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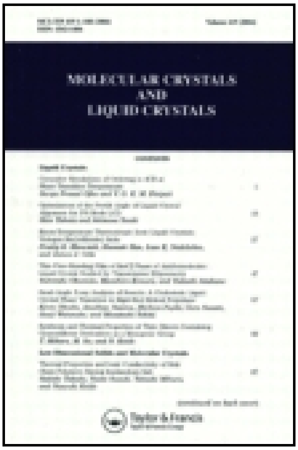

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CRYSTALLINE STRUCTURE OF Li-AND Cs-GRAPHITE SUPERDENSE PHASES

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Abstract Highly saturated lithium- and cesium- graphite intercalation compounds (of a composition LiC_2-LiC_4, CsC_4) synthesized under high pressure conditions were investigated using X-ray diffraction. It was shown an hexagonal unit cell with lithium with a = 8.63 Å and c = 11.1 Å (c = $3I_c$). With cesium, the orthorhombic unit cell presents the following parameters : a = 4.945 Å, b = 8.565 Å and c = 4 I_c= 23.48 Å.

INTRODUCTION

High pressure syntheses have given highly saturated LiC_2 and CsC_4 compounds, which should contain very short M-M distances, confirmed by IR spectroscopy[1] and NMR[2]. Both NMR and IR investigations have pointed out the decomposition of LiC_2 with time under the experimental conditions, but even after one year of keeping the samples under normal pressure and temperature conditions, the highly saturated phase remains in the sample. X-ray diffraction (including hk0 reflexions) was used in order to determinate the nature of this highly saturated phase.

EXPERIMENTAL

The samples, based on HOPG, were synthesized under high pressure conditions as described elsewhere[3]. Composition was controlled by measuring the volume of the sample and by DTA[4]. We have examined both ool and hko reflexions. The compounds present a bright yellow color, slightly lighter than that of the normal LiC_6 and CsC_8 phases.

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Li-GICs

The 001 reflexions show up a repeat distance along the c axis of 3.70 Å. This value, close to that of the c parameter of the normal compound obtained by reaction of the lithium vapor on graphite, indicates that one has prepared a first stage compound in which the lithium atoms lie probably in the potential wells of the graphite, as in LiC_6[5].

The corresponding hk0 X-ray diagram is shown on Fig.1 and the reflexions are listed in Table I. It appears immediatly that the large number of observed peaks cannot be attributed only to :

- the LiC_2 type unit cell, whose a parameter should be equal to that of graphite (around 2.46 Å),
- the presence of hk0 family only : there are also some hkl reflexions due to the relatively high mosaic spread of the sample (around 15°).

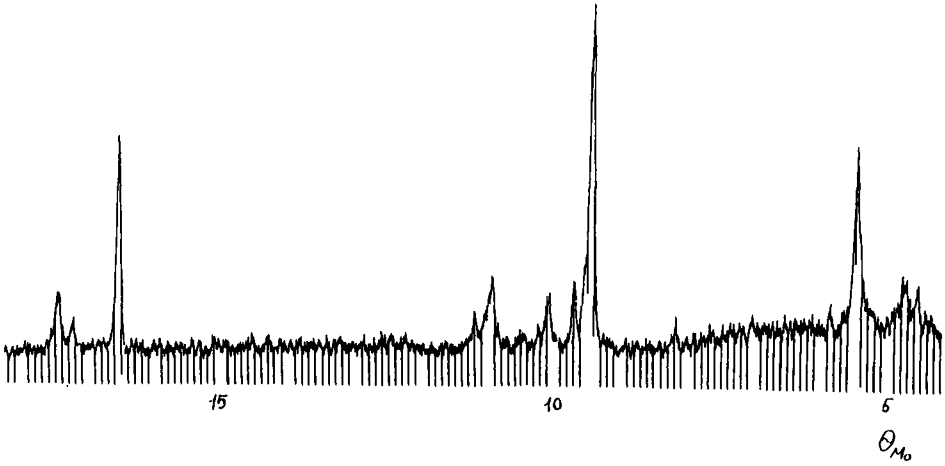

FIGURE 1 hkl X-ray diagram of Li superdense phase (Mo Kα).

