Electron Spectroscopy of NanoDiamond Surface States

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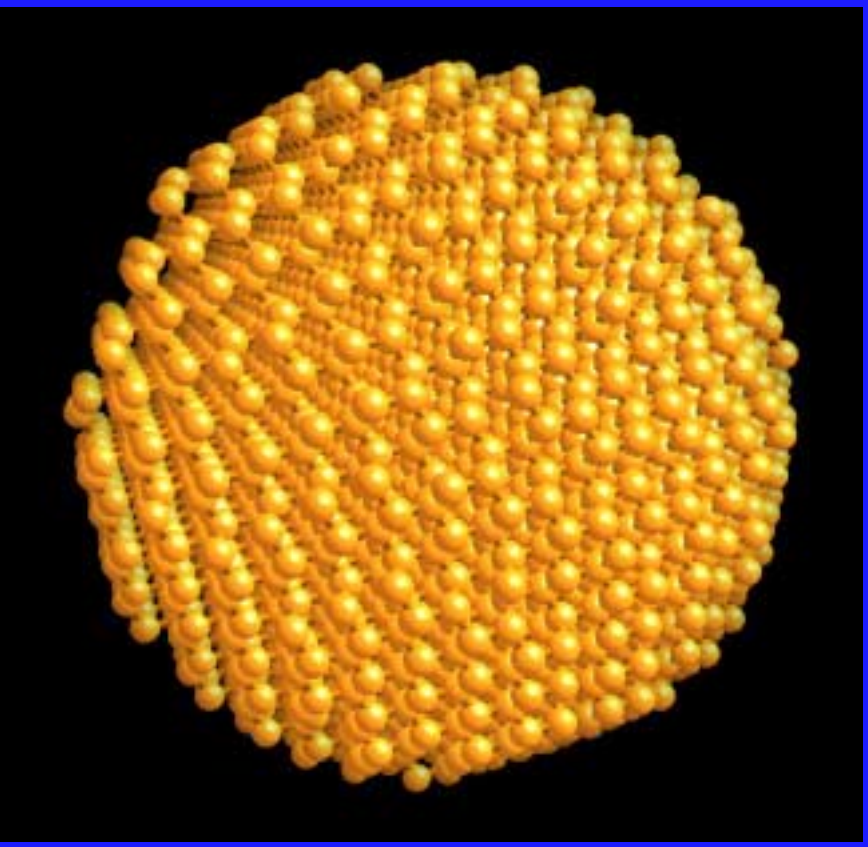
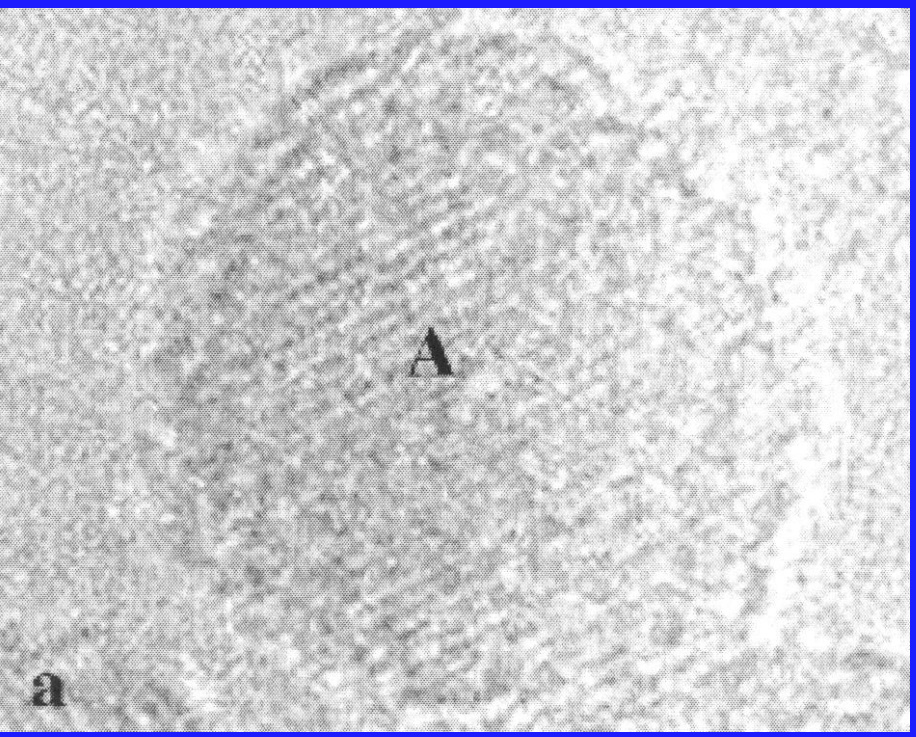
NanoDiamond Quantum Dot

