Crystal structure of low-dimensional Cu(I) iodide: DFT prediction of cuprophilic interactions†

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Density functional theory calculations of the crystal structure of copper(I) iodide encapsulated within small diameter single walled nanotubes predict edge sharing tetrahedra of copper atoms, bridged by iodine, with Cu–Cu near neighbour distances varying from 2.42 to 2.72 Å indicating a strong closed shell cuprophilic interaction.

The ability to encapsulate simple salts within carbon nanotubes, in particular single walled nanotubes (SWNTs), has led to the determination by high resolution transmission electron microscopy (HRTEM) of pseudo one dimensional (1-d) crystal structures of a number of simple binary compounds.[1–9] Much of the interest in these encapsulated structures relate to their potential as new low-dimensional materials; the encapsulated material has the potential to confer homogeneity in electronic properties on the wide diversity of synthesised nanotubes. The crystal forms that arise as a consequence of the forced low dimensionality are also of intrinsic interest. The templating effect of the nanotube inevitably modifies the atom coordination environment compared to that in the bulk structure even to the extent of producing all surface crystals. In some cases, for example KI, the 1-d structure is related to the bulk with modified coordination number. In others, for example HgTe, different coordination environments are found. HRTEM can readily image heavy atoms and when combined with through focal image restoration procedures improved signal to noise and enhanced resolution may be obtained. The positions of light atoms are a challenge and in all cases model structures must be proposed to generate images for comparison with experiment.

Computer simulation methods, in particular molecular dynamics, have been employed to investigate both the structure of crystallites and the filling mechanism. This approach has been particularly successful in the study of KI crystallites[10–13] where the interatomic forces are well described by Born–Mayer and Lennard-Jones potentials. A recent study of AgI,[14] using a similar approach, included flexibility of the nanotube to examine distortions as a result of encapsulation.

Quantum chemical calculations employing density functional theory (DFT) methods have the advantage of providing, in addition to detailed structural predictions, information on electronic structure of the composite. They have been used successfully to confirm and refine the structures of KI[15,16] and HgTe[17] encapsulates.

Recently, encapsulation of wide gap semiconductor CuI nanocrystals in the channels of metallic SWNTS has been reported with inner diameter 1–1.4 nm.[18] Capillary adsorption studies, EDX microanalysis and HRTEM imaging of CuI@SWNT demonstrated the successful filling of SWNTs with one-dimensional fine crystals of CuI oriented in [00*l*] direction along the channel with a layer spacing of 3.59 Å.[18] Raman spectra of the composite CuI@SWNT show considerable broadening of G-modes and shifts to lower frequencies, while the G^- line of metallic tubes nearly disappears indicating the shift of electronic band structure of filled SWNTs and transition of the metallic tubes to a semiconductive state.[18] Structural details are not available though studies are still underway.

In this paper, based on DFT, we predict a novel structure for CuI encapsulated in small diameter nanotubes in which cuprophilic interactions are evident.

Calculations were carried out using the SIESTA code[19–21] (full details are given in the electronic supplementary information, ESI†). Two different starting structures were used for the optimisation of 1-d CuI in the absence of a confining tube. The first was a novel structure, adopted by HgTe in SWNT,[17,22] which has 3:3 coordination with the metal in a trigonal planar coordination site and the anion having a pyramidal environment. Given that both Cu^+ and Hg^{2+} are both d^{10} ions this seemed a plausible structure for CuI. The second was a low-dimensional structure derived from the NaCl rock salt bulk structure with a 2 × 2 cross section with 4:4 coordination of the atoms.[16,23] The available experimental evidence suggests that at pressures in the region of 10 GPa CuI adopts a rock salt structure.[24–27] The shortest Cu–Cu distances in the 3:3 structure was 3.96 Å and that in the 4:4 structure was 4.11 Å.

Both structures underwent significant evolution on geometry optimisation to give final structures, **A** and **B**, in which the Cu formed a central chain of edge sharing tetrahedra. These chains were sheathed by I atoms. The two structures are shown in Fig. 1; **A** evolves from the 3:3 starting structure and **B** from the 4:4 rock salt like lattice. In **A** the I atoms bridged faces of the tetrahedra in an asymmetric fashion to give the I atoms three-fold coordination. In **B** the I atoms have two near Cu neighbours and two further ones showing a memory of the initial four-fold coordination. Structure **A** was calculated to be 0.04 eV per CuI lower in energy than **B**,

