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2006 J. Phys.: Condens. Matter 18 5129

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# Reconstructive phase transitions between carbon polymorphs: limit states and periodic order-parameters

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Received 21 February 2006, in final form 24 April 2006

Published 19 May 2006

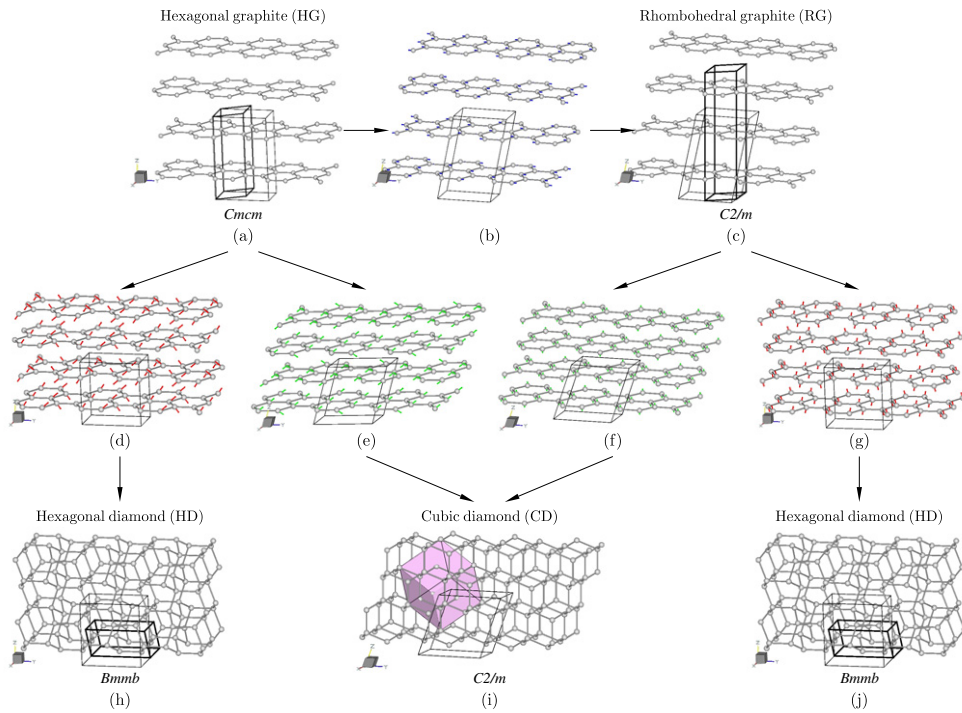
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## Abstract

The structural relations between carbon polymorphs are described as reconstructive phase transitions with displacive mechanisms occurring via a common substructure. The polymorphs are shown to correspond to limit states resulting from critical fractional displacements and critical strains. The transition order-parameters are defined as periodic functions of the displacements.

(Some figures in this article are in colour only in the electronic version)

Because of the technological importance of hexagonal graphite and cubic diamond, the phase diagram of carbon has been investigated intensively for many decades. Despite this effort the transformation mechanism from graphite to diamond is not yet fully understood. In particular the role played in this mechanism by rhombohedral graphite [1] or hexagonal diamond [2] is still questioned. On theoretical grounds the different models proposed for the graphite–diamond transition [3–9] involve a hybridization change for the bonding electrons, and structural mechanisms describing the conversion from one structure to the other in terms of reordering in the hexagonal layer stacking, supplemented by macroscopic strains. However, to our knowledge there exists no description of the structural mechanisms leading to the carbon allotropes as *symmetry breaking processes*. In this study we show that the structural changes between carbon polymorphs can be described in a unified way as reconstructive transitions of the displacive type, the transitions occurring via a common substructure of monoclinic or orthorhombic symmetry. In this description the polymorphs appear as *limit states* resulting from definite critical displacements and critical strains. The critical displacements are shown