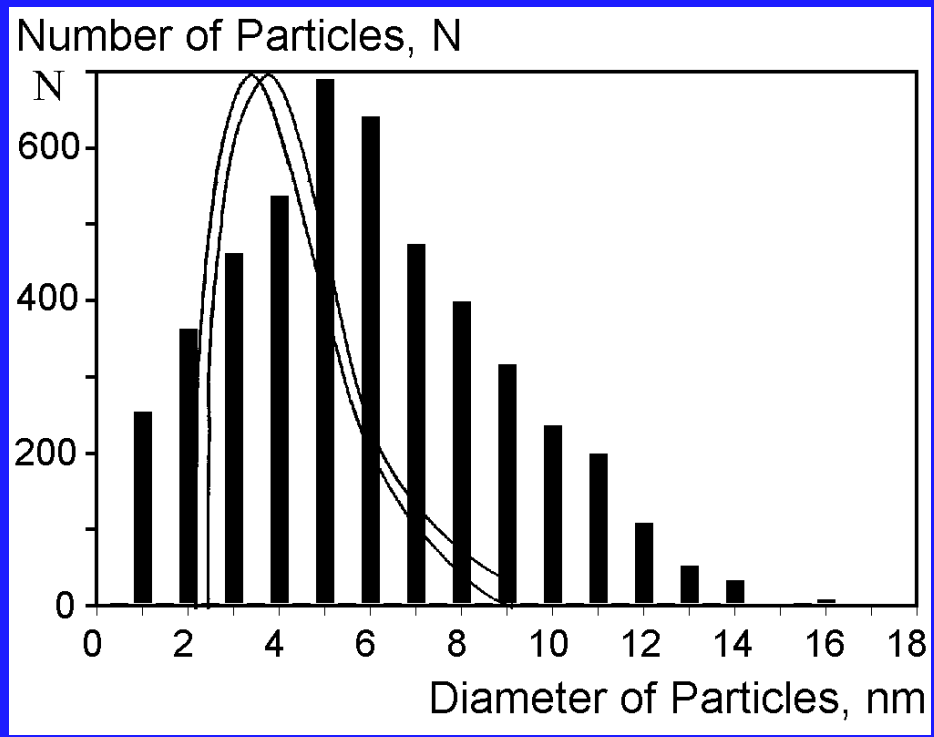


- Diamond quantum dot
  - V. S. Gorelik 1995
    - Phys Solid State, **37**, No 10
  - It was earlier in Sci folklore
    - Exact ref is not published
  - NDQD is introduced in 2001
    - Alicante (Spain)
  - V.V. Zhirnov et al. 2002
    - Lyon & Saratov
- ND
  - 5 nm, ~ 60,000 electrons, de Broglie energy ~ 0.1 eV

