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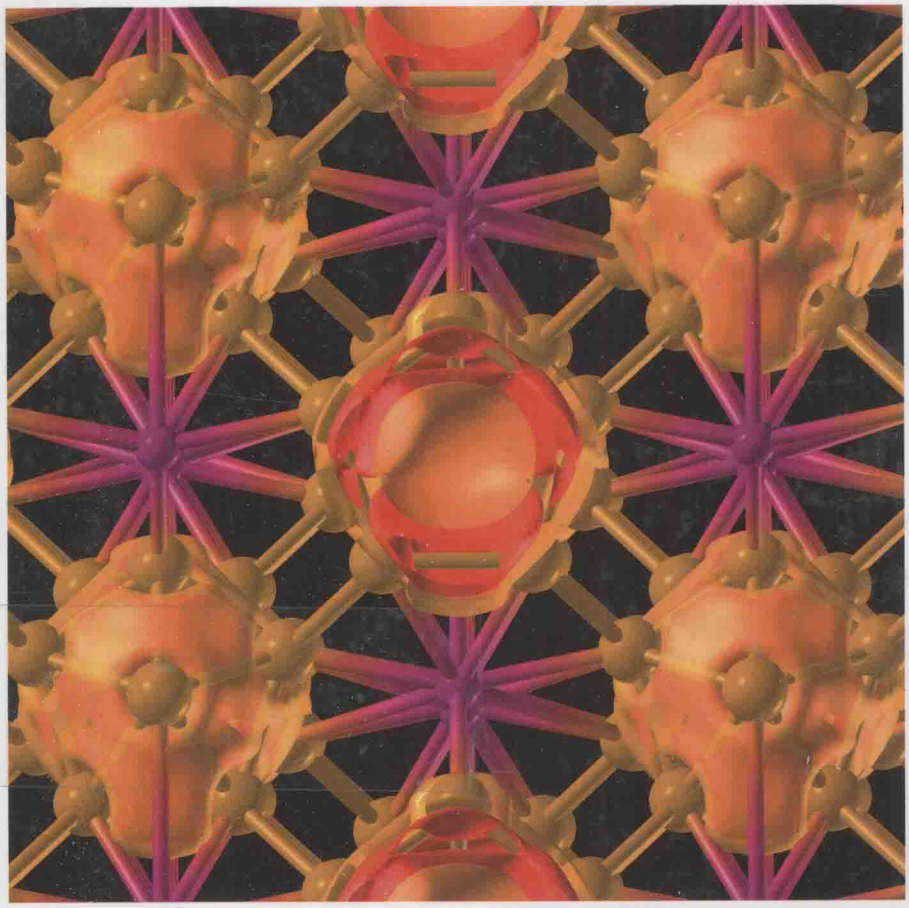
Modern Methods of Crystal Structure Prediction



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Modern Methods of Crystal Structure Prediction

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Introduction: Crystal Structure Prediction, a Formidable Problem

Artem R. Oganov

The famous 1988 editorial in *Nature* by John Maddox [1] stated:

> *"One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition".*

The central topic of the present volume is to review the state of the art in resolving this "scandal". Crystal structure is arguably the most important piece of information about a material, as it determines – directly or indirectly – pretty much all properties of a material. Knowing the structure, one can compute a large number of properties of a material, even before it is synthesized – hence the crucial importance of structure prediction for computational materials design. When the structure is unknown and cannot be predicted, very little can be said about the material.

Until recently, it was widely believed that crystal structures are fundamentally unpredictable [1–3] – as human behavior, or earthquakes, or long-term behavior of stock exchange. However, the situation began to change dramatically in 2003–2006, and this avalanche-like development of this important field can be called a scientific revolution that continues to this day. The aim of this book is to present some of the most important modern approaches to the formidable problem of crystal structure prediction.