**Figure 1.** Structural mechanisms for the reconstructive phase transitions between carbon polymorphs via a common substructure: (1) HG  $\rightarrow$  HD ((a)  $\rightarrow$  (d)  $\rightarrow$  (h)), (2) HG  $\rightarrow$  CD ((a)  $\rightarrow$  (e)  $\rightarrow$  (i)), (3) HG  $\rightarrow$  RG ((a)  $\rightarrow$  (b)  $\rightarrow$  (c)), (4) RG  $\rightarrow$  CD ((c)  $\rightarrow$  (f)  $\rightarrow$  (i)) and (5) RG  $\rightarrow$  HD ((c)  $\rightarrow$  (g)  $\rightarrow$  (j)). The conventional hexagonal (HG, RG and HD) and cubic (CD) unit-cells are represented by thick lines in (a), (c), (h), (j) and (i). The unit-cells of their common substructures are shown in all figures by thin lines. The small arrows in (b), (d), (e), (f) and (g) represent the real magnitudes of the atomic displacements.

to coincide with minima of the effective free-energies, formed as polynomial expansions of the order-parameters defined as periodic functions of the displacements.

Figure 1 represents the assumed displacive mechanisms transforming hexagonal graphite (HG), rhombohedral graphite (RG), hexagonal diamond (HD) and cubic diamond (CD) into each other. Figures 1(a), (c), (h) and (i) show that the carbon structures possess a common substructure displaying an orthorhombic  $Cmcm$  (HG),  $Bmmb$  (HD) or monoclinic  $C2/m$  (RG, CD) symmetry, whose basic vectors ( $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$ ) are related with the basic vectors of the conventional hexagonal (HG, RG, HD) or cubic (CD) unit-cells of the different allotropes by:

$$\begin{aligned} \mathbf{a} &= \mathbf{a}_{\text{HG}} = \mathbf{a}_{\text{RG}} = -\mathbf{a}_{\text{HD}} = 1/2(\mathbf{a} + \mathbf{b})_{\text{CD}} \\ \mathbf{b} &= (\mathbf{a} + 2\mathbf{b})_{\text{HG}} = (\mathbf{a} + 2\mathbf{b})_{\text{RG}} = \mathbf{c}_{\text{HD}} = -1/2(\mathbf{a} + \mathbf{b} - 2\mathbf{c})_{\text{CD}} \\ \mathbf{c} &= \mathbf{c}_{\text{HG}} = 1/3(\mathbf{a} + 2\mathbf{b} + 2\mathbf{c})_{\text{RG}} = (\mathbf{a} + 2\mathbf{b})_{\text{HD}} = 1/2(\mathbf{a} + \mathbf{b} + 2\mathbf{c})_{\text{CD}} \end{aligned} \quad (1)$$

in accordance with the observed orientational relations reported in [10] that  $[001]_{\text{HG}} \parallel [120]_{\text{HD}}$ ,  $[100]_{\text{HG}} \parallel [100]_{\text{HD}}$  and  $[120]_{\text{HG}} \parallel [001]_{\text{HD}}$ . The lattice parameters of the transformed unit-cells are given in table 1. The atomic displacement field transforming HG into HD is shown in the figures 1(a)  $\rightarrow$  (d)  $\rightarrow$  (h). It consists of antiparallel *fractional* displacements:  $\pm \frac{1}{16}\mathbf{b}$  and  $\pm \frac{1}{12}\mathbf{c}$ , combined with  $\pm \frac{5}{48}\mathbf{b}$  and  $\pm \frac{1}{12}\mathbf{c}$ , the carbon atoms initially in  $2b$  and  $2c$  positions of  $P6_3/mmc$  being shifted to positions  $4f$ . The HG  $\rightarrow$  HD transition involves a drastic compression of about 35% along  $\mathbf{c}$  and small decompression (2%) and compression (6%) along  $\mathbf{a}$  and  $\mathbf{b}$ , respectively.