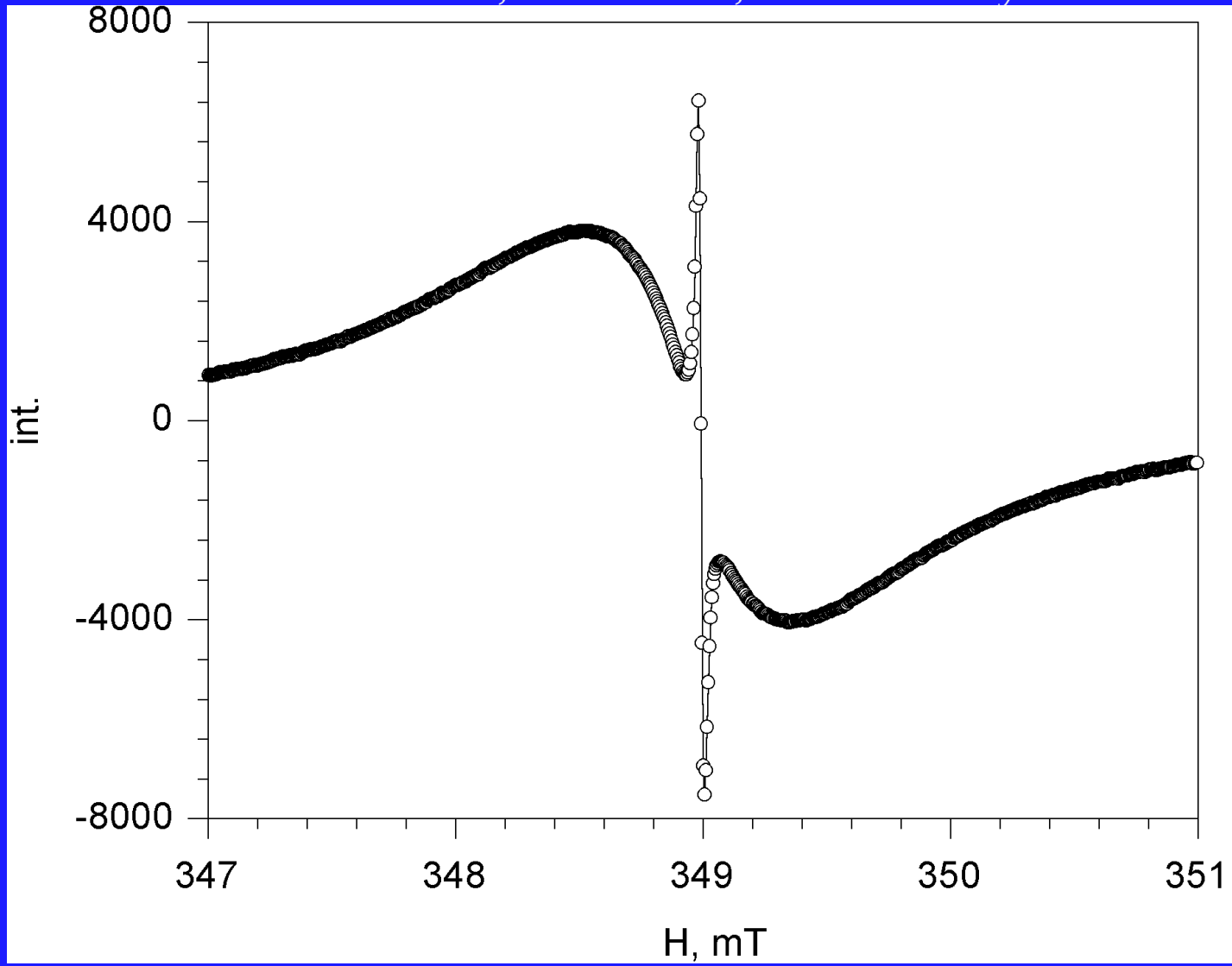
Molecular-mass (size) distribution

- ND 4 nm in diameter
- Size distribution of ND





The EPR spectra of ND

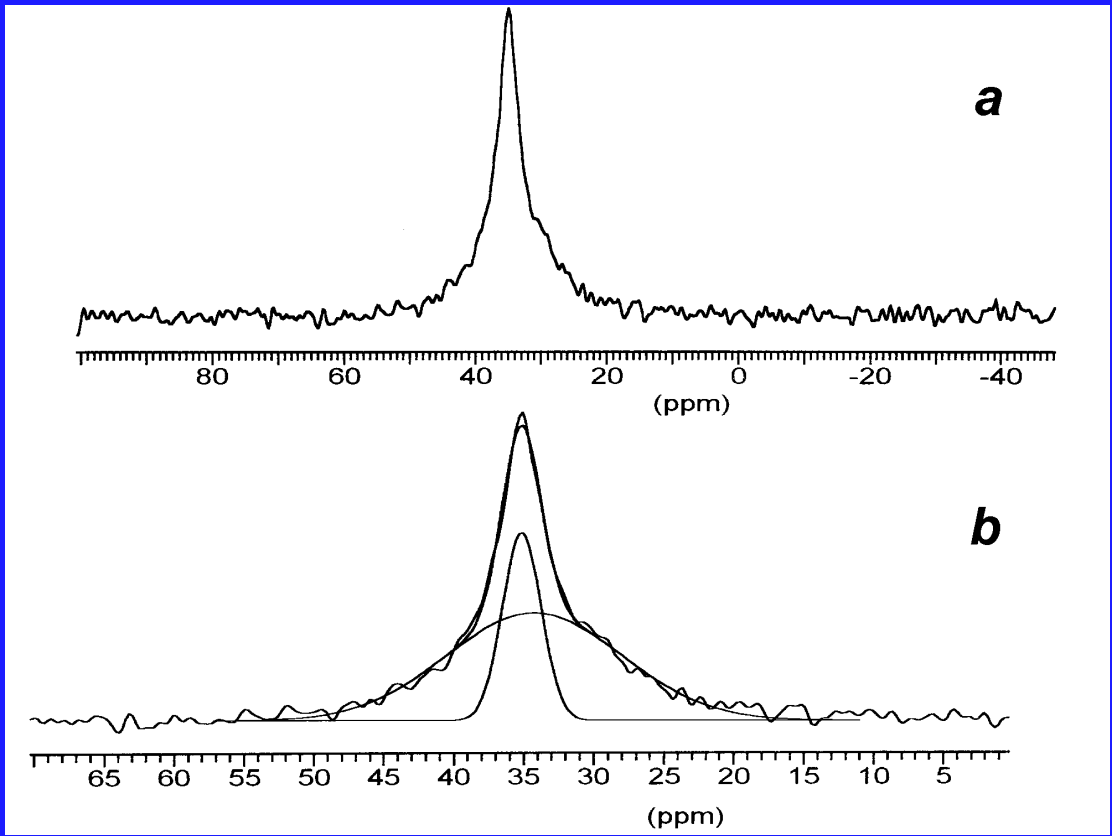


- **Central part** of the **EPR spectrum** (EMX EPR Bruker) **of ND** in the NDC 10 nanocomposite **with** the **Li standard (*g* = 2.0023).** The scan and the modulation are 50 and 0.01 mT.

Paramagnetic invariant of ND

- The concentration of unpaired spins (N) is equal to $4*10^{19}$ spin / g of the nanocomposite, powder etc.
- N is about one spin per nanodiamond particle.
- g-value, the magnitude of $g = 2.0027 \pm 10^{-4}$
- EPR linewidth, $\Delta H = 0.86 \pm 0.02$ mT.
- These values remain constant within the experimental error and are independent of the
  - temperature (77 - 1000 K),
  - composition,
  - structure,
  - and state of the nanodiamond surface.
- The paramagnetic invariant of ND exists

The ^{13}C NMR spectra of ND



Nos.	Position		Width		Amplitude, arb. units	Relative integral intensity
	Hz	ppm	Hz	ppm		
1	3532	35,104	278	2,763	4,18	27,83
2	3445	34,236	1261	12,532	2,39	72,17

- The ^{13}C NMR were taken using a CXP-400 Bruker spectrometer with a magnetic field H_0 = 9.4 T at a frequency of 100.6 MHz.
- The interaction with protons was suppressed, and the rotation under the magic angle at a frequency exceeding 1 kHz was used.
- The number of spectra accumulated attained 500.
- Decomposition into two Gaussian components:
  - 1 - 30% normal sp^3
  - 2 - 70% distorted sp^3