What do we exactly mean by "crystal structure prediction problem"? For each chemical composition there are an infinite number of possible atomic arrangements that can, in principle, be obtained in the laboratory – these correspond to all possible local minima of the free energy. Among these, at each thermodynamic conditions (pressure, temperature, chemical potential) there are a finite number of special structures, extreme in some sense – the lowest energy (i.e. the most stable structures), the highest/lowest value of some other property (hardness, density, band gap, superconducting Tc, ...), or highest rate of nucleation (corresponding to kinetically preferred phases). Prediction of these structures is a well-defined and crucially important problem. In the simplest and most important case, by crystal structure prediction we mean finding, at given P-T conditions, the stable crystal structure knowing only the chemical formula.

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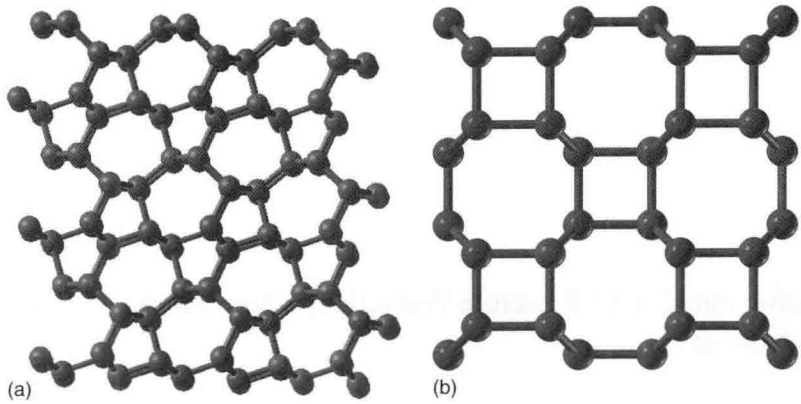

Figure 1 Structures of metastable superhard sp^3-bonded allotropes of carbon: (a) M-carbon [5] and (b) bct4-carbon [6].

Many types of approaches have been proposed to address this problem. Some are topological (as reviewed in the chapter by Blatov and Proserpio [4]) and aim at constructing the simplest topologies consistent with what we know about the chemistry of the system. This way, assuming sp^2-hybridization of carbon atoms one would arrive at 2H-graphite structure, and assuming sp^3-hybridization one would find the diamond and lonsdaleite structures – and a vast array of interesting metastable structures, including clathrates, M-carbon (Figure 1a), bct-carbon (Figure 1b) and other possible allotropes.

Topological approaches often appeal to symmetry, since in the vast majority of cases stable crystal structures do display some symmetry – the asymmetric point group 1 (or corresponding to it space group P1) is very rare (see Table 1). The ubiquity of symmetry may simplify the task of structure prediction, and not only in topological approaches.

Other approaches are based on empirical correlations and involve either *structural diagrams* [8–10] or *data mining approaches* [11, 12]. In either case, a large database of known stable crystal structures is required. While data mining approaches involve advanced machine learning concepts and are capable of predicting not only stable structures, but also the likelihood of compound formation in multinary systems (a formidable task too!), structural diagrams are much more empirical and limited in their scope. In these, one frequently uses ionic radii or the so-called "pseudopotential radii" [9], both of which (especially the latter) lack strict physical meaning and uniqueness. Instead of the "pseudopotential radii" one could use other quantities, such as the chemical scale or the Mendeleev number – the resulting empirical structure diagrams seem to have a good ability to separate structure types (e.g., Figure 2), and thus have predictive power.

The most unbiased, non-empirical and hence most generally applicable approaches are based on *computational optimization* – i.e. explicit calculations of the (free) energy and exploration of its landscape with the aim of finding the most stable arrangement of the atoms. These approaches are the main focus of

Table 1 Distribution of 280 000 chemical compounds over the 32 point groups. Note somewhat different frequencies for inorganic (I) and organic (O) compounds. (data collected by G. Johnson and published in [7]).