**Table 1.** Lattice parameters of the conventional unit-cells and the common substructure calculated after (1) for the carbon polymorphs.

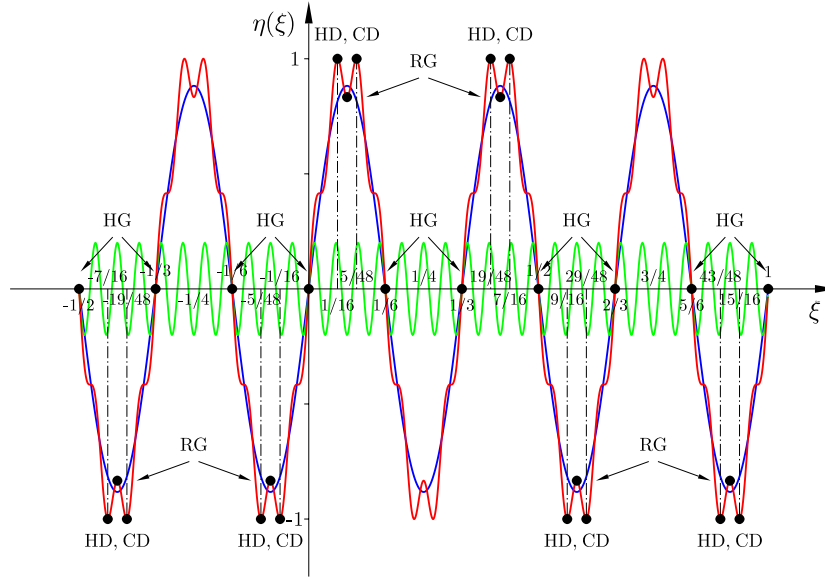
Polytype	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\alpha$	$\gamma$	Space group
HG	2.464	2.464	6.708		120	$P6_3/mmc$
	2.464	4.268	6.708			$Cmcm$
RG	2.456	2.456	10.041		120	$R\bar{3}m$
	2.456	4.254	6.843	78.040		$C2/m$
HD	2.522	2.522	4.119		120	$P6_3/mmc$
	2.522	4.119	4.369			$Bmmb$
CD	3.567	3.567	3.567			$Fd\bar{3}m$
	2.522	4.368	4.368	70.529		$C2/m$

A similar mechanism, represented in figures 1(a)  $\rightarrow$  (e)  $\rightarrow$  (i), holds for the HG  $\rightarrow$  CD transition. Starting from the transformed unit-cell of HG, the CD structure results from a reduction of the angle  $\alpha$  from  $90^\circ$  in HG to  $70.529^\circ$  in CD, and a set of antiparallel fractional displacements:  $\pm\frac{1}{16}\mathbf{b}$  and  $\pm\frac{1}{16}\mathbf{c}$ , combined with  $\pm\frac{5}{48}\mathbf{b}$  and  $\pm\frac{1}{16}\mathbf{c}$ . The CD unit-cell, in which the carbon atoms occupy the positions 8a of space group  $Fd\bar{3}m$ , is deduced from the monoclinic unit-cell by shifting the origin by  $p = (0, \frac{1}{16}, \frac{5}{16})$ , a large compression of 35% along  $\mathbf{c}$  and small decompressions (2%) along  $\mathbf{a}$  and  $\mathbf{b}$ .

Natural graphite, as well as synthetic samples, may contain up to 30% of rhombohedral graphite (RG) in combination with HG. Although RG is considered as an unstable allotrope of graphite, or as an extended stacking fault, it has been often invoked in the transformation mechanisms between carbon polymorphs [6, 8, 11]. The HG  $\rightarrow$  RG transition mechanism, shown in figures 1(a)  $\rightarrow$  (b)  $\rightarrow$  (c), consists of a reduction of  $\alpha$  from  $90^\circ$  in HG to  $78.040^\circ$  in RG, and of fractional displacements of the carbon atoms by  $\pm\frac{1}{12}\mathbf{b}$  (figure 1(b)). The hexagonal RG unit-cell (figure 1(c)) is deduced from the monoclinic unit-cell by shifting the origin by  $p = (0, 1/2, 0)$ .