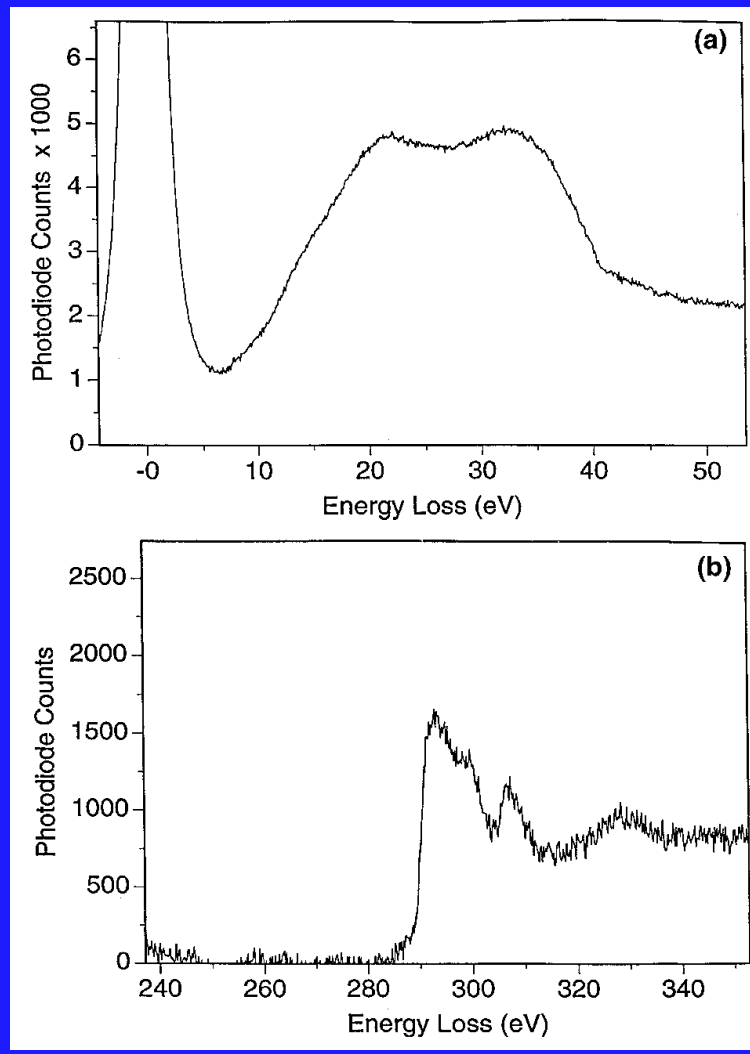
Interpretation of 1 free spin per ND

- (Traditional) The existence of local paramagnetic centers or dangling bonds is considered a conventional interpretation of one free spin per molecule (ND).
- (Novel) In addition, there are grounds to suggest that a collective unpaired electron can reside at surface Tamm levels that stabilize the de Broglie (associated) wave having a wavelength λ = 4 nm and an electron energy of about 0.1 eV.
- This implies that in each spherical particle consisting of ~ 10^4 carbon atoms, the neutralization of the surface charge (on the order of one electron per particle) is, probably, accompanied by the formation of a radical state of ND with a 1 / 2 spin.