In Table I are listed the different Miller indices of the observed reflexions, the calculations were made on the basis of an hexagonal unit cell with $a = 8.63$ Å and $c = 3_*I_c = 11.10$ Å. This unit cell, commensurate with respect to the graphite network ($a = 2a_G\sqrt{3}$) contains 3_*24 carbon atoms. Then the chemical composition should be $Li_{3x}C_{3*24}$. Since there was a partial decomposition of the starting LiC_2 material, one cannot know the exact value of x, which should be between 12 and 4 which corresponds respectively to LiC_2 and LiC_6, the phase known to be stable under ambient pressure and temperature.

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TABLE I hkl reflexions of Li_{3x} C_{72}

θ (°)	d (Å)	hkl	I%exp.	I%calc. ($Li_{27}C_{72}$)
4.57	4.45	102	10.8	6.5
4.75	4.28	110	12.1	15.5
5.52	3.687	003	53	939
5.85	3.48	103	8.4	4
7.05	2.89	210	3.6	3
8.18	2.49	212-300	6	5
9.47	2.1553	220	100	100
9.7	2.105	105-303	19.3	2
10.08	2.026	214	13.3	1
10.95	1.867	223	18.1	730
11.18	1.829	304-006	8.4	5
14.3	1.436	330	2.4	3
14.52	1.414	414-226	2.4	41.6
15.10	1.361	235-333	3.6	5
16.55	1.248	326-600	61.4	344
17.25	1.196	432-520-521-119	8.4	4
17.46	1.182	603	16.9	220

The experimental hkl intensities are compared to those calculated for x=9 ($Li_{27}C_{72}$). Several stackings of the Li planes were tested and the values in Table I correspond to the best agreement. The discrepency between those values can be due either to a misorientation for the hkl reflexions (we are in position for the hk0 planes) or to the presence of several phases which differ by their composition or stacking along the c axis (Fig. 2). However, the missing hk0 peaks are either very small or non-existent. All observed hkl peaks have been indexed which confirms the proposed unit cell.

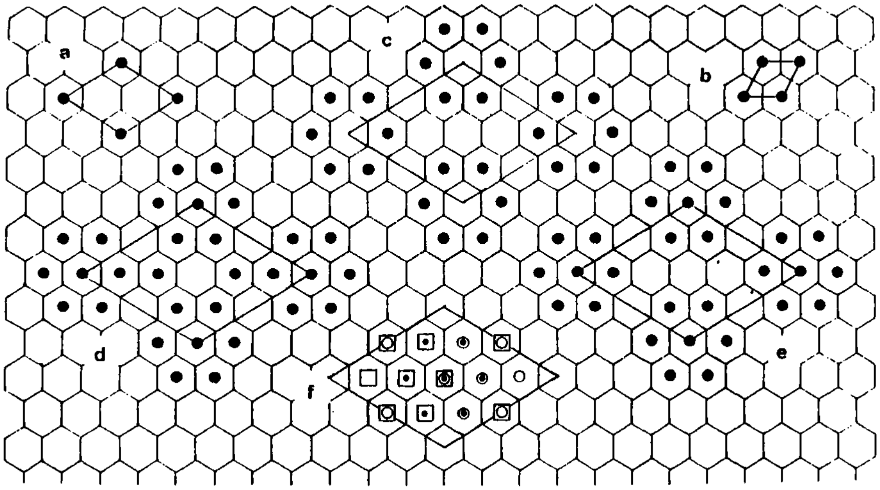

FIGURE 2 Some structures of layers for : a)LiC_6, b)LiC_2, c)Li_6C_{24}, d)Li_9C_{24}, e)Li_7C_{24}, f)Example of stacking for Li_{21} C_{72}.

