change of the slope (Fig. 3) and I_c of the 2nd stage increases more slowly with increasing N_2/CsC_{24} content. Actually below 170 K, the 2nd stage N_2-Cs layers are progressively saturated by additional N_2 molecules so that a first stage N_2-Cs ternary graphitide is formed. An example of neutron diffraction pattern at 150 K is shown in figure 5. The 001 peak of this new structure interstratified with the previous CsC_8 and $Cs(N_2)_xC_n$ phases is visible but the 002 line is included in the 003 line of the 2nd stage phase, explaining that this peak is larger than the others of the same family (Fig 5). According to a simple model in which the N_2 molecules would be parallel to the graphite planes, the identity period I_c of the first stage N_2-Cs ternary can be estimated to be $2r_{N2}+d_G=6.45$ Å (where r_{N2} and d_G are respectively the Van der Vaals radii of Nitrogen : 1.55 Å and the distance between two graphite layers : 3.35 Å) in good agreement with the experimental value of 6.4 Å. However, the measured value of $2r_{N2}$ was found to be 2.86 Å [2] yielding $2r_{N2}+d_G=6.21$ Å so that the measured identity period (6.4 Å) could be explained by the tilt of the nitrogen molecules in relation to the graphite planes.

At 100 K, complete physisorption is achieved. Indeed, from T=100 K to 10 K the *00l* intensities remain unchanged, and only the identity period of the 2nd stage slowly decreases with decreasing temperature (Fig 3). Due to the freezing of the cesium atoms at low temperature [4] the motion of the cesium atoms cannot occur anymore, and as a consequence the system remains a mixture of the three structures previously described. However changes were observed in the *hk* lines (Fig. 5) appearing at T<160 K, attributed to the 2D order of nitrogen and cesium.

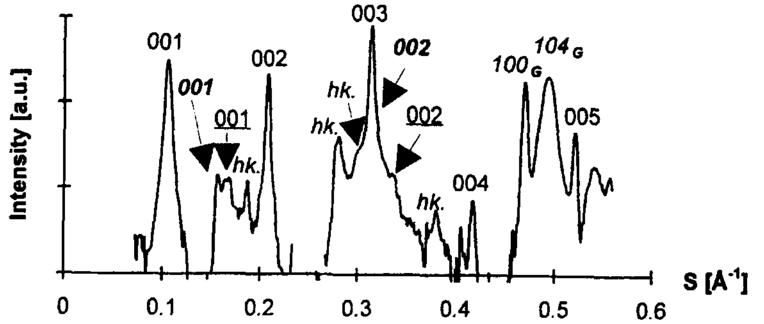

Figure 5 : Experimental scan of CsC_{24} saturated with N_2 at 150 K. The pattern consists of *00l* lines of a first stage CsC_8 (underlined indexes) and a first stage $Cs(N_2)_yC_m$(bold indexes) with the lines belonging to the 2nd stage $Cs(N_2)_xC_n$ (normal indexes).

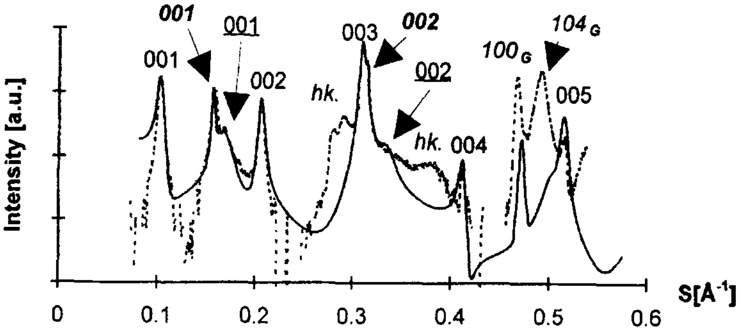

Figure 6 : Logarithmic intensity plot of an experimental scan of CsC_{24} saturated with N_2 at 160 K (dotted line). The continuous line is the result of a model of the *00l* lines with a mixture of 25% first stage $Cs(N_2)_{1.8}C_{16}$ (I_c=6.37 Å, bold indexes) and 17% of the binary first stage CsC_8 (I_c=5.98 Å, underlined indexes) interstratified in the 2nd stage $Cs(N_2)_{2.1}C_{32}$(I_c=9.71 Å, normal indexes).

Intercalation at higher pressure

When high pressure (>2.7 bar) was applied on the system cooled at 70 K, part of the nitrogen was physisorbed in the 2nd stage layers and liquid nitrogen was also formed. When lowering temperature, reversible liquid-solid transition of nitrogen was observed. Upon heating, the nitrogen pressure applied to the system increase dramatically leading above T=150 K to the formation of a first stage N_2-Cs ternary graphitide (I_c=6.37 Å) together with 2nd stage $Cs(N_2)_xC_n$ (n>24) and pure stage one CsC_8. When the system is submitted to more than 9 bar at T=165 K, the content of first stage derivative was found about seven times higher than at 1.3 bar. This result indicates that the proportion of this first stage N_2-Cs ternary graphitide is related to the pressure and as a consequence, the rate of N_2 intercalated increases with increasing pressure applied to the system. Fitting the *00l* lines intensities (Fig. 6), it can be deduced that the compound at 160 K is a mixture of 25% segregated first stage $Cs(N_2)_{1.8}C_{16}$ (I_c=6.37 Å) and 17% binary first stage CsC_8 (I_c=5.98 Å) interstratified with the 2nd stage $Cs(N_2)_{2.1}C_{32}$ (I_c=9.71 Å). The first stage ternary graphitide structure reversibly disappears at 170 K and only 2nd stage $Cs(N_2)_xC_n$ (n>24) and pure CsC_8 remain stable above this temperature.

CONCLUSION

In agreement with previous results, it was found that due to its larger interlayer distance, CsC_{24} is a best sorptive agent than RbC_{24} and KC_{24} [1-2]. As decreasing the temperature, the N_2 molecules firstly intercalates in the 2nd stage $Cs(N_2)_xC_n$ (n>24) and at T<170 K a first stage ternary Cs-N_2 graphitide is formed. The sorption phenomena is enhanced by applying high pressure and it is completely achieved at T=100 K. Upon decreasing the temperatures, the N_2 molecules firstly intercalates in the cesium layers. Pressure effect leads to the redistribution of cesium giving a mixture of 2nd stage $Cs(N_2)_xC_n$ (n>24) and 1st stage CsC_8. Below 170 K, increasing the amount of intercalated nitrogen leads to transferring a part of the 2nd stage $Cs(N_2)_xC_n$ into 1st stage $Cs(N_2)_yC_m$. At 100 K, the mobility of the cesium atoms becomes so low that further intercalation cannot proceed. Applying high nitrogen pressure enhances drastically the amount of 1st stage ternary graphitide which is obviously the ultimate step of nitrogen intercalation.

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