	I	O		I	O
1	0.67%	1.24%	422	0.40%	0.48%
$\bar{1}$	13.87	19.18	4mm	0.30	0.09
2	2.21	6.70	$\bar{4}$2m	0.82	0.34
M	1.30	1.46	4/mmm	4.53	0.69
2/m	34.63	44.81	6	0.41	0.22
222	3.56	10.13	$\bar{6}$	0.07	0.01
mm2	3.32	3.31	6/m	0.82	0.17
mmm	12.07	784	622	0.24	0.05
3	0.36	0.32	6mm	0.45	0.03
$\bar{3}$	1.21	0.58	$\bar{6}$m2	0.41	0.02
32	0.54	0.22	6/mmm	2.82	0.05
3m	0.74	0.22	23	0.44	0.09
$\bar{3}$m	3.18	0.25	m3	0.84	0.15
4	0.19	0.25	432	0.13	0.01
$\bar{4}$	0.25	0.18	$\bar{4}$3m	1.42	0.11
4/m	1.17	0.67	m3m	6.66	0.12

this book. Among the advantages are (i) the explicit calculation of the optimized quantity of interest (e.g., the energy), (ii) unbiased search techniques for exploring the energy landscape can – unlike the previously mentioned approaches, assuming knowledge of material's chemistry and likely crystal structures – arrive at completely unexpected results and truly novel structures. For instance, who would guess (based on whatever chemical knowledge) that boron under pressure would assume a NaCl-type structure composed of B_2 and B_{12} clusters with partially ionic bonding between the two? Who would guess that, when compressed to 2 million atmospheres, sodium assumes a structure unknown for any other element and becomes a transparent dielectric? Nevertheless, this is exactly what happens [13, 14], and these phenomena were first predicted using optimization techniques and only then confirmed experimentally.

When considering crystal structure prediction as an optimization problem – i.e. the problem of finding the global minimum of the energy landscape, certain properties of this landscape need to be explored. First, the number of distinct points on the landscape can be estimated as:

$$C = \binom{V/\delta^3}{N} \prod_i \binom{N}{n_i} \tag{1}$$

where N is the number of atoms in the unit cell of volume V, δ is a relevant discretization parameter (for instance, 1 Å) and n_i is the number of atoms of i-th

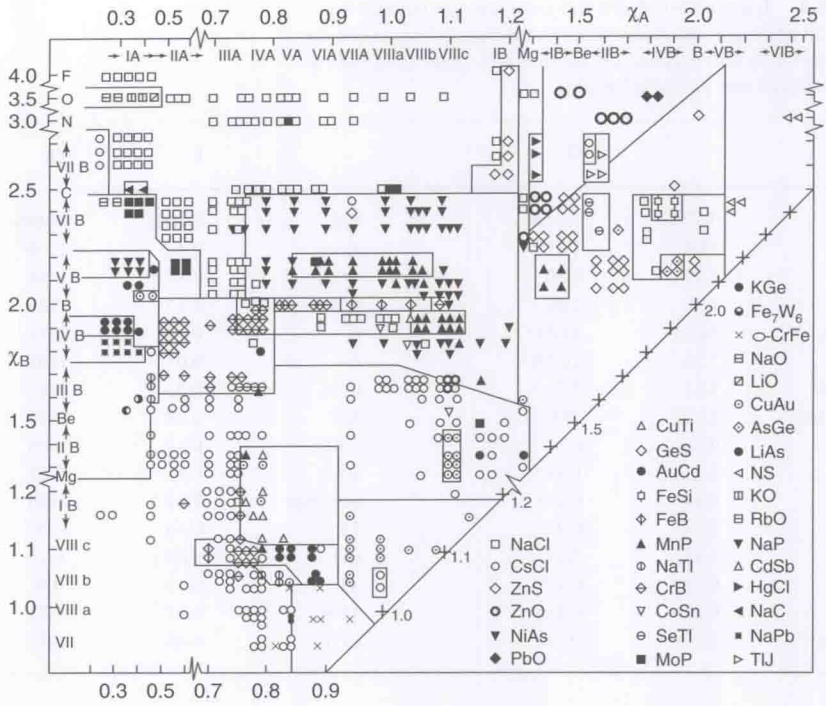

Figure 2 Pettifor's structure diagram for 574 AB compounds (from [10]).

