Graphite intercalation compounds under pressure: A first-principles density functional theory study

Gábor Csányi,^{1,*} Chris J. Pickard,² B. D. Simons,¹ and R. J. Needs¹

¹Theory of Condensed Matter Group, Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge CB3 0HE,

United Kingdom

²School of Physics and Astronomy, University of St Andrews, North Haugh, St Andrews KY16 9SS, United Kingdom (Received 6 January 2007; published 21 February 2007)

Motivated by recent experimental work, we use first-principles density functional theory methods to conduct an extensive search for low enthalpy structures of C_6Ca under pressure. As well as a range of buckled structures, which are energetically competitive over an intermediate range of pressures, we show that the high-pressure system (≥ 18 GPa) is unstable toward the formation of a class of layered structures, with the most stable compound involving carbon sheets containing five- and eight-membered rings. As well as discussing the energetics of the different classes of low enthalpy structures, we comment on the electronic structure of the high-pressure compound and its implications for superconductivity.

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I. INTRODUCTION

Although the history of graphite intercalation compounds (GICs) dates back more than a century, they first became prominent in the early 1960s when superconductivity was discovered in some alkali metal GICs.¹ Interest in these compounds has been reignited by the recent discovery that at least two compounds, C_6Ca and C_6Yb , have superconducting transition temperatures that, although modest by the standard of cuprate compounds, are an order of magnitude higher than those found previously for GICs.^{2,3} Soon after this discovery, electronic structure calculations revealed that a threedimensional band, originating from the intrinsic interlayer band of graphite and a metal ion band of the intercalant, plays a crucial role in facilitating superconductivity in GICs (Ref. 4) (see also Ref. 5). Subsequently, first-principles calculations for C₆Ca and C₆Yb (Refs. 6 and 7) provided evidence that the out-of-plane phonons of the graphene sheets and the in-plane phonons of the metal atom couple to the electrons in this three-dimensional band and provide a basis for understanding the superconductivity within a conventional BCS framework. A brief review of the work to date is given in Ref. 8.

As well as superconductivity, evidence for a reversible pressure-driven phase transition has been reported in both C_6Ca and C_6Yb .^{9,10} As the pressure is increased from ambient, the superconducting transition temperature increases markedly, rising in C₆Ca from 11.5 to 15 K at 7 GPa, above which it drops abruptly to 5 K. Similar behavior is reported in C₆Yb with a transition at approximately 2.2 GPa. Since the transition is reversible and calculations have shown softening of a phonon mode with increasing pressure, it was conjectured that a structural phase transition takes place.^{11,12} The reversible nature of the observed transitions suggest that they involve small atomic displacements.²² However, the various observations motivate an investigation of the wider landscape of structures of GICs under pressure, including the possibility of large-scale rearrangements of the atoms. In this paper, we report a study of possible structures of C₆Ca under pressure, finding that large-scale atomic rearrangements are favored at quite low pressures. We find that the behavior of the C_6 Yb shares a similar phenomenology.

II. RESULTS

Before discussing the methodology, let us first summarize the main findings. The results below reveal that the low enthalpy structures of C_6Ca (and other GICs) can be broadly classified into different classes. While the planar structure of C_6Ca is stable at ambient pressure, structures involving a buckling of the graphene sheets become energetically competitive over a range of intermediate pressures. At a comparatively low pressure of approximately 18 GPa, however, we find that the familiar honeycomb lattice structure of the graphene layers becomes unstable toward a rearrangement involving large- and small-diameter carbon rings, with the former accommodating the metal ion intercalate. With such an arrangement, the volume may be reduced without greatly increasing the internal energy, which results in a low enthalpy.

To arrive at these conclusions, we have carried out an extensive search within the "space of possible structures" of C_6C_a by relaxing a large number of random structures at a constant pressure of 15 GPa. (The general methodology parallels that described in Ref. 13.) This approach allows a search of the structure space with unbiased initial conditions. The calculations were performed within density functional theory¹⁵ using the CASTEP package,¹⁴ with a plane-wave basis set and ultrasoft pseudopotentials. To remain consistent with our previous work on the electronic structure of C₆Ca,⁴ we chose to use the local-density approximation¹⁶ for the exchange-correlation functional and used the pseudopotentials that come with the CASTEP package, dividing the electrons into two core electrons and four valence electrons for C, ten core and ten valence electrons for Ca, and forty-two core and twenty-eight valence electrons for Yb. We tested the relative stability of the most stable structures with a generalized gradient approximation¹⁷ and found no significant changes. The initial conditions for the geometry optimizations consisted of a unit cell containing 1 f.u. (seven atoms) with random atomic positions and random lattice vectors, the latter bounded so that the unit cell volume was within a factor of 2 of ambient value. For the structure-space search, we used a medium quality of plane-wave cutoff energy (270 eV) and Brillouin-zone integration (0.07 Å⁻¹) so that the optimizations were fast, thus enabling a larger number of runs to be carried out using the available computing resources (32-processor Xeon cluster). The search is believed to be nearly exhaustive over the range of seven-atom cells because the low enthalpy structures came up repeatedly during the search. The *Pmma* structure with a 14-atom unit cell was built by hand using the intuition gained from the results of the random search.

