Nanoclusters as special structural form of matter

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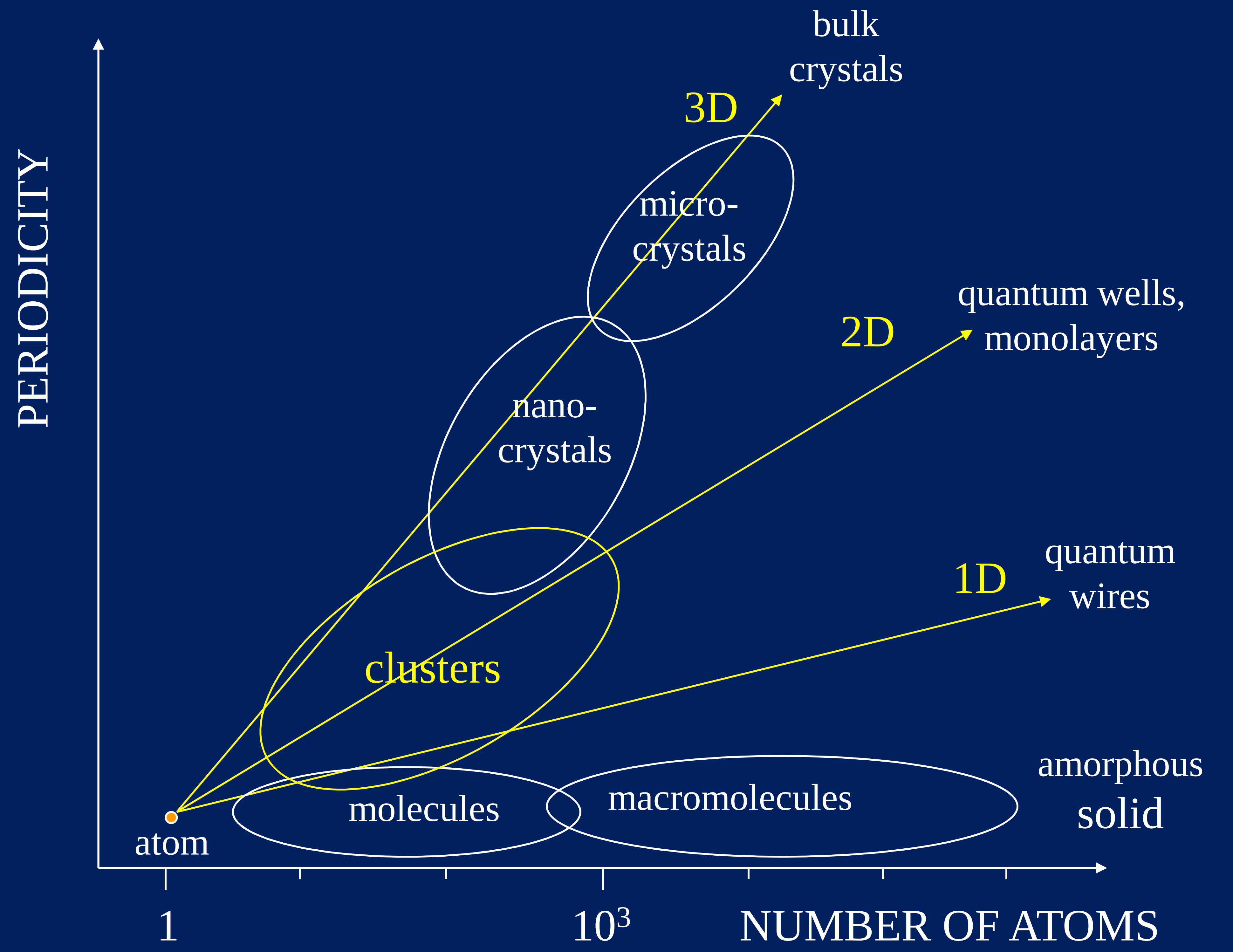
Outline

- Terms and definitions
- Classification of nanoclusters
- Preparation and characterization
- Specific properties of nanoclusters
- Magic numbers
- Examples of clusters of different types
- New kind of nanoclusters of $A^{II}B^{VI}$ compounds


PERIODICITY
bulk crystals
3D
micro-crystals
quantum wells, monolayers
2D
nano-crystals
quantum wires
1D
clusters
amorphous solid
macromolecules
molecules
atom
1
10^3
NUMBER OF ATOMS

