Correlation of Structural and Electronic Properties in a New Low-Dimensional Form of Mercury Telluride

Robin Carter,¹ Jeremy Sloan,^{1,*,§} Angus I. Kirkland,^{2,†,§} Rüdiger R. Meyer,² Phillip J. D. Lindan,^{3,‡,§} Grace Lin,³ Malcolm L. H. Green,¹ Alexis Vlandas,¹ John L. Hutchison,² and John Harding⁴

¹Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, United Kingdom

²Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, United Kingdom

³School of Physical Sciences, University of Kent, Canterbury, CT2 7NR, United Kingdom

⁴Department of Engineering and Materials, Mappin Street, Sheffield, S1 3JD, United Kingdom

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Using high resolution electron microscopy and first principles quantum mechanical calculations we have explored the fundamental physics and chemistry of the semiconductor, HgTe grown inside single wall carbon nanotubes. This material forms a low-dimensional structure based on a repeating Hg_2Te_2 motif in which both atom species adopt new coordination geometries not seen in the bulk. Densityfunctional theory calculations confirm the stability of this structure and demonstrate conclusively that it arises solely as a consequence of constrained low dimensionality. This change is directly correlated with a modified electronic structure in which the low-dimensional form of HgTe is transformed from a bulk semimetal to a semiconductor.

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Filled single wall carbon nanotubes (SWCNTs) [1] are ideal model systems for studying atomically regulated crystal growth and for investigating the fundamental physics of low-dimensional materials [2-9] and their application [10-12]. These tubes, with a typical diameter range of 1-2 nm, can be synthesized in gram scale quantities [13,14] and are formed from rolled sheets of sp^2 graphene carbon.

SWCNTs have been filled with a variety of materials including ionic halides, metals, and molecular species [2,4-9] and for many of these, new encapsulated structures that are different from those of the bulk, have been identified. Previous studies [4,6-9] have described only the structural modifications arising from low-dimensional confinement and there are no reports describing the correlation between these and the resultant physical or chemical properties.

In this Letter we report, for the first time, the detailed characterization of an encapsulated 1D semiconductor crystal with a nominal stoichiometry, HgTe, that adopts a new structure based on a local coordination not observed in the bulk arising solely as a result of low-dimensional confinement. We further report the results of densityfunctional theory (DFT) calculations that demonstrate the global stability of this structure and predict an electronic structure substantially modified from that of the bulk material.

Figures 1(a) and 1(b) show the phase of the exit plane wave function [15,16] restored from a focal series of images of two separate HgTe filled SWCNTs. Focus levels measured from subregions I to IV indicate that the filled SWCNT shown in Fig. 1(a) is oriented orthogonally with respect to the electron beam incident direction. Similarly, focus levels measured from subregions V to VIII indicate that the second SWCNT [Fig. 1(b)] is tilted by ca. 25° relative to that in Fig. 1(a). Careful examination of the restored phase of these two fragments reveals that they have closely related structures derived from a common motif. In Fig. 1(a) this motif is identified as a regular repeat of two bright atom columns of equal intensity along the SWCNT axis, separated by a layer that changes contrast from an unresolved linear feature to three distinct atom columns with differing intensities. These features are consistent with two orthogonally stacked layers of Hg₂Te₂ dimers and this has been confirmed by comparison with extensive image simulations.



FIG. 1. (a), (b) Composite restorations of the phase of the exit plane wave function of two separate SWCNTs with diameters of 1.36 and 1.49 nm, respectively, containing crystalline HgTe. The boxes indicate individually restored subregions as described in the text which were also used for establishing relative focus levels along the SWCNT axis.



FIG. 2 (color online). (a) Generalized Hg₄Te₄ motif with both Hg₂Te₂ dimers delineated. This motif is shown with a local rotation angle (ϕ) = 0, intralayer Hg-Te-Hg angle (γ) = 70°, and relative tilt angle (θ) = 0. (b) Subsets of optimized simulations of the phase of the specimen exit plane wave with (θ) = 0 and 25°, respectively, for fixed (γ) = 70° and for values of (ϕ) as indicated. (c) Detail from Fig. 1(a). (d) Simulation matching (c). (e) Structure model corresponding to the indicated region in (d). (f) Detail from Fig. 1(b). (g) Simulation matching (f). (h) Structure model corresponding to the indicated region in (f).