EELS of ND

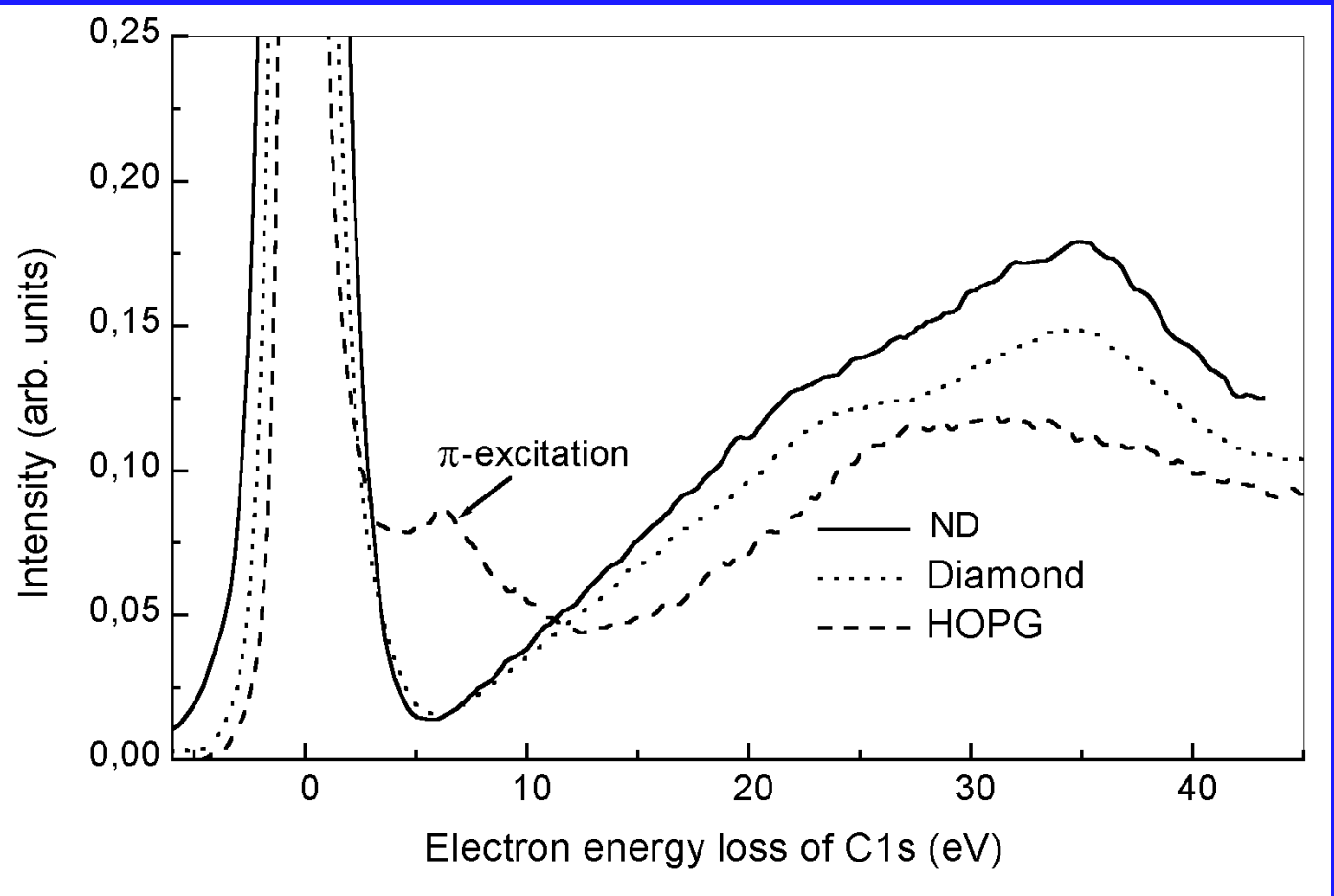
Low-loss (a) and core-loss (b) electron energy loss spectra of ND powder.

- The peak at 33 eV in the low-loss spectrum corresponds to the bulk plasmon in diamond, whereas the peak at 23 eV originates from the surface phonon.
- The size of the clusters as estimated from HRTEM and EELS is 4÷5 nm.
- Note that the line shape of K-edge in the core-loss spectrum does not display any evidence of the 1s to π^* transition at 294 eV which is the characteristic signature for the presence of sp^2 bonded carbon.



S. Prawer, K.W. Nugent, D.N. Jamieson, J.O. Orwa, L.A. Bursill, J.L. Peng. The Raman spectrum of nanocrystalline diamond *Chem. Phys. Lett.*, 332 (1-2), 93-97 (2000).

