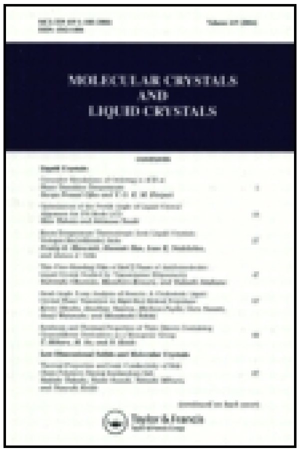

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In-Plane Structure and Thermal (In)Stability of $LiC_{2.18}$ Based on Boron-Doped Graphite

Cetna Bindra [a] , Vera A. Nalimova [b] & John E. Fischer [c]

[a] Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA, 19104, USA

[b] Department of Chemistry, Moscow State University, Moscow, 119899, Russia

[c] Department of Materials Science and Engineering and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA, 19104, USA

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In-Plane Structure and Thermal (In)Stability of $LiC_{2.18}$ based on Boron-Doped Graphite

CHETNA BINDRA[a], VERA A. NALIMOVA[b] and JOHN E. FISCHER[c]

[a]Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA 19104, USA; [b]Department of Chemistry, Moscow State University, Moscow 119899 Russia; [c]Department of Materials Science and Engineering and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA 19104, USA

LiC_2, the super-dense high pressure phase of lithium intercalated graphite retains a high Li density upon pressure release; it stabilizes at $LiC_{2.18}$ if 0.5 at.% boron-substituted graphite is used for synthesis. We investigate it's in-plane structure and thermal decomposition using high resolution X-ray powder diffraction. This yields a $2\sqrt{3}$ hexagonal cell with a = 8.54 Å and c = 3.71 Å. $LiC_{2.18}$ is stable indefinitely at ambient T and P. Above 100°C, a decomposition product $LiC_{3.4-3.8}$ is observed, corresponding to the stable phase at ambient conditions *without* boron. In both cases, we attribute the decomposition to Li diffusion with formation of (meta)stable Li_7 clusters; we speculate that the boron impurity impedes this process and thereby 'pins' the denser of the two superlattices.

Keywords: graphite; intercalation; high pressure

INTRODUCTION

LiC_2, synthesized from Li metal and graphite at high pressures decomposes at 1 atm. to $LiC_{3.4-3.8}$ (or $Li_7C_{24} \sim Li_{21}C_{72}$ (with 3 inequivalent Li layers)) with a commensurate hexagonal cell $\mathbf{a}=3\mathbf{a}_{gr}$ = 8.63 Å and c = 11.1 Å (3× 3.7 Å) [1]. We found a dramatic enhancement in the stability of the high Li density using 0.5 at.% boron-substituted graphite [2]; the $00l$ intensities followed for many months at 1 atm., showed an average composition of $LiC_{2.2}$, the first example of a stable phase denser than $LiC_{3.4}$. Here we report high resolution synchrotron powder X-ray diffraction studies of hkl reflections to understand the in-plane structure and thermal stability. We find a $2\sqrt{3}$ hexagonal cell with a = 8.54 Å and c = 3.71 Å with single layer stacking. The stable composition observed is $LiC_{2.18}$. The in-plane C-C distance 1.438 Å in $LiC_{2.18}$ is the same as in LiC_6 (and $LiC_{3.4}$ [1]) indicating similar total charge transfer from Li to C; this supports the idea of the excess Li density, in $LiC_{2.18}$, being localized and forming planar Li clusters due to Li-Li 'bonding'. $LiC_{2.18}$ is stable indefinitely at ambient T and P, while we observe a decomposition product close to $LiC_{3.4-3.8}$ at 175°C. This corresponds to the stable phase at ambient pressure in the absence of boron, in which it is stable up to 100°C, retaining the $Li_{21}C_{72}$ superlattice. In both cases, we attribute the decomposition to Li vacating specific sites, such that Li_7 clusters are preserved; we speculate that the boron impurity impedes this process and thereby 'pins' the denser of the two superlattices. This enhanced stability suggests the application of these phases in high-capacity primary batteries.