Cross correlation of individual layers in the experimentally restored phase along the SWCNT axis with a generalized motif has been carried out for both nanotubes [Fig. 2(a)] [21]. In these calculations the local rotation angle of the motif with respect to the incident beam direction (ϕ) and the internal Hg-Te-Hg angle (γ) were varied for the two tube inclinations ($\theta = 0^{\circ}$ and 25°) corresponding to the experimentally determined values. This has enabled the full three-dimensional structure of the nanocrystal to be determined from the two experimental projections. An optimum fit (based on the maximum in the correlation coefficient) was obtained for both crystal fragments with a fixed value of $\gamma = 70^{\circ}$. Two subsets of simulations for varying ϕ which closely match the experimental images in Figs. 1(a) and 1(b) are shown in Fig. 2(b). These simulations confirm that the structure of both encapsulated crystals is identical (with $\gamma = 70^{\circ}$ in both cases) but that they are rotated with respect to each other (by 32°) and are inclined at different angles (0° and 25°) with respect to the incident beam direction [Figs. 2(a)-2(h)]. Both fragments are also twisted by ca. 15° along the tube axis. Optimized structural models are shown in Figs. 2(e) and 2(h) corresponding to the indicated subregions of the simulations shown in Figs. 2(d) and 2(g), respectively, with values for ϕ , γ , and θ indicated.

The measured interatomic spacing within the encapsulated nanocrystal equals the 0.28 ± 0.01 nm Hg-Te bond

distance (within experimental error) found in the bulk sphalerite form of HgTe [23]. However, the bond angles at both Hg and Te are altered significantly from the tetrahedral coordination of the bulk. The Hg atoms have three coplanar bonds disposed at 120° and the Te atoms have bonds disposed at 120°, 90°, and 90°. This clearly demonstrates that the local coordination is substantially altered in this low-dimensional state and that the bulk site symmetry equivalence of Hg and Te is broken. We also note that the nanotube wall contrast does not alter along the tube axis and that its diameter remains constant in contrast to previously reported results for the ionic material CoI₂ [9], thus suggesting an absence of any strong interaction between the crystal and the tube wall.

It is possible to rationalize this modified Hg coordination geometry in terms of formal hybridization. In bulk HgTe both atomic species are tetrahedrally coordinated (corresponding to formal sp^3 hybrids). The planar trigonal configuration at Hg observed here in the low-dimensional state is known for various discrete compounds of Hg and Te including a series of 1D chain anions [24] and is attributed in these structures to sp^2 hybridization. The conventional octahedral coordination in group VI species (described using d^2sp^3 hybrids) is not a possible explanation in this system since DFT calculations (see later) agree with the observed structure without any explicit representation of the Te d electrons. Therefore, we regard the trigonal-planar Hg coordination as arising from $[HgTe_3]^-$ units in which the 6 valence electrons are accommodated in three sp^2 hybrids with an unoccupied pzorbital normal to these. To obtain the distribution of Hg-Te-Hg angles observed, we further require that a Te lone pair occupy one of the orbitals in the sp^2 plane and the other orbitals bond to Hg. This hybridization is also consistent with the experimentally observed difference in site symmetry between Hg and Te.

We have also used first principles quantum mechanical calculations [25] to further investigate the observed structure and to predict its properties. In a bulk covalent material such as HgTe changes in the bonding arising directly from low dimensionality are the dominant driving force towards structural change, and interactions with the tube wall (predominantly van der Waals) are of secondary importance. Accordingly, we have used free quasi-1D crystals as the basis for our calculations, with no explicit representation of the nanotube present and the validity of this approach is apparent from the results obtained. Four starting configurations for DFT calculations were used, three generated from bulk sphalerite and wurtzite forms of HgTe together with a fourth using the optimized geometry obtained from the experimental data. After complete structural optimization, all starting structures yield 1D HgTe polymorphs of comparable energy, but that derived from the experimental data gave the lowest-energy structure (at -679.15 eV/atom [28]. A detail showing the optimized



FIG. 3 (color online). Optimized geometry of the lowdimensional form of HgTe showing local bond lengths and angles calculated from DFT. The equivalent experimentally determined bond lengths and angles are given in the text.

calculated geometry is shown in Fig. 3 demonstrating excellent agreement in both bond distances and angles (within experimental error) with the experimental data.