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From IR spectroscopy, one knows that the LiC_x dense phases are characterized by the presence of equisided triangles, parallel to the carbone planes, with a very short Li-Li distance[1] and we have already discussed in other papers[2,6] the possible presence of "Li_7" clusters in such compounds, this is one of the reasons why we have chosen the in-plane arrangement for the lithium atoms, which form, in some cases, "flowers" of metal atoms.

Cs-GICs

The ool reflexions of CsC_4 and the corresponding Fourier transform are shown in Fig 3. It corresponds to the CsC_4 composition, but the metal layers are slightly splitted, maybe due to ionic repulsion between $Cs^{+\delta}$ which are at the same in-plane coordinates. The distance between the Cs layers is : 0.4 Å. The hk0 scan is shown in Fig 4. The experimental data can be explained on the basis of a simple orthorhombic unit cell with a = 4.945 Å ($2a_G$), b = 8.565 Å ($2\sqrt{3}a_G$) and c = 23.48 ($4I_c$) (Table II). It presents raws of cesium atoms with very short Cs-Cs distances (~ 2.46 Å) in spite of the large size of the Cs atoms (Fig. 4).

TABLE II hkl reflexions of the CsC_4 compound

θ (°)	d(Å)	h k l	$I_{exp.}$	$I_{calc.}$
4.75	4.28	020-110	-	25.1
4.88	4.17	021-111	-	49.2
5.12	3.97	022-112	39.1	46.2
5.25	3.876	023-113	16.5	42.1
5.63	3.615	024-114	10.9	37.4
6.70	3.04	025-115	7.8	32.8
6.81	2.96	026-116-(+008)	10.9	28.6(+141.8)
8.32	2.45	131-201	40	36.7
8.43	2.42	132-202	24.8	64.2
8.54	2.39	133-203	17.4	34.1
8.91	2.29	029-119-135-205	15.7	48.6
9.53	2.1419	220-040	100	100
10.13	2.016	136-206	41.3	74.5
12.68	1.62	150-240-151-241-311	28.7	50
12.8	1.61	152-242-312	13	40.1
13.0	1.58	153-243-313	8.7	20
13.1	1.56	154-244	7.8	12.6
13.47	1.52	155-425-315-156-426-316	10.9	59
14.45	1.42	060-330-04 12-22 12	16.1	11.9
16.65	1.238	260-400	58.7	105
17.38	1.19	171-351-172-352-420	16.1	40
18.18	1.14	268-408-176-356-426	7	120

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The observed intensities are decreasing as the l Miller index is increasing, this is due to the fact that the sample was fixed for hk0 refexions study. The presence of hkl in this case is only due to the mosaic spread of the sample. Because of the relatively high symmetry of the orthohexagonal unit cell represented below, many hk0 reflexions present a zero intensity value.