EXPERIMENTAL DETAILS

LiC_2 was synthesized from Li metal and highly oriented pyrolitic graphite(HOPG) as well as 'B-HOPG' (containing 0.5 at.% substitutional boron). Pressure was generated in an anvil apparatus by compressing the ampoule at 50 kbar and 300°C under quasi-hydrostatic conditions for a few hours. The sample was grated into a powder and loaded into 0.5 mm quartz capillaries. X-ray powder diffraction patterns were recorded at beam-line X7A at the National Synchrotron Light Source, Brookhaven National Laboratory. We used a Ge(111) double crystal monochromator in the incident beam, a flat Ge(220) analyzer after the sample and a NaI:Tl scintillation detector. Data was collected at 0.01° steps with $\lambda = 0.70019$ Å in the temperature range 25°C and 250 °C. The raw data is shown in Figure 1 and 2 for both samples.

X-RAY DIFFRACTION

Analysis of these x-ray patterns requires a multi-phase Reitveld refinement completely identifying all the unit cells and the relative amounts of the various phases present. The primary phase of interest however was found to be incommensurate. Present Reitveld refinement techniques do not deal with incommensurate structures and enabling this kind of an analysis would have proved to be very difficult in the present circumstances. On the other hand, data analysis by means of comparison to calculated models has been carried out, yielding a great deal of new and interesting information.

The "LiC_2" (Li-HOPG) decomposition product after pressure release yields the Li_9C_{24} phase [1] which has a hexagonal unit cell, $a = 8.63$ Å, $c = 11.1$ ($3 \times I_c$)Å, where $I_c = 3.7$ Å. This includes the allowed reflections of various other phases ($Li_{11}C_{24}$, Li_9C_{24}, Li_7C_{24} and LiC_6, Figure 2), the *intensities* depending on the stoichiometry of each phase. The overlapping of allowed reflections for the above phases implies that the (*hkl*) intensities are not a good index of the global composition; the most reliable factor instead being the 00*l* integrated intensities, as they reflect the total intercalated metal concentration and are independent of in-plane structure, i.e. the phase mixture.

Hence, the data analysis has been performed by fitting the x-ray profiles with Gaussian functions from the viewpoint of evaluating 00*l* relative integrated intensities to reveal the total intercalated metal content, and identifying *hkl* reflections that do not occur for LiC_6. The room temperature x-ray patterns are fit to model calculations for various Li stoichiometries and in-plane arrangements, as shown in Figure 2.

The observed peaks have been tracked with temperature variation, so as to observe Li out-diffusion and evolution of the superlattices.

Boron-HOPG - $LiC_{2.18}$: In-Plane Structure

The room temperature X-ray powder pattern of the B-HOPG - "LiC_2" is shown in Figure 1A and graphs of data taken at varying temperatures are shown in the lower panels. The experimental peak positions (D in Å) and intensities are derived from Gaussian fits. Comparison to model calculations show a "best-fit" with the $Li_{11}C_{24}$ structure, in Figure 2(c). The salient features of the data for the 'B-HOPG' case and the comparison to model are the following:

(a) The experimental 00*l* intensity ratios are in excellent agreement with the model i.e. a hexagonal cell with **c** = 3.71 Å. A ratio of 21% for 002/001 yields a stoichiometry of $LiC_{2.18}$ for the B-HOPG sample. In contrast, the ratio for LiC_6 is ~ 10%. (b) There is a high angle shoulder on the 001 peak at **d** = 3.66 Å. This peak indexes as (020) and is lower in **d** than the corresponding (001), which is at **d** = 3.69 Å. For this *hk*0 (020) to appear at this position, an **a** parameter less than **a** = 8.57 Å is required for an interlayer spacing of 3.71 Å, as deduced from the fit profiles and the calculations (At **a** $\geq$ 8.57 Å, the (020) is at a higher **d** value than (001)). **a** = 8.54 Å provides the best fit, taking into account the relative intensities and the peak positions. (c) We note that **c** = 3.71 Å, instead of 11.1 (3 x 3.7(I_c)) Å. There are no higher order *hkl*'s observed here, in contrast to the HOPG (25°C) case in Figure 3A, which contains in-plane peaks at lower 2θ values than the (001) peak at ~ 11°. Additionally, there are some peaks that appear in the pattern that do not index on a 3.71 Å cell, however they appear at the same **d** value in the HOPG case also. In light of the different **a** parameter, these peaks are assigned to the presence of a small amount of the HOPG phase ($Li_{21}C_{72}$). All other peaks can be indexed on the hexagonal cell with **a** = 8.54 Å; **c** = 3.71 Å. This implies a greater symmetry in the higher density (B-HOPG) compound.