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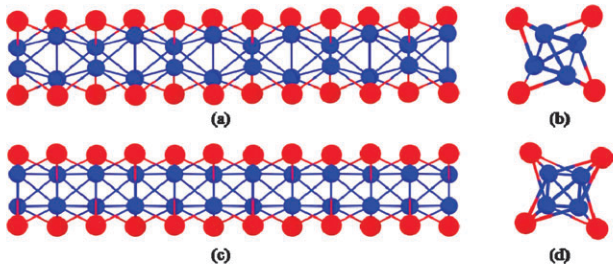

Fig. 1 Optimised geometries of 1-d CuI with periodic boundary conditions (a) and (b) **A** (Cu–Cu = 2.49, 2.70 Å; Cu–I = 2.62, 2.63 Å) and (c) and (d) **B** (Cu–Cu 2.42, 2.69 Å; Cu–I 2.58, 2.98 Å). Cu blue, I red.

hence structure **A** was selected for encapsulation into the SWNTs.

The Cu–Cu distance in elemental copper is 2.556 Å and that in bulk CuI is 4.28 Å, thus the distances found in the 1-d structure of Cu–I represent significant metal–metal bonding interactions. Normally two closed shell metal cations might be expected to repel each other. However, there are many examples of complexes of Group 11 metals in the +1 oxidation state with short metal–metal bond lengths.[28] Most examples relate to Au(I) chemistry where the term aurophilic has been coined to describe the gold–gold interaction. Authentification of cuprophilic interactions has been more controversial.[29] The computed strength of the interaction has been found to be a function of the level of theory and the quality of the basis sets employed. Correlation effects are deemed to be important, reinforced by relativistic contributions for heavier metals such as gold. We have tested the model with finite 1-d structures up to $Cu_{32}I_{32}$ using other functionals and larger basis sets and found equivalent results. The size of the systems modelled here precludes the highest level of theory.

The supercell lengths for a CuI crystal comprising three (Cu_8I_8) unit cells ($Cu_{24}I_{24}$, supercell length = 2.444 nm) and a (n,n) SWNT (n = 8, 9, 10) comprising 10 unit cells (SWNT supercell length 2.435 nm) are very close to each other. We applied periodic boundary conditions to supercells of $Cu_{24}I_{24}@(n,n)$ in order to model the entire supercell (SWNT + CuI) as an infinite system. Fig. 2 shows the modelled CuI crystals encapsulated within SWNT. The indices of the chosen nanotubes were (8,8), (9,9) and (10,10) which have diameters of 10.85, 12.36 and 13.56 Å, respectively, sizes corresponding to the experimental report.[18] Geometry optimisation of the composites retained the structure **A** found for the isolated crystal. The resulting bond lengths are given in Table 1 where they are compared to those of bulk CuI.

Table 1 Bond lengths, charges and binding energies per CuI calculated for CuI@SWNT, an isolated 1-d CuI crystal and bulk CuI: d_t is the diameter of the (empty) SWNT

	d_t/Å	Cu–Cu/Å	Cu–I/Å	Charge	$E_{binding}$/eV
CuI@(8,8)	10.85	2.42–2.66	2.52	−0.40	+0.35
CuI@(9,9)	12.36	2.53–2.72	2.65	−0.23	−0.17
CuI@(10,10)	13.56	2.51–2.70	2.67	−0.13	−0.14
1-d CuI	—	2.51–2.70	2.63		
Bulk CuI		4.28	2.62		

The values for the Cu–Cu and Cu–I distances are similar to those found for structure **A** for the (10,10) and (9,9) tubes but when contained within the smallest diameter (8,8) tubes there is evidence of compression of the CuI crystal. This is confirmed by the energetics (Table 1) which show that insertion of the crystal into a SWNT is exoergic for the two larger tubes but endoergic for the (8,8) tube. The distance from I to the nearest carbon atoms also decreases with tube diameter (3.83 Å, 10,10; 3.33 Å, 9,9; 3.00 Å, 8,8).

Mulliken population charge analysis was carried out to estimate the charge transfer between the CuI crystals and the tubes. Analysis indicates that there is a small charge transfer to the CuI crystals from the tubes (Table 1).

Density of states (DOS) and partial density of states (PDOS) were calculated both for 1-d CuI and bulk CuI (Fig. 3). Whereas bulk CuI is wide gap semiconductor, change to a 1-d structure decreases the band gap considerably to 0.1 eV. In previous studies on KI[16] and HgTe[17] lowering the dimensionality of the crystal was found to increase the band gap. The reduction is in part due to the Cu–Cu interactions that broaden the 3d and 4s bands. The 3d levels predominate at the top of the valence band and the 4s states at the bottom of the conduction band (see ESI†).