As mentioned above, the search produced a number of structures which can, broadly, be grouped into two families. The first consists of the well-known rhombohedral or trigonal $R\bar{3}m$ structure, which is the stable low-pressure phase of C₆Ca, and its lower-symmetry variants in which the bonding topology of the graphene sheets remains intact, but the sheets are buckled (see Fig. 1). In these buckled configurations, the Ca ions occupy the troughs between the buckled sheets, which results in a small reduction in the overall volume. The principal difference between the Cm and the C2/m structures is that, in the former, the metal sheets are stacked in an $\alpha\beta\gamma$ sequence, just as in the $R\bar{3}m$ structure, whereas the latter has an $\alpha\alpha$ stacking. Structures consisting of nanoporous carbon framework filled with Ca atoms were also found, but they were higher in enthalpy at these pressures.

Despite the buckling of the sheets, the integrity of the hexagonal carbon ring structure in this family of compounds is maintained. In the second family of low enthalpy compounds, the carbon and Ca atoms maintain a planar geometry, but the hexagonal ring structure is replaced by a network of different sized rings. The Pmma structure has five-, six-, and seven-membered rings, whereas the Cmmm structure has only five- and eight-membered rings. A useful way to think about these bonding topologies is that they result from one (Pmma) or two (Cmmm) Stone-Wales (SW) bond rotations,¹⁸ starting from the regular hexagonal graphene network. The last two structures are reminiscent of those of a class of ternary boride compounds, whose prototype is YCrB₄. To our knowledge, its structure, consisting of metal ion layers and boron sheets with five- and seven-membered rings, was first proposed by Kuz'ma.¹⁹ Several other members of the class have since been identified.^{20,21}

To further increase the accuracy of the procedure, we chose promising representative structures from the different families and refined them using a higher plane-wave cutoff energy (480 eV) and Brillouin-zone sampling (0.05 Å⁻¹). The converged lowest enthalpy structures obtained are defined in Table I. Figure 2 shows the enthalpies of the new structures, referenced to the $R\bar{3}m$ structure, as a function of external pressure. The buckled *Cm* structure is slightly less stable than the $R\bar{3}m$ structure at pressures up to about 18 GPa, but at higher pressures it becomes more favorable. In fact, the $R\bar{3}m$ and buckled structures are always close in enthalpy, and their relative stability cannot be conclusively asserted because of inherent systematic errors in the local-



FIG. 1. Low enthalpy structures of C₆Ca found during the structure space search. The top panel shows the familiar $R\overline{3}m$ structure, which is stable under ambient conditions. The Ca ions (large) are situated between the layers, occupying sites above the centers of the hexagonal rings in an $\alpha \alpha$ stacking arrangement. The following two panels show lower-symmetry variants, with C2/m and Cm structures, where in each case the graphene sheets are buckled (as depicted in the side views shown as insets) and the Ca ions are rearranged. While all of these buckled structures are energetically competitive, it is not possible to conclude from our calculations whether any become globally stable at intermediate pressures. The bottom two panels show structures in which the hexagonal carbon rings of the graphene sheets are transformed, by a sequence of Stone-Wales bond rotations, into five-, six-, and seven-membered (Pmma) or five- and eight-membered rings (Cmmm). At high enough pressure, the latter structure is expected to become globally stable.

TABLE I. Details of C_6Ca structures at 15 GPa, calculated at the higher level of precision.

Space group	Lattice parameters (Å, deg)			Atomic coordinates (fractional)			
Cmmm	a=9.07 $\alpha=90$	b=3.66 $\beta=90$	$c = 3.54$ $\gamma = 90$	C1 C2	0.079 0.175	0.000 0.308	0.000
				Ca	0.500	0.000	0.500
R3m	<i>a</i> =4.24	<i>b</i> =4.24	c=12.28	С	0.000	0.333	0.167
	<i>α</i> =90	β=90	γ=120	Ca	0.000	0.000	0.000
Pmma	<i>a</i> =4.82	<i>b</i> =3.74	<i>c</i> =6.7	C1	0.250	0.500	0.117
	<i>α</i> =90	β=90	γ=90	C2	0.514	0.500	0.210
				C3	0.750	0.500	0.091
				C4	0.596	0.500	0.417
				Ca	0.250	0.000	0.350
C2/m	<i>a</i> =7.30	<i>b</i> =4.23	c=4.15	C1	0.000	0.334	0.500
	<i>α</i> =90	$\beta = 102$	γ=90	C2	0.171	0.168	0.532
				Ca	0.000	0.000	0.000
Cm	a=7.32	<i>b</i> =4.24	<i>c</i> =6.4	C1	0.246	0.166	0.513
	<i>α</i> =90	$\beta = 105$	γ=90	C2	0.054	0.332	0.474
				C3	0.413	0.333	0.512
				Ca	0.531	0.500	1.000