On the whole, the peak *positions* agree very well between the experiment and the model and there is semi-quantitative *intensity* agreement. As mentioned earlier, the presence of overlapping peaks makes exact intensity agreement with *one* phase difficult, due to the presence of various phases differing by average composition or stacking along the *c* axis. It is not clear that $Li_{11}C_{24}$ is the *only* phase present, however it has been suggested as a primary phase.

An important observation is the position of the graphite in-plane reflection (020) at **d** = 2.158 Å, indicating a C-C distance of 1.438 Å. This brings up two points, the first being that **a** = 8.54 Å is not equal to 6 × 1.438 (C-C), indicating a minor degree of incommensurability. The second point is that the de-localization of the intercalate valence electrons enhances the π electron density in graphite. This screening effect is responsible for weakening the in-plane C-C bonds and is reflected in a measurable dilation of the bond length [7,8]. We note that the C-C distance for $LiC_{2.18}$ (B-HOPG) as well as for the $LiC_{3.4-3.8}$ (HOPG) is 1.438 Å and is similar to that in LiC_6 (1.436 Å). Pristine graphite has a C-C bond length of 1.42 Å. This directly indicates a similar total charge transfer from the Li layer to the graphite in all three compounds, however, *less* charge transfer *per* Li atom in $LiC_{2.18}/LiC_{3.4}$, in light of their larger Li density. This supports the idea that the excess electronic charge present in "LiC_2" is localized near the Li layer and forms Li clusters *via* short, covalent Li-Li 'bonds'. This idea has been suggested before and the existence of Li clusters has been confirmed by IR spectroscopy [5] and ^{7}Li NMR-spectroscopy [6].

Thermal Decomposition of B-HOPG $LiC_{2.18}$

Upon heating, the change in the x-ray pattern of $LiC_{2.18}$ is very interesting. As the temperature is increased slightly to 50°C, shown in Figure 1B, a slight reduction of overall intensities is observed. However, the relative intensities remain unaltered, the 002/001 ratio for the B-HOPG case still being ~ 21% and no additional superlattice peaks appear. This indicates little or no reduction of the intercalated metal in the sample.

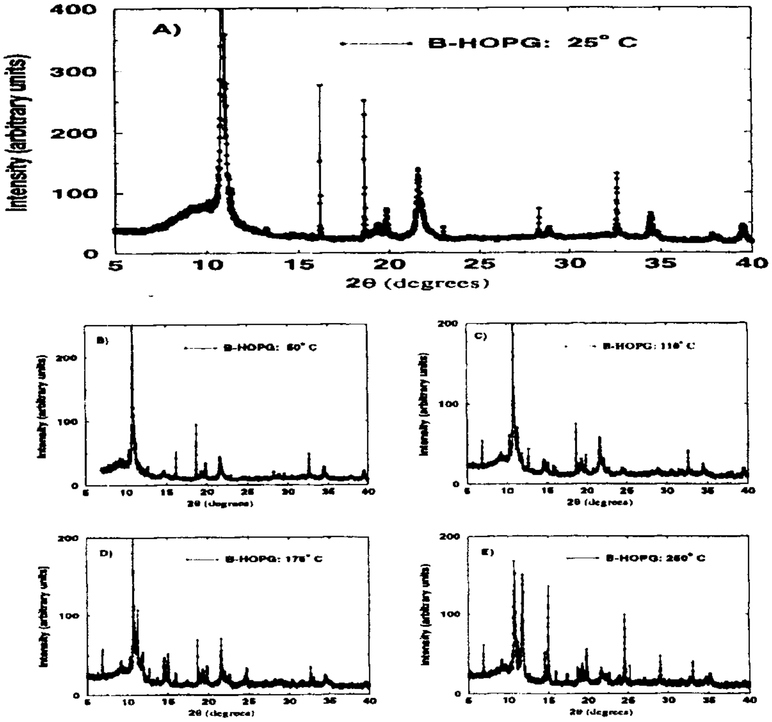

FIG. 1. Synchrotron X-ray powder diffraction data (λ = 0.70019 Å) for the B-HOPG ($LiC_{2.18}$ at 25C) between the range 25C and 250C.

