

Is there theoretical evidence for a metallic carbon polymorph with space group symmetry $Fm\bar{3}m$ at ambient conditions?

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Abstract

Quantum mechanical calculations based on density functional theory and the generalised gradient approximation show that the equilibrium lattice parameter of a carbon polymorph with space group symmetry $Fm\bar{3}m$ would be 3.08 Å, and hence very different from that of diamond. No local minimum in the dependence of the total energy on the lattice parameter has been found. Such a polymorph would be approximately 5 eV atom⁻¹ less stable than diamond, suggesting that its synthesis is very unlikely. This finding is consistent with older density functional calculations and contradicts recent results of LCAO calculations, which have been used to support the interpretation of experimental data as showing the existence of a metallic carbon polymorph with space group symmetry $Fm\bar{3}m$. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, Konyashin et al. [1] reported the observation of a metallic modification of carbon with space group symmetry $Fm\bar{3}m$ and a lattice parameter of 3.56 Å, confirming results obtained earlier by Palatnik et al. [2]. In the paper by Konyashin et al. [1], the argument for the existence of the metallic carbon polymorph with space group $Fm\bar{3}m$ with a lattice parameter very close to that of diamond is based on: (i) the analysis of electron diffraction patterns; (ii) the results of EELS investigations; and (iii) semi-empirical model calculations. The relationship between the two structures is shown in Fig. 1. The observation of strong reflections, such as the 200 reflection, in electron diffraction experiments, which are forbidden by symmetry for the dia-

mond lattice, had already lead Palatnik et al. [2] to conclude that their synthesis produced a metallic carbon modification with a very low density of 1.59 g cm⁻³. The experimental observations will not be addressed in the current paper, although we note that several mechanisms are known which lead to the violation of extinction rules, leading to the observation of forbidden reflections [3–5].

Konyashin et al. [1] used linear combination of atomic orbitals (LCAO) calculations to support their analysis of the electron diffraction patterns. They report that their calculations show a distinct minimum of the binding (total) energy at 3.68 Å, which corresponds to a volume of 12.46 Å³ atom⁻¹. They do not, however, discuss their computed general dependence of the binding energy as a function of the lattice parameter. This dependence (Fig. 1 in [1]) clearly shows that the global minimum of the total energy curve seems to be at a significantly lower lattice parameter. No further details, such as the quality of the basis set, are reported in that

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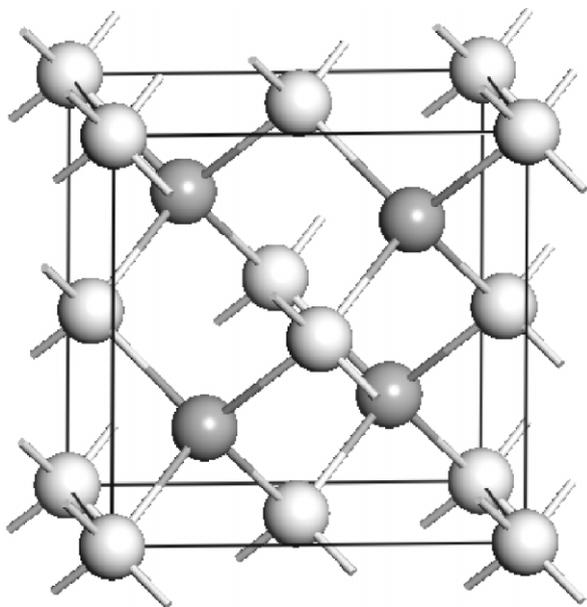


Fig. 1. The structure of the hypothetical polymorph with space group symmetry $Fm\bar{3}m$ can be derived from the diamond structure by removing the dark-grey atoms.

paper. It is this result which we address here by quantum mechanical calculations.

The model used in the present paper is based on density functional theory, the generalised gradient approximation and a plane wave basis set in conjunction with ultrasoft pseudopotentials. This quantum mechanical approach can be considered as the current state-of-the-art in parameter-free modelling of perfect crystal structures in the athermal limit. This model provides accurate phase relations for binding energies differing by more than ≈ 0.2 eV atom⁻¹ and gives lattice parameters with an accuracy of 2–3%. It is undoubtedly more reliable than the LCAO method in conjunction with empirical matrix elements used by Konyashin et al. [1].

Earlier density functional calculations based on the local density approximation have been already used to address the existence of a polymorph with $Fm\bar{3}m$ symmetry. For example, Yin and Cohen [6] investigated whether an $Fm\bar{3}m$ polymorph would be stabilised by pressure. In these calculations, the ground state structures of the simple cubic, body-centered cubic, hexagonal close packed and the $Fm\bar{3}m$ polymorphs were all significantly less stable than diamond, and the latter had a unit cell volume larger by 28% than that of diamond. Similarly, the calculations of Mailhiot and McMahan [7] show that $Fm\bar{3}m$ carbon is less stable by 4.23 eV atom⁻¹ than diamond, and they predict a bulk modulus of 233 GPa for the $Fm\bar{3}m$ modification. These calculations gave a volume of 7.01 Å³ atom⁻¹. Hence, the

results are in agreement with those presented in Yin and Cohen [6], where $Fm\bar{3}m$ carbon was computed to be less stable by 4.59 eV/atom with the volume of 7.28 Å³ atom⁻¹.

