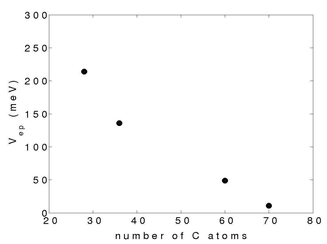
C_{28}-derived Molecular Solids: Structure, Doping & Electron-Phonon Interaction

Nichols A. Romero, Jeongnim Kim, and Richard M. Martin

Department of Physics, Materials Research Laboratory and
Materials Computation Center, University of Illinois, Urbana, IL 61801

Motivation and Objective

Motivation: Recall that $T_c \sim \exp(-1/\lambda)$, and $\lambda = N(0) V_{ep}$ for molecular solids.



Smaller fullerenes have a larger electron phonon interaction potential:† $V_{ep} \propto$ curvature‡

$$V_{ep} = \sum_{\nu} \frac{1}{M\omega_{\nu}^2} \frac{1}{g^2} \sum_{i,j}^{g} |\langle i|\varepsilon_{\nu}\cdot\nabla V|j\rangle|^2$$

Objective: Find C_{28}-derived molecular solids which are potential high-T_c superconductors.

†. Figure data taken from N. Breda *et al*., PRB **62**, 130 (2000) and references therein
‡. V. H. Crespi, PRB **60**, 100 (1999).

How to make a fullerene superconductor?

In the spirit of C_{60}:

Step 1: Choose a small fullerene with a large V_{ep}. Try to do better than C_{60}.

→ Next most abundant fullerenes are C_{36}† and C_{28}.

Step 2: Make a molecular solid with weakly broadened bands resulting in a large DOS at the band edges.

→ Need a close-shell molecule with a large gap, $C_{24}B_4$, $C_{24}N_4$, $C_{28}H_4$, and then find a solid that weakly interacting solid..

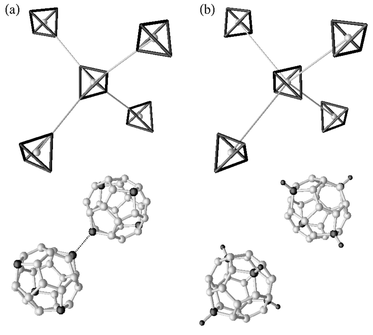
Step 3: Electron-dope the conduction band within a rigid band donor picture picture.

→ Intercalate alkali atoms into solid.

† M. Cote et. al, Phys. Rev. Lett. **81**, 697 (1988).

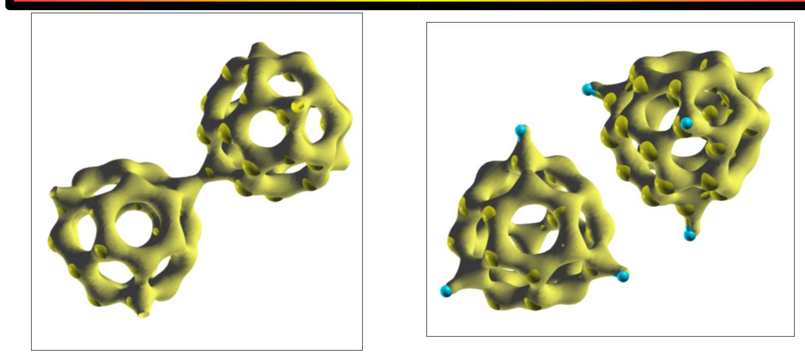
Hyperdiamond Solids

Hyperdiamond (HD) solids are diamond lattices with fullerene (tetrahedral symmetry) as a basis.



Schematic diagrams of the 1st nearest-neighbor (n.n.) in the HD structures (top) with examples of pairs of C_{28}-derived molecules shown below. The lattice sites in the solid are highlighted by the grey spheres enclosed in the tetrahedra. The two distinct orientations of the constituent molecules are represent by those of the tetrahedra. The n.n. pairs show two distinct bonding configurations:
(a) *apex-bonded* C_{28} HD forms covalent bonds†
(b) *face-bonded* $C_{28}H_4$ HD forms weak bonds
†E. Kaxiras et. al, Phys. Rev. **B** 49, 8446 (1994).

Covalent vs. Molecular Solid



Isocharge density surface for (*Left*) apex-bonded C_{28} HD and (*Right*) face-bonded $C_{28}H_4$ HD. Notice the lack of bonds in the molecular solid $C_{28}H_4$.

