

SUBSURFACE COLLECTIVE ELECTRON STATES IN NANODIAMOND

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Despite relative simplicity of covalent crystals electronic structure, significant discrepancies between theory and experiment are still present for nanodiamond particles, e.g. nature of paramagnetic invariant and disordered shell cannot be described even qualitatively. It is possible to resolve the problem and provide qualitative agreement with experiment if one takes collective electron states into account. Collective electron states are widely used and accepted when it comes to metallic compounds, while applicability of the concept to semiconductor and dielectric materials remains at least questionable. In our research we have studied existence and localization of the collective electron states in nanodiamond particles both by solving one-particle one-dimensional Schrödinger equation in Kronig-Penney potential and by *ab initio* computations of ground state wave functions and eigenenergies of diamondoids $C_{123}H_{100}$, $C_{211}H_{140}$ and $C_{302}H_{172}$ at the DFT R-B3LYP level of theory with 6-31G(d,p) basis set done in the GAMESS-US software package.

Three distinct classes of collective electron states have been found: collective bonding orbitals resembling 3D-modulated particle-in-a-box solutions; subsurface-localized binding states for deformed nanodiamond and surface-localized nonbonding conductive Tamm's states.

Existence of deformed surface layer is experimentally proved by PEELS, EPR and NMR experiments. It was shown by our calculations that this deformation results in localization shift of lower binding orbitals from core to thin subsurface layer (Fig. 1).

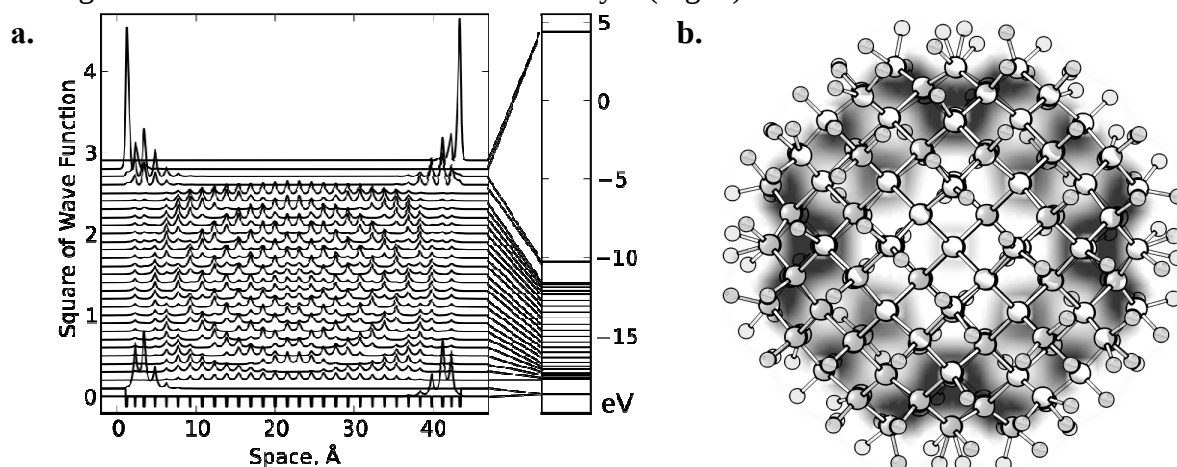


Fig. 1. (a) Wave functions for 1D chain of 30 potential holes with smooth deformation of side holes (binding orbitals model) (b) map of subsurface orbital in $C_{159}H_{124}$ diamondoid.

This model agrees with experimentally determined subsurface localization of unpaired spins. We suggest that spread nature of collective bonding states may increase significance of spin-density fluctuations and lead to singlet instability of the ground state solution like in the well-known case of π -conjugated polyene chains. We would like to emphasize that paramagnetic invariant behavior of nanodiamond with respect to field strength and temperature is explained if spin density fluctuations of deep bonding states are considered, while subsurface localization of these states is consistent with g-factor independence of chemical modification of nanodiamond surface. Subsurface collective electron states localization and particle deformation are closely interrelated, i.e. self-consistency between wavefunctions and nuclear positions is satisfied in nanodiamond molecule.

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