Classification

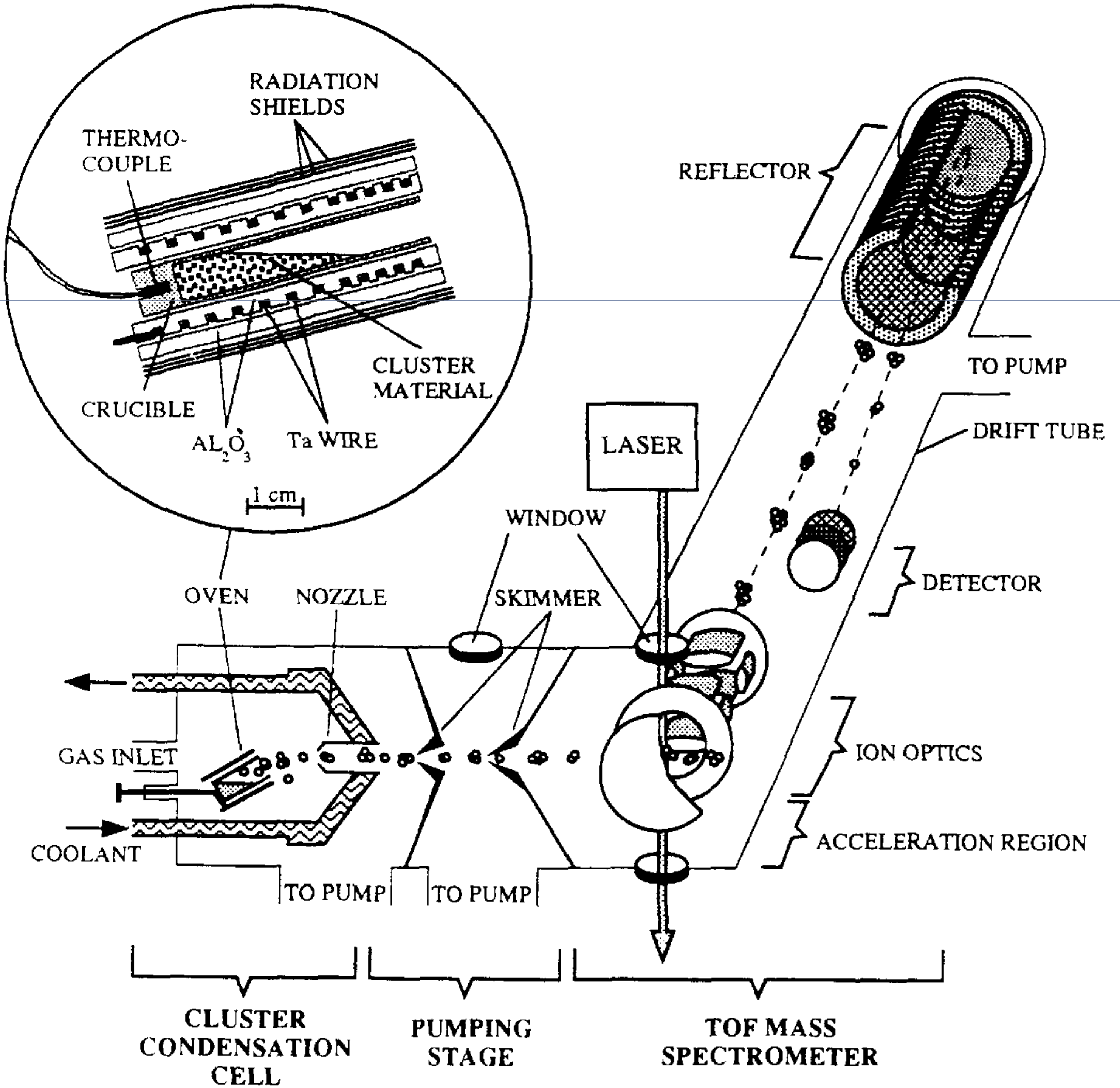
- by composition: atomic, binary, ternary, multinary
- by structure: pieces of bulk crystal, shell structures, special kinds of structure
- by bond types: covalent, ionic, metal, hydrogen, van der Waals