Upon temperature variation, the x-ray pattern and the 00*l* intensities are very stable until ~ 100°C, beyond which a few variations appear. The high *Q* *hk*0 shoulder on the 00*l* peak disappears (or probably overlaps with the 00*l*). This indicates a larger unit cell with the a parameter value approaching 8.63 Å (3 x a_{gr} or 6 x C-C), implying "out-diffusion" of Li atoms and expansion of the unit cell as the sample decomposes. The intensities of various reflections change, and new superlattice peaks appear corresponding to the staggered layers along the c-axis; the intensities vary in the direction expected, toward the HOPG unit cell.

Li diffusion takes place transforming the compound from $Li_{11}C_{24}$ to $Li_{21}C_{72}$ (or 3 x Li_7C_{24}). This changes the unit cell to one with a larger in-plane parameter a = 8.54 Å → 8.63, as well as disturbs the registry between successive layers as c goes from I_c to 3 x I_c. Qualitatively, the B-HOPG pattern in Figure 1, Graph (C, 110°C) resembles the HOPG pattern shown in Figure 3, Graph (A, 25°C).

It is impossible to list all the intensities for each temperature; however, it is important to note that the B-HOPG sample is relatively stable up to ~ 110°C, beyond which essential LiC_x decomposition is noted. At no point is pure LiC_6 obtained. In addition, the decomposition seems to proceed as $Li_{11}C_{24}$ → Li_7C_{24}, continually preserving the Li_7C_{24} superlattice consisting of Li_7 clusters.

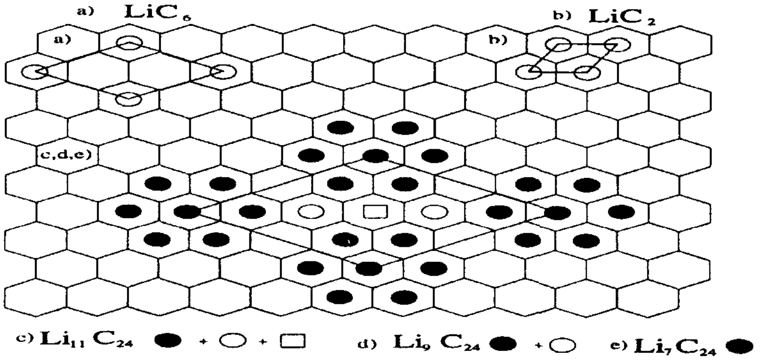

FIG. 2. Li-graphite inplane superlattices: a) LiC_6, b) LiC_2, c) $Li_{11}C_{24}$ ($LiC_{2.18}$); (filled + empty circles + square) d) Li_9C_{24} ($LiC_{2.7}$); filled + empty circles and e) Li_7C_{24} ($LiC_{3.4}$); only filled circles). Thermal decomposition: LiC_2 → $Li_{11}C_{24}$ → Li_9C_{24} → Li_7C_{24}

HOPG - $LiC_{3.4}$

The HOPG sample was also x-rayed for comparison purposes. The X-ray powder pattern at room temperature is shown in Figure 3A; data at varying temperatures are shown in the lower panels. Fitted peak positions (D in Å) and intensities are compared and "fit best" to model calculations based on the $Li_{21}C_{72}$ structure (Figure 2(e)), completely consistent with earlier results [1]. The pattern has many higher order ***hkl*** peaks that correspond to a larger superlattice and are not observed in the B-HOPG case. In addition, the 002/001 intensity ratio is close to 13%, corresponding to a stoichiometry of $LiC_{3.4-3.8}$, with a hexagonal unit cell of $a = 8.63$ Å (6 × C-C) and $c = 11.1$ Å ($3 \times I_c$). Here too the agreement is the same as in the B-HOPG case, i.e. excellent peak position, however, semi-quantitative peak intensity agreement.