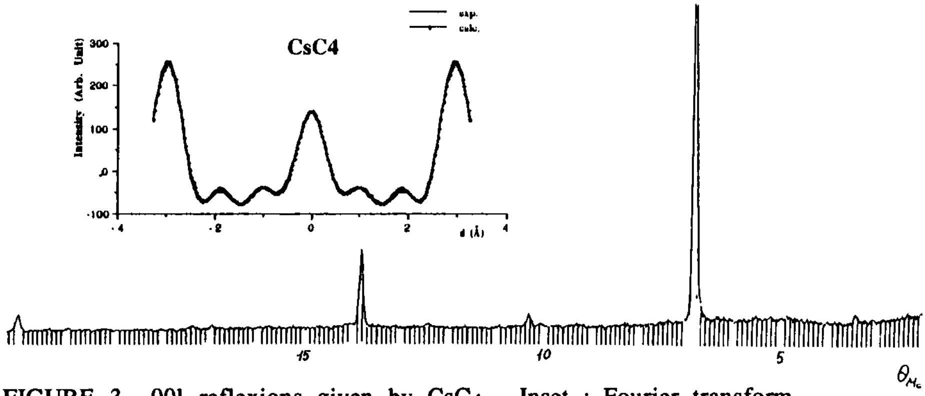
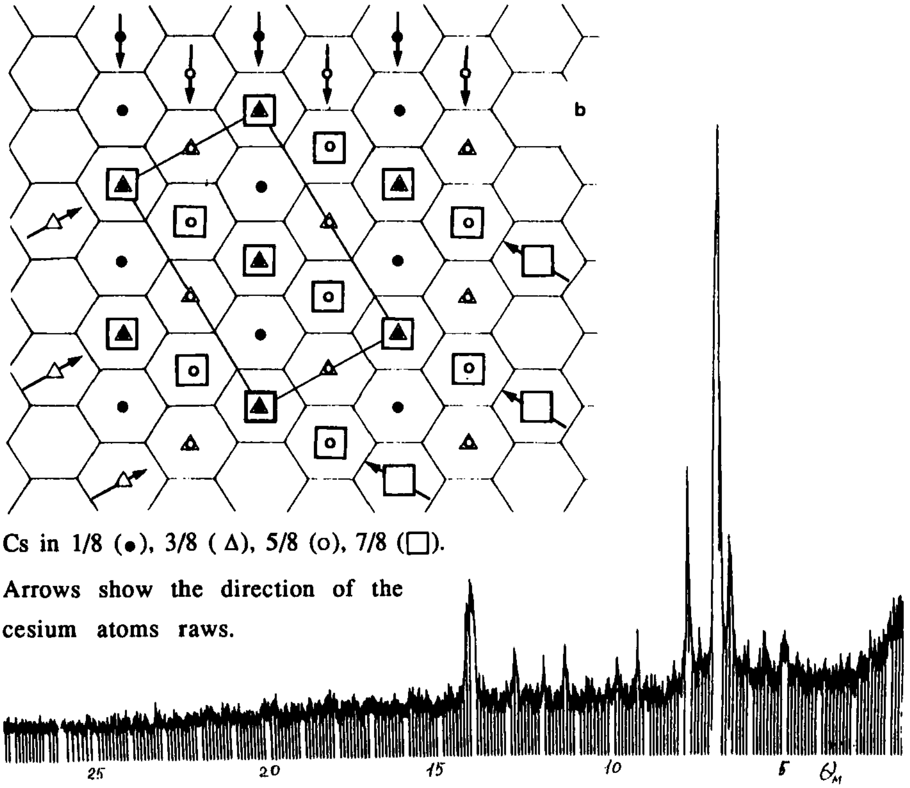


FIGURE 3 001 reflexions given by CsC_4 - Inset : Fourier transform.



Cs in 1/8 (●), 3/8 (△), 5/8 (o), 7/8 (☐).
Arrows show the direction of the cesium atoms raws.

FIGURE 4 hkl reflexions of CsC4 and the stacking of the four Cs layers.

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DISCUSSION

The value of 8.63 Å for the **a** parameter of our lithium compound involves an in-plane C-C distance of 1.438 Å, a value slightly larger (1.3%) than that in graphite (1.42 Å), this value is very close to that in LiC_6 : 1.436 Å. This means that, in spite of a ratio Li/C much higher in our compounds than in LiC_6, the charge transfer to the carbon is very close in both cases. This is, once again, in favour of a partial covalent in-plane bonding between the lithium atoms.

Such a situation is even more pronounced in the cesium compound : the in-plane C-C distances in CsC_4 are shorter than in the CsC_8 phase : 1.427 Å and 1.431 Å respectively. The charge transfer to carbon is less in CsC_4 than in CsC_8 in spite of twice as much Cs per carbon atom.

CONCLUSION

The fact that the unit cell corresponds to the right composition could involve that the CsC_4 phase is not decomposed when the pressure is released, contrarily to what happens with the lithium superdense compounds. This relatively low stability of the LiC_x compounds explains the difficulty to assign the positions for the lithium atoms inside the hexagonal unit cell which is well defined.

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