2. Computational details

The quantum mechanical calculations performed here are based on density functional theory, DFT. While DFT itself is exact [8], practical calculations require an approximation for the treatment of the exchange and correlation energies. Here we use the ‘generalised gradient approximation’, GGA [9]. Results based on GGA calculations are generally in better agreement with experiment than those obtained with the local density approximation, LDA [10–13]. Total energy differences between polymorphs are usually small and their evaluation requires precise calculations of the total energy. The computational scheme which we use here allows such accurate calculations. It is based on an expansion of the charge density and electronic wavefunctions in a basis set of plane waves. However, as it is impractical to explicitly consider tightly bound core electrons when using a plane-wave basis set, pseudopotentials have to be used to mimic the screening of the Coulomb potential of the nucleus by the core electrons. A number of approaches for the construction of pseudopotentials have been presented in the literature [14,15]. The state-of-the-art is the efficient ‘ultrasoft’ pseudopotential, leading to calculations that require a comparatively small number of plane waves [16,17]. Such ultrasoft pseudopotentials were used here, with a maximum cut-off energy of the plane waves of 310 eV. In addition to the cut-off energy, only one further parameter determines the quality of the calculations, namely the density of points with which the Brillouin zone is sampled. Here, we use a sampling of reciprocal space such that distances between grid points are ≈ 0.03 Å⁻¹. The present calculations are restricted to the athermal limit, in which temperature effects and zero-point motions are neglected. For all calculations, we used academic and commercial versions of the CASTEP program, which has been described elsewhere [18–20].

3. Results

The computed dependence of the total energy on the atomic volume is shown in Fig. 2. The minimum of the total energy curve corresponds to the equilibrium lattice parameter in the athermal limit, and is found at 3.08 Å. This implies a density of 2.73 g cm⁻³, in between that of diamond (3.51 g cm⁻³) and graphite (2.26 g cm⁻³), and a volume of 7.3 Å³ atom⁻¹. There is no local minimum in the dependence of the total energy on the unit cell volume at larger lattice parameters. The data points can be fitted with a third-order Birch–Murnaghan

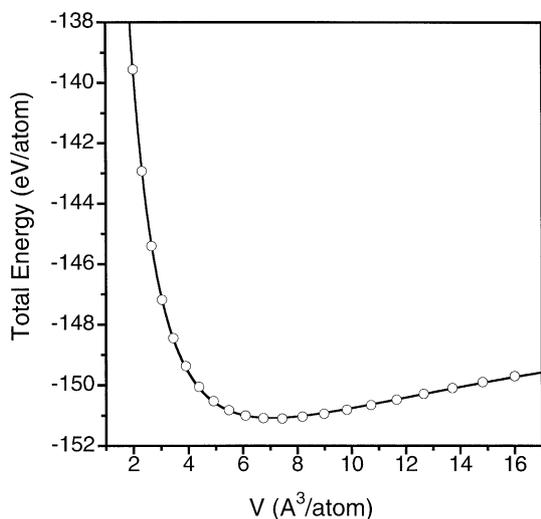


Fig. 2. Dependence of the total energy of the hypothetical metallic carbon modification on the volume per atom. Points show computed values, the line represents a fit with a third-order Birch–Murnaghan equation of state. There is no local minimum at volumes larger than $7.3 \text{ \AA}^3 \text{ atom}^{-1}$ ($29.22 \text{ \AA}^3 \text{ unit cell}^{-1}$).

equation of state. This gives a bulk modulus of $B = 130\text{--}146 \text{ GPa}$ and a pressure-derivative $B' = 3.7\text{--}3.9$, depending on the interval which is used to fit the equation of state.

The accuracy of the current calculations can be checked by comparing results obtained for diamond. In this case, we compute a lattice parameter of 3.537 \AA , in good agreement with the experimental value of 3.567 \AA .

4. Discussion

The calculations presented here are consistent with results obtained earlier by density functional theory calculations [6,7]. A comparison with results obtained for diamond also confirms that the current calculations are accurate. Hence, our conclusion is that if a carbon polymorph with space group symmetry $Fm\bar{3}m$ existed, it would have had a lattice parameter close to 3.08 \AA , i.e. very different from that of diamond. It would have had a significantly lower density ($\rho_{\text{theo}} = 2.727 \text{ g cm}^{-3}$) than diamond ($\rho_{\text{theo}} = 3.607 \text{ g cm}^{-3}$), and thus it is unlikely to be a high-pressure polymorph. We therefore have shown that the LCAO calculations presented by Konyashin et al. [1] gave results which cannot be reproduced at a higher level of theory, and hence they cannot be used to support the existence of a metallic carbon polymorph with space group symmetry $Fm\bar{3}m$. The total energy calculation shows that this polymorph would be approximately 5 eV atom^{-1} less stable than diamond. This makes it extremely unlikely that such a polymorph could be synthesized.

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