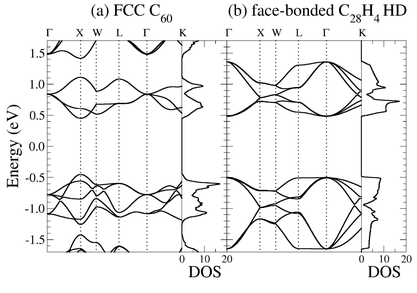
Structural and Electronic Properties

Ab initio calculations performed within DFT-LDA using SIESTA.

molecule	apex-bonded HD	face-bonded HD
$C_{24}B_4$	molecules break apart	molecules break apart
$C_{24}N_4$	covalent solid	hybridization
$C_{28}H_4$	sterically hindered	molecular solid

properties of solid/molecule	C_{60}	$C_{28}H_4$
lattice constant	13.9	16.3
conduction bands DOS (eV/spin/molecule)	8--10	4--5
binding energy (eV/molecule)	0.6	0.2
LUMO-HOMO gap (eV)	1.6	2
V_{ep} (meV) [Intramolecular phonons only]	64	169

Band Structure and DOS: C_{60} *vs.* $C_{28}H_4$

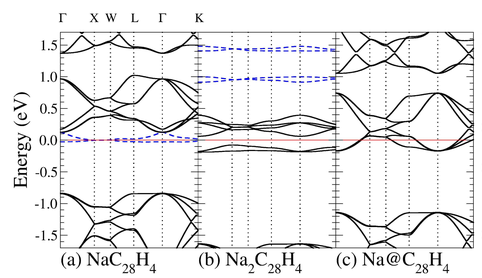


(a) For the C_{60} solid, the set of three (five) bands above (below) the gap are derived from the three (five)-fold degenerate LUMO (HOMO) of the C_{60} molecule.
(b) For the $C_{28}H_4$ solid, the set of six bands above and below the gap are derived respectively from the three-fold degenerate LUMO and HOMO for each $C_{28}H_4$ in the two-molecule cell.

Similarities include: weakly broadened bands & large band gaps.
NOTE: Units of DOS (states/eV/spin/cell)

Alkali doping of face-bonded $C_{28}H_4$ HD

Band structure comparison among three doping scenarios:
(a) Intercalation of Na atoms into tetrahedral site
(b) Intercalation of Na atoms into interstitial site between opposing six-membered rings on n.n. $C_{28}H_4$
(c) Encapsulation of Na atom into the $C_{28}H_4$ cage



Legend: **Solid $C_{28}H_4$ bands**;
Dopant bands;
Femi Level.

(a) Sodium and Hydrogen *s* states hybridize lead to dopant bands at Fermi level.
(b) Lattice constant increases from 16.3 Ang. to 18.1 Ang; Jahn-Teller Effect in $C_{28}H_4^-$ leads to a gap opening in the solid.
(c) Ideal doping case → rigid band donor

T_c for Solid $Na@C_{28}H_4$

The superconducting transition temperature T_c can be estimated using McMillan's solution to the Eliashberg Equations:

$$T_c = \frac{\omega_{\ln}}{1.2} \exp\left[-\frac{1+\lambda}{\lambda-\mu^*(1+0.62\lambda)}\right]$$

1. $\mu^* \approx 0.22$ (for C_{60} and $C_{28}H_4$)
2. $\omega_{\ln} \approx 1000$ K (for C_{60} and $C_{28}H_4$)
3. λ ($Na@C_{28}H_4$) $\approx 1.5\lambda$ (K_3C_{60})
4. T_c(K_3C_{60}) = 19.3 K leads to λ (K_3C_{60}) = 0.84
5. T_c($Na@C_{28}H_4$) $\approx 3T_c$(K_3C_{60}) $\approx$ 58 K

Estimated T_c for $Na@C_{28}H_4$ is higher than that of Cs_3C_{60} (40 K).

Conclusions

1. $C_{28}H_4$ forms a molecular solid similar to C_{60}.
2. Conventional doping of alkali atoms into interstitial sites in $C_{28}H_4$ solids is problematic.
3. Endohedrally doped $C_{28}H_4$ may superconduct with $T_c \approx 58$ K.

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