The HD and CD structures can be obtained from RG as shown in figures 1(c)  $\rightarrow$  (f)  $\rightarrow$  (i) and figures 1(c)  $\rightarrow$  (d)  $\rightarrow$  (j). The RG  $\rightarrow$  HD transition requires an increase of  $\alpha$  from  $78.040^\circ$  to  $90^\circ$ , and antiparallel displacements, shown in figure 1(g), by  $\pm\frac{1}{48}\mathbf{b}$  and  $\pm\frac{1}{12}\mathbf{c}$ . It yields the HD unit-cell (figure 1(j)), which involves compressions along  $\mathbf{c}$  (36%) and  $\mathbf{b}$  (3%) and decompression along  $\mathbf{a}$  (3%). The RG  $\rightarrow$  CD transition follows a similar scheme with a reduction of  $\alpha$  from  $78.040^\circ$  to  $70.529^\circ$  and antiparallel displacements (figure 1(f)) by the  $\pm\frac{1}{24}\mathbf{c}$  fractions, with a compression along  $\mathbf{c}$  (36%) and decompressions (3%) along  $\mathbf{a}$  and  $\mathbf{b}$ .

In terms of a Landau symmetry analysis the order-parameters associated with the transitions from HG to the other carbon polymorphs are of two types. (1) Macroscopic strains which consist of (i) the shear strain  $e_{yz}$ , which expresses the changes in the angle  $\alpha$  and reduces the hexagonal HG symmetry to monoclinic, (ii) the tensile strain  $e_{xx} - e_{yy}$  corresponding to an orthorhombic deformation of the hexagonal cell, (iii) the non-symmetry-breaking component  $e_{zz}$  which accounts for the compression along  $\mathbf{c}$ . (2) A cooperative set of fractional symmetry-breaking displacements along  $\mathbf{b}$  and  $\mathbf{c}$ . Both types of order-parameter are activated for obtaining the polymorphic structures which appear as *limit states* arising for definite atomic displacements and critical strains. This is consistent with the theoretical approach proposed for *reconstructive* phase transitions of the displacive type [12, 13] in which the critical displacements coincide with extrema of the effective order-parameters defined as periodic functions of the displacements. The periodic character of the reconstructive transition mechanisms is shown in figure 2, in which the order-parameter  $\eta$  is plotted as a function of the atomic displacements  $\xi$  along the [120] direction in HG. The periodic function  $\eta(\xi)$  representing the effective order-parameter associated with the HG  $\rightarrow$  (HD, CD, RG)