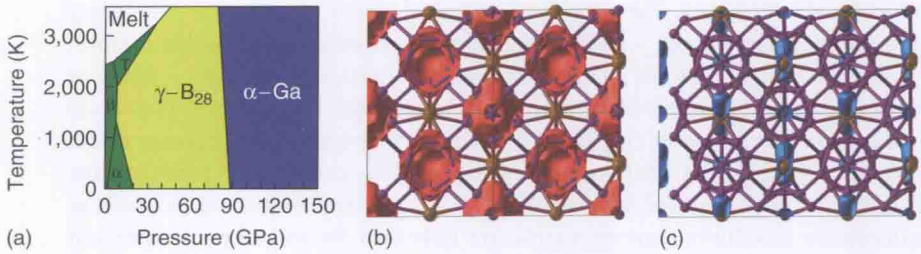

Figure 3 Boron: (a) its schematic phase diagram (from [13]) and distribution of electrons corresponding (b) bottom and (c) top of the valence band in γ-B_{28} [15].

type in the unit cell. C is astronomically large (roughly, $\sim 10^N$ if one uses $\delta = 1$ Å and typical atomic volume of 10 Å^3).

It is useful to consider the dimensionality of the energy landscape:

$$d = 3N + 3 \tag{2}$$

where $3N$-3 degrees of freedom are the atomic positions, and the remaining six dimensions are lattice parameters. For a system with 100 atoms in the unit cell, the landscape is 303-dimensional!

Equation (1) implies that the difficulty of crystal structure prediction increases exponentially with system size (or landscape dimensionality) and it thus poses an NP-hard problem (which is a shorthand of "non-deterministic polynomial-time hard", meaning that the scaling of the problem with the system size is faster than any polynomial). Such high-dimensional problems with astronomically large numbers of possible solutions imply that simple exhaustive search strategies are unfeasible.

Great simplification of the problem can be achieved if structures are relaxed, i.e. brought to the nearest local energy minima. During relaxation, certain correlations between atomic positions set in – interatomic distances adjust to reasonable values, and unfavorable interactions are avoided. The intrinsic dimensionality is thus equal to a reduced value:

$$d^* = 3N + 3 - \kappa \tag{3}$$

where κ is the (non-integer) number of correlated dimensions. Just doing relaxation, great simplifications of the global optimization problem can be achieved – for example, the dimensionality drops from 99 to 11.6 for $Mg_{16}O_{16}$ (a really simple system), while the decrease is less substantial for chemically complex systems – from 39 to 32.5 for $Mg_4N_4H_4$. To appreciate this simplification of the problem, we remind that the number of local minima depends exponentially on the intrinsic dimensionality:

$$C^* = \exp(\beta d^*) \tag{4}$$

This implies that any efficient search method must include structure relaxation (i.e. local optimization). Even simple random sampling, when combined with local optimization, can deliver correct solutions – although only for very small systems, roughly $N < 8$–10 ([17, 18], see chapter by Tipton and Hennig [19] in this volume). Much larger systems can be treated by more advanced methods, such as simulated annealing ([20, 21], see chapter by Schön and Jansen [22]), metadynamics ([23, 24], see chapter by Martoňák [25]), basin hopping ([26], see chapter by Wales in this volume [27]), minima hopping ([28], see chapter by Goedecker [29]), or evolutionary algorithms ([5, 30, 31], see chapter by Lyakhov et al. [32]). Many of the above methods rely on the fact that in usual chemical systems good (i.e. low energy) structures share some similarities, i.e. are located relatively close to each other on the landscape, forming the so-called energy funnels, low-energy regions of configuration space. This gives the landscape a benign overall shape – such as the one shown in Figure 5. Exploiting the fact (assumed for a long time by chemists, but now proven on real systems – see, e.g. [16]) that in real chemical systems there are only a few (or just one) energy funnels, allows further gains of efficiency of structure predictions. Nowadays, systems with a few hundred degrees of freedom can be treated by some of these methods – perfectly adequate for most inorganic and organic systems. Extending this limit to much larger systems may