density approximation (commonly estimated as 0.05 eV/atom for total energy differences). The Pmma and *Cmmm* structures show a steep decline in relative enthalpy, indicating that they would be favored at high pressure. Considering the geometry of these structures, it can be seen that the energy cost of the SW bond rotations is offset by a significant reduction in volume (up to 20%), as the metal ions are accommodated within the larger rings. The enthalpypressure curve of *Pmma* has a lower slope than that of *Cmmm* because it involves one SW bond rotation rather than two, so that the rings in which the Ca atoms sit are smaller and the volume reduction is not as large.



FIG. 2. (Color online) The enthalpy differences per C₆Ca f.u. of our new structures, referenced to the $R\bar{3}m$ structure.



FIG. 3. The band structure of the *Cmmm* structure (left) and the corresponding "empty" structure with the metal ions removed (right). The two panels have been aligned vertically using the bottom of the sigma bands (not shown); the respective Fermi levels are indicated by dashed lines. Since the space group of this structure is almost hexagonal, we have used the corresponding notation for the points of high symmetry in the Brillouin zone and indicated the small discrepancy by using primed letters. Note the increase in the Fermi level upon intercalation, accompanied by the lowering and subsequent occupation of the dispersive interlayer band (marked by an arrow).

Figure 3 shows the band structure corresponding to the *Cmmm* structure. Comparing it to that of the "empty" carbon skeleton (after removal of the metal ions), it can be seen that, upon intercalation, a new dispersive band becomes occupied in much the same way as in the parent $R\overline{3}m$ structure.⁴ However, the density of states (DoS) (shown in Fig. 4) at the Fermi level is significantly lower (on both the Ca and C atoms) in the *Cmmm* structure, suggesting that the conditions for superconductivity are likely to be less favorable. In addition, the general shape of the DoS looks much less like that of graphite as compared with the $R\overline{3}m$ structure.

III. DISCUSSION

Taken together, these findings present a coherent picture of the behavior of C_6Ca under pressure. At low pressures, the



FIG. 4. Density of states, resolved into contributions on the C and Ca atoms, corresponding to the *Cmmm* (top) and $R\overline{3}m$ (bottom) structures, calculated at 15 GPa.

graphene sheets remain flat, leading to the familiar $R\overline{3}m$ structure. However, this parent structure is but one member of a larger family of compounds in which the integrity of the hexagonal rings is maintained, while the graphene sheets become buckled to accommodate Ca atoms within the troughs. The troughs allow more space for the Ca atoms, so these structures are favored over $R\overline{3}m$ at higher pressures, although the gain in enthalpy is limited. At still higher pressures, another more drastic solution emerges in which the bonding topology of the carbon atoms is disrupted by SW bond rotations within the graphene layer. A single SW bond rotation results in five-, six-, and seven-membered rings, as in the Pmma structure, and two SW bond rotations result in fiveand eight-membered rings, as in the Cmmm structure. The SW mechanism results in large-diameter carbon rings, within which the Ca atoms sit, giving a substantial volume reduction, and these structures become stable at pressures above about 18 GPa. The accompanying phase transition is expected to be strongly first order, and the electronic structure of the large-diameter-ring structures is strongly modified from that of $R\overline{3}m$. In summary, and recalling the experimental evidence for a phase transition, we conclude that our simulations strongly predict a transition to a structure similar to *Pmma* or *Cmmm* at sufficiently high pressures, but due to the intrinsic errors associated with DFT, it is uncertain whether the observed transition is this one. It is possible that one of the buckled structures becomes the most stable one for an intermediate range of pressure, in which case we predict a *second* phase transition at higher pressure.

Further calculations show that the bonding between the metal and carbon atoms is stronger than might be expected, and all the structures considered here are stable against phase separation into diamond and/or graphite and pure fcc and/or bcc Ca. We have also studied the stability of the above phases of C₆Yb under pressure, and again we find that structures with Yb atoms sitting within larger membered rings are stable at pressures above about 18 GPa. We conjecture that the occurrence of such rings accommodating the intercalate atoms might be a general feature of graphite intercalation compounds under high pressures.

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- *Present address: Department of Engineering, University of Cambridge, Trumpington Street, Cambridge CB2 1PZ, United Kingdom.
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