The in-plane C-C distance is the same as that in B-HOPG, indicating similar charge transfer in both cases. The temperature variation of the x-ray pattern is not as significant in this case. There are two important observations. First, the "HOPG-$LiC_{3.4-3.8}$" sample does not seem as stable as the B-HOPG as a multitude of peaks appear on heating. Second, at no point, even at 250°C, is there any sign of "pure" LiC_6.

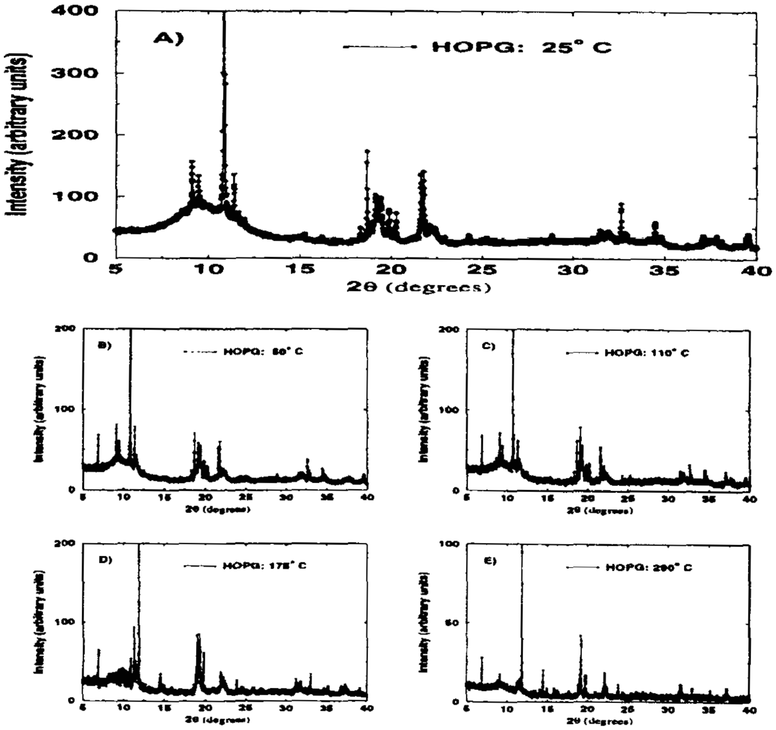

FIG. 3. Synchrotron X-ray powder diffraction data ($\lambda = 0.70019$ Å) for the HOPG ($LiC_{3.4}$ at 25C) between the range 25C and 250C.

SUMMARY

In summary, there are important differences in the HOPG and B-HOPG samples. (1) The B-HOPG sample retains a very high Li density ($LiC_{2.18}$) with a small hexagonal cell. It is stable at ambient conditions and maintains its stability up to 110°C. (2) Beyond 110°C, thermally assisted decomposition occurs of the B-HOPG sample, proceeding in the direction of lower Li density and a larger hexagonal cell. The decomposition product is similar in stoichiometry and structure to the ambient pressure phase obtained with HOPG - $LiC_{3.4-3.8}$.

(3) The HOPG sample at ambient conditions has a lower Li density relative to B-HOPG-$LiC_{3.4-3.8}$, in agreement with [1]. (4) Various superlattice peaks appear with increasing temperature, indicating that the HOPG based sample decomposes faster upon heating. On the other hand, "pure" LiC_6 is never observed as a decomposition product, even at 250°C.

In both cases, we attribute the decomposition to Li diffusion such that the Li_7 clusters (filled circles 7 Li atoms in Figure 2) are preserved. These probably serve as the stabilizing factor of the high Li density. This is supported by *ab initio* quantum calculations by Fateev *et al.* [10], showing the stability of small planar Li_7 clusters in this geometry. In the case of B-HOPG, it is suggested that the boron impurity arrests the decomposition of "LiC_2" to $LiC_{3.4}$ by pinning the metastable superlattice at $LiC_{2.2}$ with $\sim$ 1 boron atom per unit cell.

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