The minor relaxations observed verify that the experimental structure is reliable and represents a thermodynamic minimum at low dimensionality. However, we note that within the error of the DFT calculation there exists a competitive structure [28] but that this has never been observed experimentally. These calculations also clearly demonstrate that the tube-wall interaction is not a significant influence other than to confine the material to one dimension. We further note that the relaxed structures obtained from the alternative starting configurations also display a preference for threefold coordination of both chemical species: trigonal planar for case of Hg and trigonal bipyramidal for Te despite starting from structures with exclusively tetrahedral bond angles. We have also calculated the electronic band structure of the low-dimensional form which reveals that the structural change observed also leads to a radical modification of the electronic properties, in that all three materials become semiconducting, with a band gap of at least 1.2 eV [29], in contrast to the bulk material which is a semimetal. An interesting comparison may be made with calculations on HgTe clusters [30], where the same trigonal-planar structural motif appears on the surfaces of those clusters that have semiconducting character. Finally, our calculations reveal a charge transfer of 0.28e from Hg to Te compared with bulk Mulliken populations, consistent with our earlier interpretation of the bonding and if the bonding in the bulk is considered to be semi-ionic, then this transfer lessens that ionic character.

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*Present address: Advanced Technology Institute, School of Electronics and Physical Sciences, University of Surry, Guildford, GU2 7NX, United Kingdom. Electronic address: jeremy.sloan@chem.ox.ac.uk [†]To whom correspondence should be addressed. Electronic address: angus.kirkland@materials.ox.ac.uk [‡]Electronic address: p.lindan@kent.ac.uk [§]Corresponding author.

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- [15] SWNTs were synthesized using a modified high-yield arc synthesis technique [14] and then filled with molten highly pure HgTe (99.9%, STREM) by capillary filling [2]. Specimens were examined using a 300 kV field emission gun high resolution transmission electron microscope (JEOL JEM-3000F, $C_s = 0.57$ mm, point resolution = 0.16 nm). Images of discrete HgTe filled nanotubes located over holes in a carbon support film were acquired at a magnification of 600 000X using a 1024-pixel charge coupled device camera.
- [16] The complex exit plane wave function was reconstructed from a 20-image through focal series under a linear imaging model according to an established procedure [17,18]. Individually restored subregions of the exit wave were used to generate a composite of the entire field of view. Focus levels determined from these subregions [19] were also used to estimate the inclination of the

SWCNT with respect to the incident beam direction. The antisymmetric coefficients of the wave aberration function were independently determined from an additional tilt azimuth data set [20].

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tials as written into the CASTEP code [26]. The separation between the 1D crystals and their periodic images was at least 1.2 nm and ultrasoft pseudopotentials were used with core charges of 6 (Te) and 12 (Hg), and a plane-wave cutoff of 370 eV. *k*-point sampling was chosen such that the maximum spacing between points was less than 0.3 nm^{-1} . Exchange and correlation were treated under the local-density approximation [27] and full structural relaxation meant that no ionic force exceeded 0.2 eV/nm.

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- [28] The three configurations derived from the bulk were constructed by extracting columns of atoms along the [100] direction. (a) From sphalerite, a 6 atoms repeat unit, (b) from wurtzite, an 8 atoms repeats unit, and (c) also from wurtzite a 12 atom repeat unit. After complete structural optimization their stabilities relative to the experimentally derived structure were (a) 0.17, (b) 0.17, and (c) 0.03 eV/atom, respectively.
- [29] The gap between occupied and unoccupied states for the four structures considered were (a) 1.3 eV, (b) 1.3 eV, (c) 1.9 eV, and (d) 1.2 eV. It is accepted that DFT underestimates the real band gap by ca. 30%.
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