EELS of C1s XPS



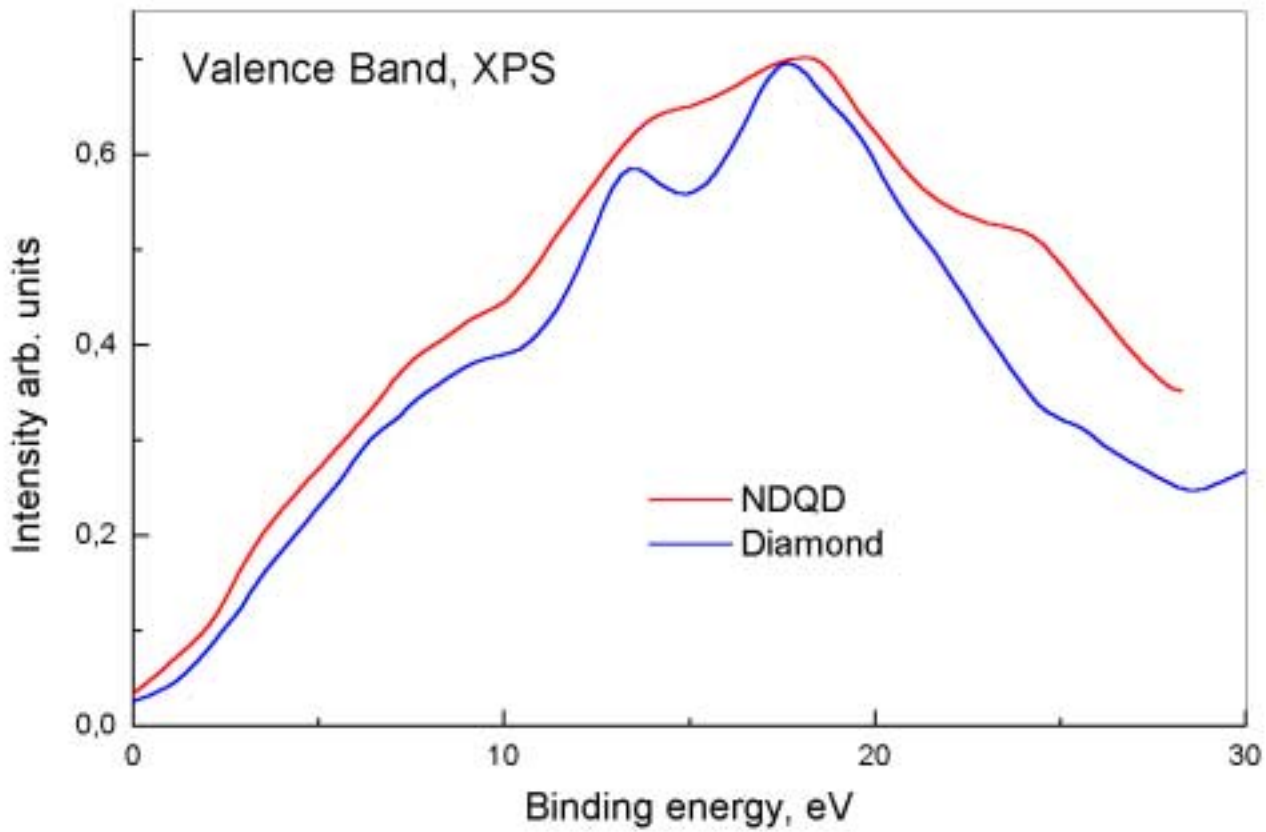
- There is no line of K-edge of ND at 294 eV
  - 1s to π* transition (1486.6 eV, X-ray excitation)