The DOS of the CuI@(9,9)SWNT composite is compared with that of the empty (9,9) tube in Fig. 3(c). Both are pinned with zero at their respective Fermi levels. It is apparent that the combined DOS is a sum of the two components. The shift of readily identifiable features of the SWNT DOS to higher energies is consistent with charge transfer to the CuI 1-d crystal populating the CuI conduction band and a lowering of the Fermi level for the nanotube. Population of the conduction band of the CuI 1-d crystal may lead to interesting electronic properties. Similar patterns are observed in the DOS of both CuI@(8,8) and CuI@(10,10) with respect to their respective nanotube hosts.

Preliminary studies indicate that similar structures are likely for all MX structures where M = Cu, Ag and Au and X = Cl, Br and I.

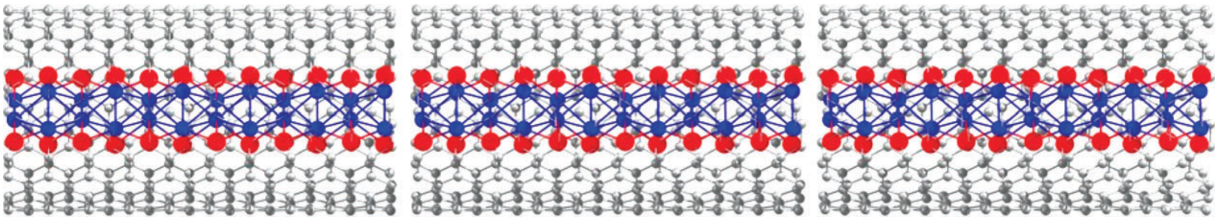

Fig. 2 Structure of infinite CuI crystals inside an infinite SWNT. The breaks in the structure indicate the periodic boundary conditions.

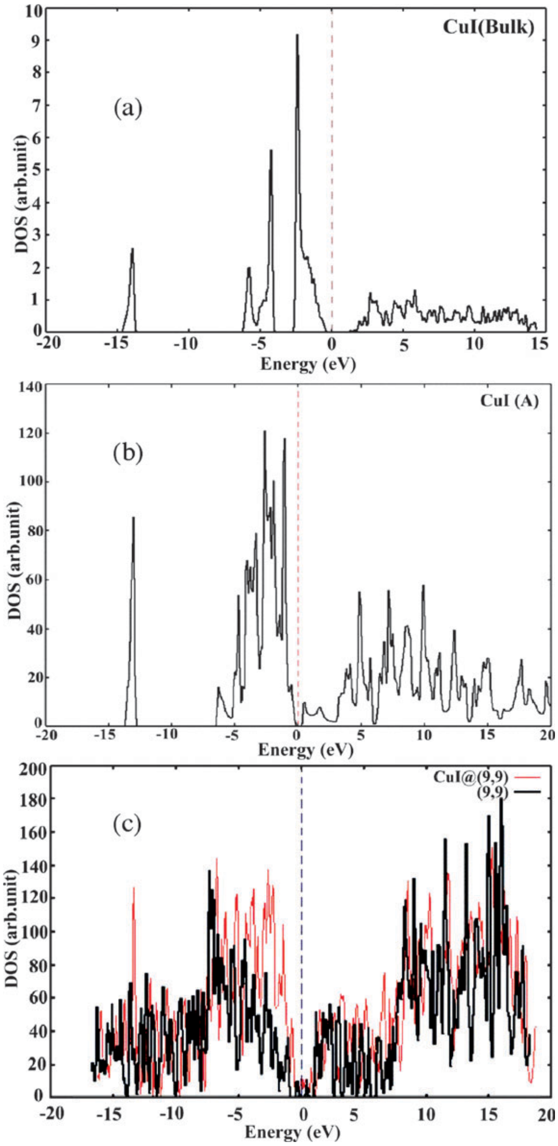

Fig. 3 Density of states (DOS) for (a) bulk CuI (b) 1-d CuI (c) CuI@(9,9) (red) and a (9,9) SWNT (black).

In conclusion, encapsulation of CuI in nanotubes, and the consequent enforcement of low dimensionality on the ensuing crystal, results in an unprecedented structure in which cuprophilic interactions give edge-linked tetrahedra of Cu atoms sheathed by iodine. The band gap of the encapsulate is considerably reduced compared to the bulk leading to small but significant charge transfer from the nanotube. Such composites promise a greater homogeneity in electronic properties than are manifested by the assembly of single walled nanotubes.

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