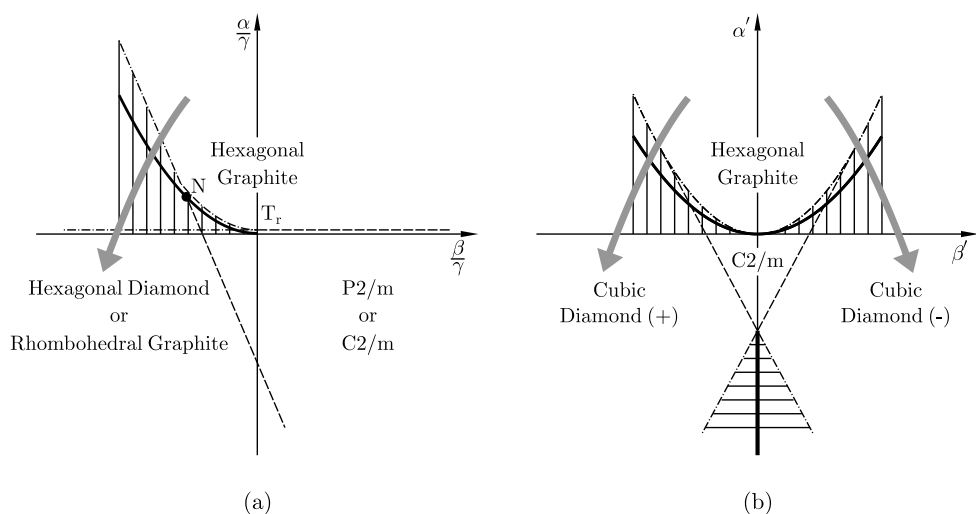


**Figure 2.** Periodic dependence (red (dark grey) curve) of the effective transition order-parameter  $\eta(\xi)$ , defined by (2), associated with the transitions from hexagonal graphite (HG) to rhombohedral graphite (RG), cubic (CD) and hexagonal (HD) diamonds, in function of the displacements  $\xi$  along  $[120]_{\text{HG}}$ . The curve in blue (black) represents the periodicity of the displacements giving rise to the RG structure (first term in (2)). The green (light grey) curve is a higher harmonic (second term in (2)) whose periodicity reflects the onset of the HD and CD structures from HG and RG, respectively.

transitions is the truncated Fourier series:

$$\eta(\xi) = 0.958 \sin(6\pi\xi) + 0.125 \sin(42\pi\xi). \quad (2)$$

The first term in (2) expresses the ‘primary’ symmetry-breaking displacements giving rise to the RG structure from HG, and the second term is a higher harmonic related to secondary symmetry-breaking displacements leading to the HD and CD structures from HG and RG, respectively. Taking into account the transformation properties of the displacements  $\xi$  leading to the HD, CD and RG structures, by the symmetry operations of the HG space group ( $P6_3/mmc$ ), yields two distinct *effective* free-energies:  $F_1(\eta(\xi)) = \frac{\alpha}{2}\eta^2 + \frac{\beta}{4}\eta^4 + \frac{\gamma}{6}\eta^6$ , for the HG  $\rightarrow$  (RG, HD) transitions, and  $F_2(\eta(\xi)) = \frac{\alpha'}{2}\eta^2 + \frac{\beta'}{3}\eta^3 + \frac{\gamma'}{4}\eta^4$  for the HG  $\rightarrow$  CD transition. Minimization of  $F_1$  and  $F_2$  with respect to  $\xi$  provides the critical displacements  $\xi^c$  at which the RG, HD and CD phases arise. Their fractional character can be viewed by decomposing  $\xi^c$  into the critical displacements  $\xi_1^c$  (along  $[120]_{\text{HG}}$ ) and  $\xi_2^c$  (along  $[001]_{\text{HG}}$ ). Minimizing  $F_1$  yields the equation of state:  $\eta \frac{\partial \eta}{\partial \xi} (\alpha + \beta \eta^2 + \gamma \eta^4) = 0$ , which gives four possible stable phases. (i) The HG phase for  $\eta = 0$ , for the successive critical displacements (expressed in **b** units for  $\xi_1^c$  and **c** units for  $\xi_2^c$ ):  $\xi_1^c = \pm(0, 1/6, 1/3, 1/2, 2/3, 5/6, \dots)$ ,  $\xi_2^c = 0$ ; (ii) the HD phase for  $\frac{\partial \eta}{\partial \xi} = 0$  and  $\xi_1^c = \pm(1/16, 5/48, 19/48, 7/16, 9/16, 29/48, 43/48, 15/16, \dots)$ ,  $\xi_2^c = \pm 1/12$ ; (iii) the RG phase for  $\frac{\partial \eta}{\partial \xi} = 0$  and  $\xi_1^c = \pm(1/12, 5/12, 7/12, 11/12, \dots)$ ,  $\xi_2^c = 0$ ; (iv) the monoclinic  $P2/m$  (HG  $\rightarrow$  HD) or  $C2/m$  (HG  $\rightarrow$  RG) phases for  $\eta = \pm[\frac{1}{2\gamma}(-\beta + \sqrt{\beta^2 - 4\alpha\gamma})]^{1/2}$  and non-critical displacements  $\xi_1$  and  $\xi_2$ . Minimization of  $F_2$  with respect to  $\xi$  leads to: (i) the HG phase; (ii) the CD phase for  $\frac{\partial \eta}{\partial \xi} = 0$  and the same critical values of  $\xi_1^c$  stabilizing HD but



