Superconductivity in doped column-IV semiconductors: clathrates, diamond and silicon

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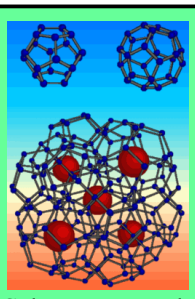
Column IV covalent clathrates



Barium-intercalated silicon clathrates are superconducting with a T_C of 8 K [Tanigaki et al., Nature Materials 2, 653 (2003)]. Calculations [1] show that the phonons involved in the transition are those of the silicon network, while Ba plays the role of dopant. It is the first exemple of a superconducting transition in doped column IV sp3 semiconductors. They are precursors of the superconudcting transition in doped carbon and silicon diamond..

Column IV covalent clathrates are composed of face-sharing X_n cages (X=Si,Ge and n=20,24 or 28). All atoms exhibit the sp^3 hybridization as in the diamond phase (Si-2). However, contrary to Si-2, the network can be doped, or intercalated, by incorporating atoms (Ba, Na, etc.) at the cage center.

In the case of the (hypothetical) carbon clathrates, the electron-phonon coupling is much larger than in fullerenes, an evolution related to that of the hybridization from π-bonding to σ-bonding.

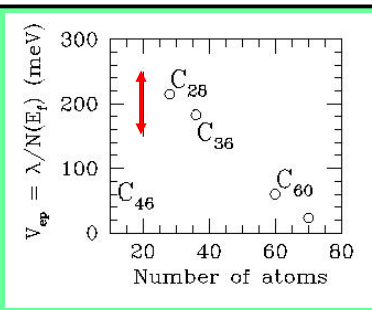


Fig: evolution of the electron-phonon potential as a function of fullerene size.. In red, the values obtained for the hypothetical carbon clathrates.

Doped diamond

Our predictions concerning sp^3 carbon-based systems have been confirmed by the discovery of a superconducting transition in heavily boron-doped diamond [E.A Ekimov et al., Nature **428**, 542 (2004)]. Assuming substitutional doping (~3%), the band structure of diamond is characterized by a Fermi level located ~0.5 eV in the valence bands (degenerate behavior).

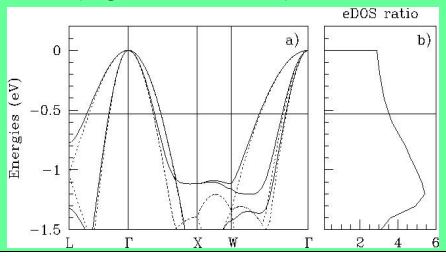


Fig: band structure of diamond: intrinsic (dashed lines)) and doped (full lines). The Fermi level is the horizontal line (supercell calculations).

Calculations [2] show again that the e-ph coupling is extremely large in such systems, much larger than in fullerenes or in MgB_2. Surprisingly, most of the e-ph coupling originates from the localized boron vibrational modes.

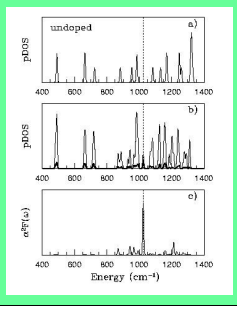


Fig: theoretical phonon spectra at zone-center. (Top) pristine diamond, (center) B-doped diamond with projection on B-atoms highlighted, and (bottom) Eliashberg function peaked on the boron vibrational modes.

Doped cubic silicon

Using laser melting of cubic Si in a boron atmosphere, boron doped cubic silicon with dopant content in the 6% range can be achieved. Upon such doping, B-doped cubic silicon becomes superconducting with a transition temperature of the order of a few tenths of a Kelvin [3]. The good agreement between experimental and theoretical evaluation of the lattice parameter compression and the phonon spectrum, including high-frequency Si-B stretching modes, put strong evidences on the substitutional nature of boron incorporation even in this large doping limit. Calculations of the electron phonon coupling lead to a ~0.3 value for the coupling constant λ.

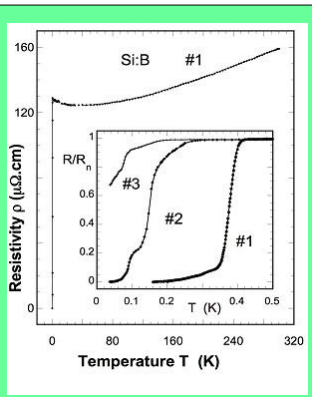


Fig: Resistivity vs temperature for three B:Si samples.

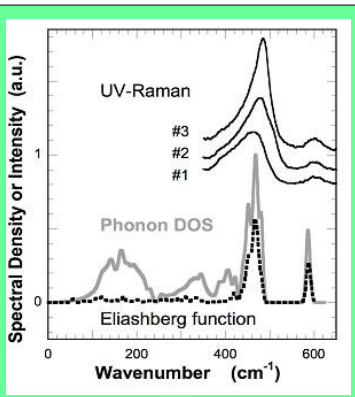


Fig: Experimental Raman spectrum and theoretical phonon density of states and Eliashberg function.

REFERENCES:

[1] D. Connétable *et al.*, Phys. Rev. Lett. **91**, 247001 (2003).

[2] X. Blase, Ch. Adessi, D. Connétable, Phys. Rev. Lett. **93**, 237004 (2004).

[3] E. Bustarret *et al.*, *Nature* (London) **444**, 465-468 (2006).