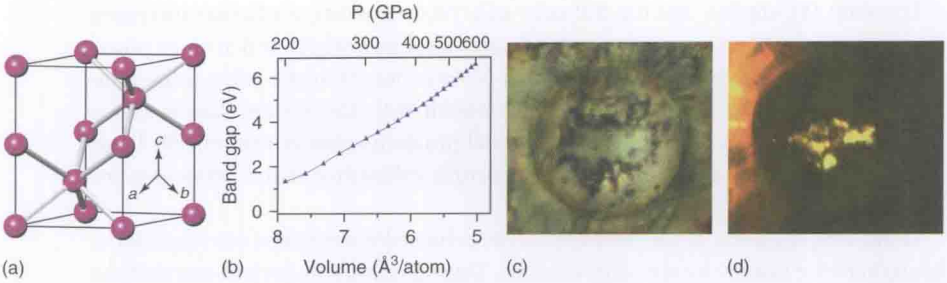

Figure 4 *hP*4 phase of sodium: (a) crystal structure, (b) band gap computed in the GW approximation, and optical photographs of a sodium sample at (c) 110 GPa (where sodium is a white reflecting metal) and (d) at 199 GPa (where it is a red transparent insulator). After [14].

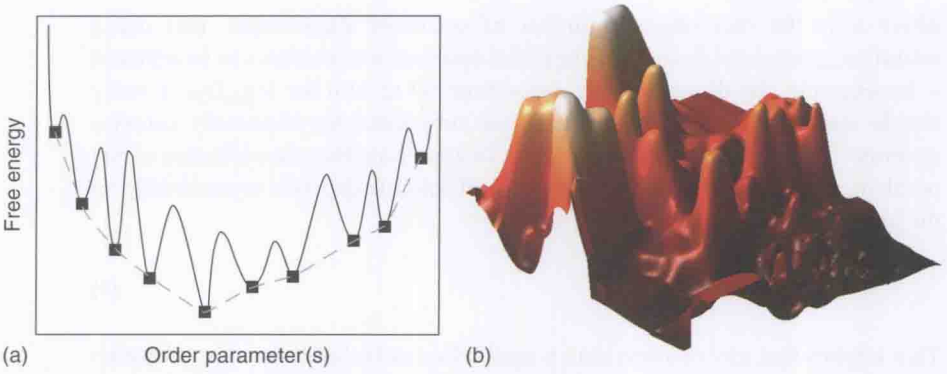

Figure 5 Energy landscape: (a) schematic illustration showing the full landscape (solid line) and reduced landscape (dashed line interpolating local minima points), (b) 2D-projection of the reduced landscape of Au_8Pd_4 (done using the method presented in [16]) showing all low-energy structures clustered in one region of configuration space.

enable us to treat biologically important systems and address such problems as protein folding. There are already some steps in this direction (see, e.g. [29]).

Next level of complexity is to ask if we can predict not just the stable structure, but also the whole set of stable chemical compositions (and the corresponding structures) in multicomponent system. This means that we are dealing with a complex landscape consisting of compositional and structural coordinates, and instead of a single ground state we should have a set of ground states located on the so-called convex hull (Figure 6). There are some encouraging steps in solving this problem [33–35].