**Figure 3.** Theoretical phase diagrams corresponding to the minimization of the (a)  $F_1$  and (b)  $F_2$  Landau free-energies with respect to the displacements  $\xi$ . Solid, dashed and dashed-dotted lines represent, respectively, first-order transition, second-order transition and limit of stability lines. The hatched areas are regions of phase coexistence.  $N$  is a three-phase point.  $T_r$  is a tricritical point. The arrows suggest the thermodynamic paths followed in carbon.

with  $\xi_2^c = \pm 1/16$ ; (iii) the monoclinic  $C2/m$  phase for  $\eta = \frac{1}{2\gamma'}(-\beta' \pm \sqrt{-\beta' - 4\alpha'\gamma'})$  and non-critical displacements.

Theoretical phase diagrams associated with  $F_1$  and  $F_2$  are shown in figures 3(a) and (b). In figure 3(a) the monoclinic phase can be reached from HG and (HD or RG) across second-order transitions whereas the  $HG \rightarrow (HD \text{ or } RG)$  reconstructive transitions are always first-order. The phase diagram of figure 3(b) reveals the existence of two anti-isostructural CD structures (denoted + and -), associated with opposed signs of  $\eta$ .

In summary, starting from the HG (or RG) structure the carbon allotropes have been described as resulting from displacive mechanisms combined with macroscopic strains. In these mechanisms the polymorphs appear as limit states stabilizing for definite critical displacements and critical strains. This interpretation was justified by expressing the effective transition order-parameters as periodic functions of the displacements, the critical displacements corresponding to minima of the free-energies and to extrema of the order-parameters.

The description of the formation of the carbon polymorphs in terms of displacive processes is in contrast with the current interpretations [6, 8, 13] which assume *ordering* mechanisms. Ordering processes are suggested by the possibility of organizing the carbon structures as different stacking of hexagonal layers and the transitions between them as a reordering in the layer stacking. Combined ordering and compression mechanisms allow one to describe the  $HG \rightarrow CD$  or the  $HG \rightarrow RG$  transitions [6], but fail to explain the formation of HD because of its orientational relationship with respect to HG. The different orientations of the hexagonal layers reported in cubic and hexagonal diamonds, with respect to HG, is essential in favour of a displacive mechanism. The fact that similar critical displacements, involving the same intermediate substructure, yield the variety of carbon polymorphs is another argument in favour of our proposed displacive approach.

This approach suggests an explanation of the simplicity of the equilibrium phase diagram of carbon, which contains only the HG and CD phases, as compared to the rich polymorphism

found in the phase diagrams of other IVa elements [14] such as Si, Ge or Sn. Starting from the ambient pressure HG phase, the thermodynamic path assumed for the HG  $\rightarrow$  CD transition differs from the paths leading to HD or RG, a further transition from CD to another structure being unlikely due to the limit character of the CD structure which makes it less sensitive to the influence of temperature or pressure. The left-or-right-hand side of the theoretical phase diagram of figure 3(b), which exhibits only the HG and CD phases, reflects the topology of the experimental phase diagram of carbon. The anti-isostructural CD variant may coincide with the cubic n-diamond structure, obtained by rapid cooling from graphite sheet shock-compressed to 65 GPa [15], which is composed of hexagonal-ring planes puckered in the opposite direction with respect to CD [16]. This is consistent with the opposite signs of the corresponding order-parameters.

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