It is = core-loss spectrum of ND

- (100 keV electron excitation) of ND

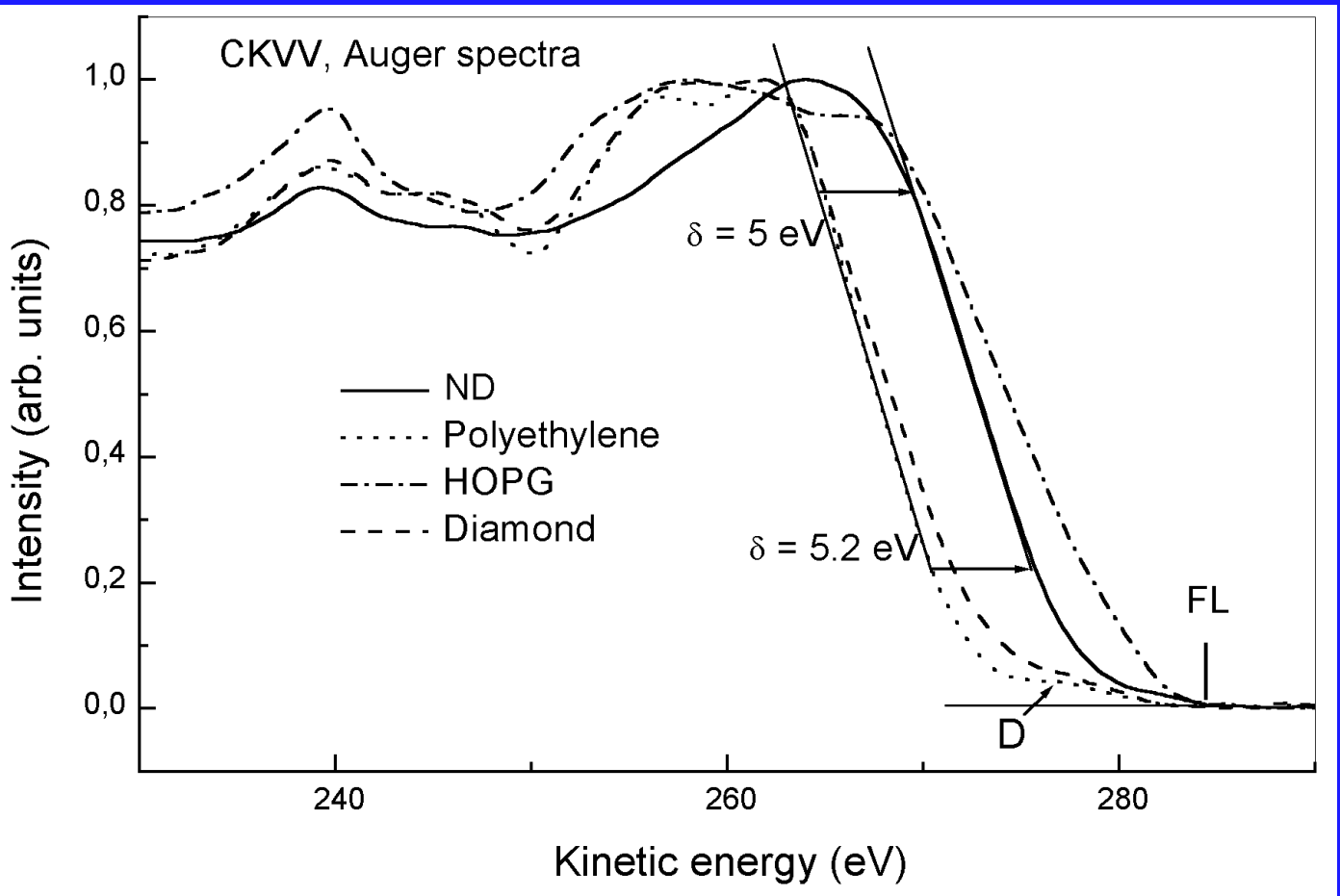
pure π bonded carbon is not presence in ND.

XPS valence band of ND



- XPS VB spectra of ND is in the consent with ^{13}C NMR data

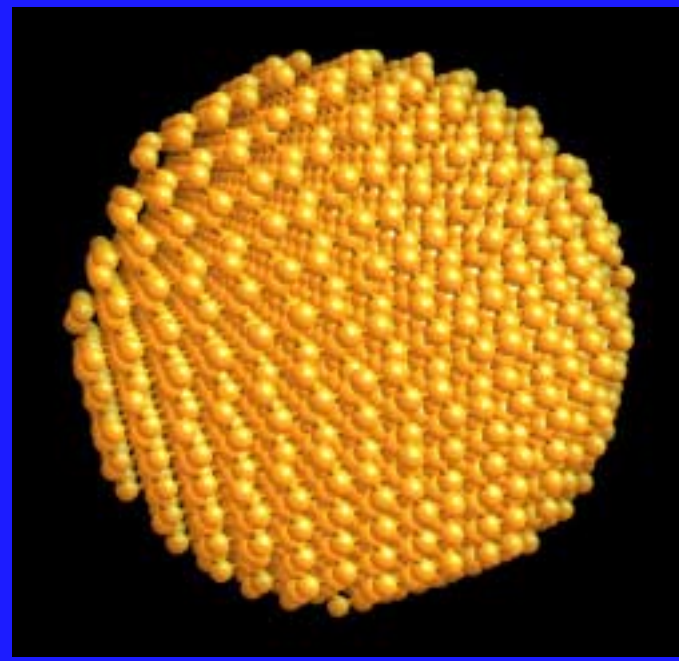
Surface electronic states of ND



According to CKVV Auger spectra the surface state of diamond is identical to that taking place on ND. Therefore we can think that uniform electronic state of ND (molecular diamond) is $\sigma_s^1\sigma_p^2\pi^1$.

CONCLUSIONS

- **NanoDiamond** is quantum dot (ball) and **has**
  - **Paramagnetic invariant**
  - **Surface plasmon**
  - **Auger decay invariant**
- Low-dimensional electronic states is
  - due to the collective formation mechanism
  - relay to Tamm surface electrons



- **ND is quantum dot** with shell ψ
  - ***ND is dot of diamond surface***