We can also consider landscapes of properties other than the (free) energy. In this case, hybrid optimization needs to be performed – combining local optimization

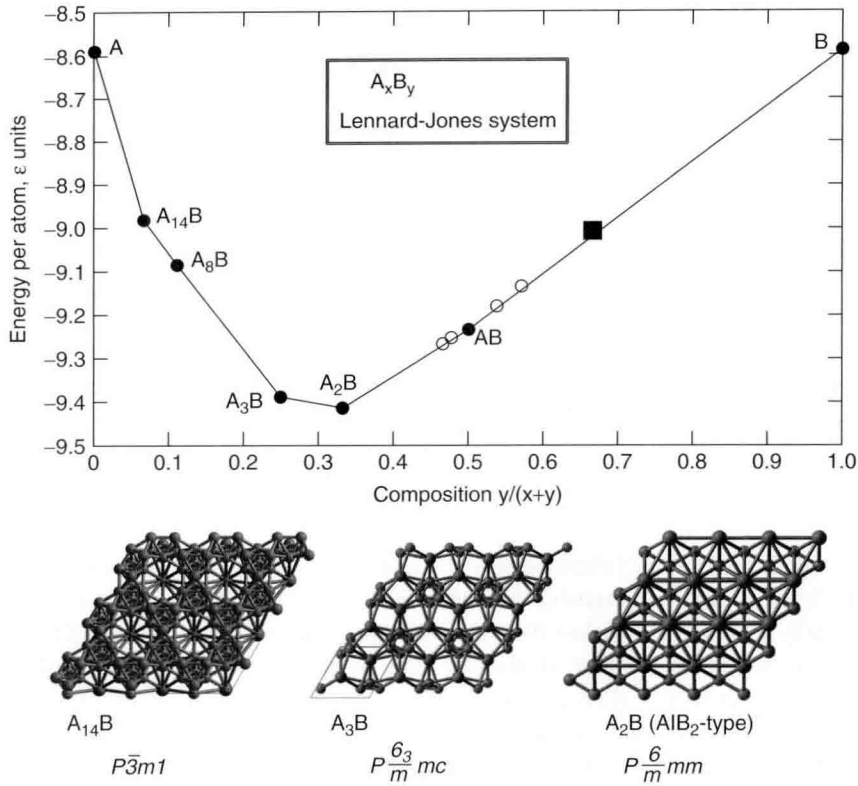

Figure 6 Examples of a simultaneous prediction of stable compositions and corresponding structures in a binary Lennard-Jones system with variable composition. Solid circles denote ground states, open circles – metastable solutions. See [35] for the potential model. From [35]. It is amazing that such a simple system gives such a wealth of complex ground states.

with respect to the energy (to find possible (quasi)equilibrium states) and global optimization with respect to the property of interest. This allows us to find structures (and compositions), corresponding to the desired values of the physical property of interest. Figure 7 gives an example of such optimization, utilizing the evolutionary algorithm [5, 30, 31] to search for the hardest possible structure of SiO_2.

This search employed the model of hardness [37] extended by Lyakhov and Oganov [36, 38], who also questioned whether diamond is the hardest carbon allotrope. The answer was that it indeed is (with the theoretical hardness of 89.4 GPa, within the error bars of to the experimental values [39]), but a number of other allotropes come close to it – for instance, lonsdaleite (89.3 GPa), bct4-carbon (theoretical hardness 84.2 GPa) and M-carbon (theoretical hardness of 83.4 GPa) shown in Figure 1. Both M-carbon [40] and bct4-carbon [6] (and private communication from a talented young researcher X.-F. Zhou, August 2009) structures were proposed as explanations for the experimentally observed new superhard allotrope

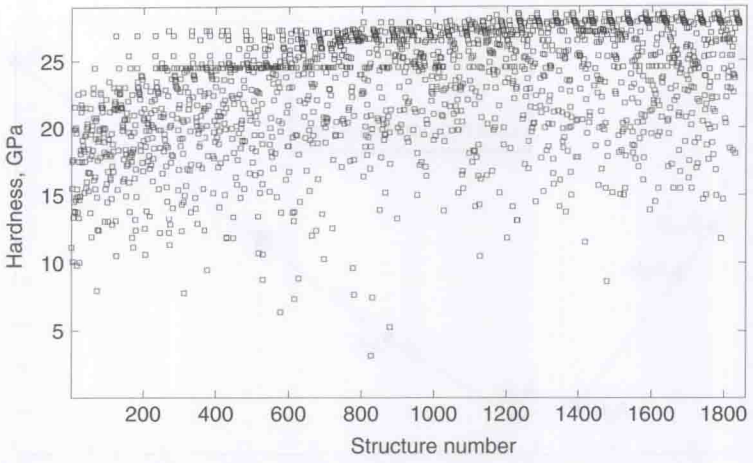

Figure 7 Evolutionary search for the hardest structure of SiO_2. From [36].

("superhard graphite") obtained by cold compression of graphite above 17 GPa [41]. Both structures are metastable and both match experimental observations almost equally well, but nevertheless there is a way of deciding which one is more likely to be the "superhard graphite" of Mao [41]. This brings us to the next major unsolved problem – *prediction of synthesizability of a metastable phase.* Indeed, the structure with optimal properties will frequently be metastable, and will be of interest only if it can be synthesized. This requires that the activation barrier for its formation from an available precursor (in this case, graphite) be lower than the barrier of formation of any other structure. The best approach for computing the absolute activation energies of solid-solid phase transitions is the transition path sampling

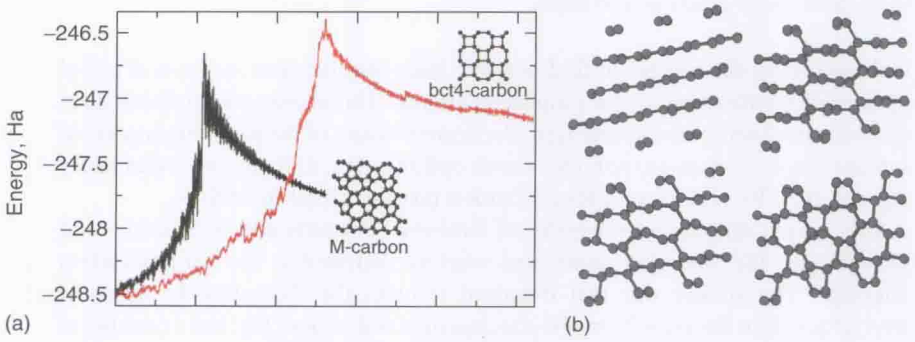

Figure 8 Synethesizability of M-carbon vs bct4-carbon: (a) energy profiles along the graphite-M-carbon (black) and graphite-bct4 (red) transition pathways and (b) the transition pathway graphite-M-carbon. The energies in given per supercell of 144 atoms. From [44]. Courtesy of S.E. Boulfelfel.

method [42], reviewed in this volume by Leoni and Boulfelfel [43]. One of the main advantages is that this method enables studies of nucleation and growth of the new phase, and its absolute activation barriers are meaningful (unlike those obtained by most other methods). As shown in Figure 8, the lower computed energy barrier clearly favors M-carbon over bct4-carbon [44].

It is my hope that this volume, reviewing most of the major methods of crystal structure prediction, all the way from topological approaches [4] to optimization methods [19, 22, 25, 27, 29, 32] and methods to appraise synthesizability of a material [43], will be useful to a wide readership of physicists, chemists, materials scientists and earth scientists. This volume also presents, in the Appendix, the first attempt to systematically compare different optimization strategies for a set of very challenging inorganic structure prediction problems [45]. The methods described in this volume should motivate further research into the structure and properties of materials, and will (probably quite soon) widely enable computational design of new functional materials. We are witnessing the dawn of a new era, where crystal structure prediction will no longer be an intractable problem.

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