Preparation

- free clusters in vacuum or inert gas
- in colloid solution
- in solid matrix
- in pores of zeolite, opal etc.
- inside big molecules

preparation

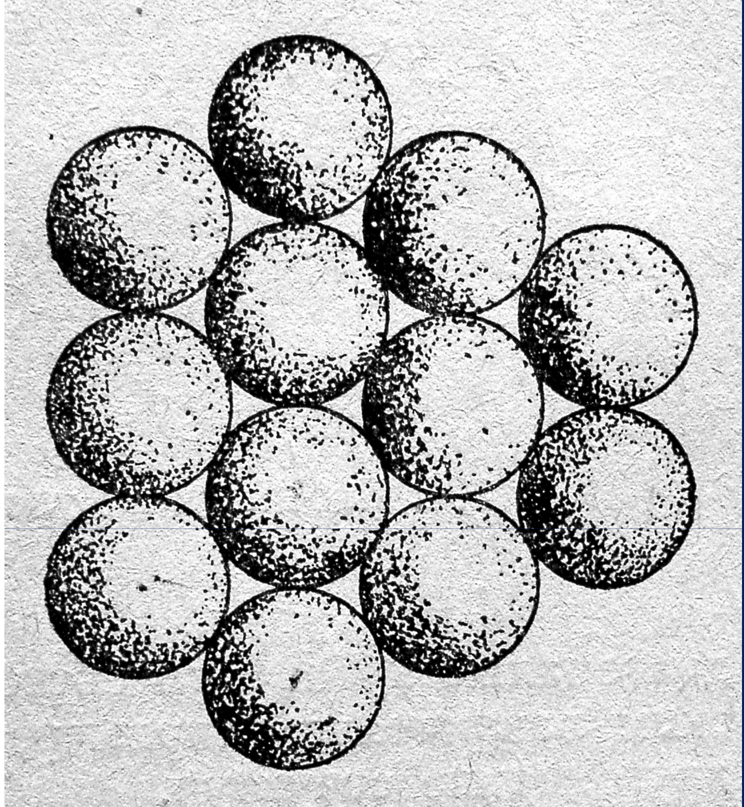
T.P. Martin / Physics Reports 273 (1996) 199–241

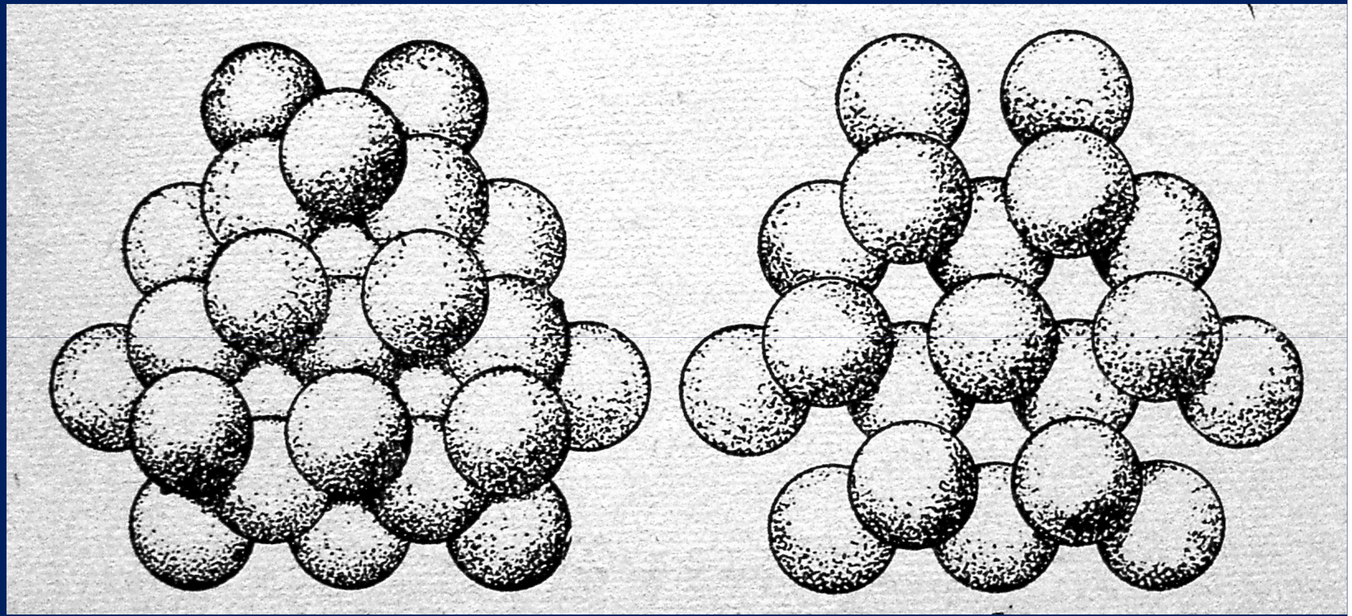


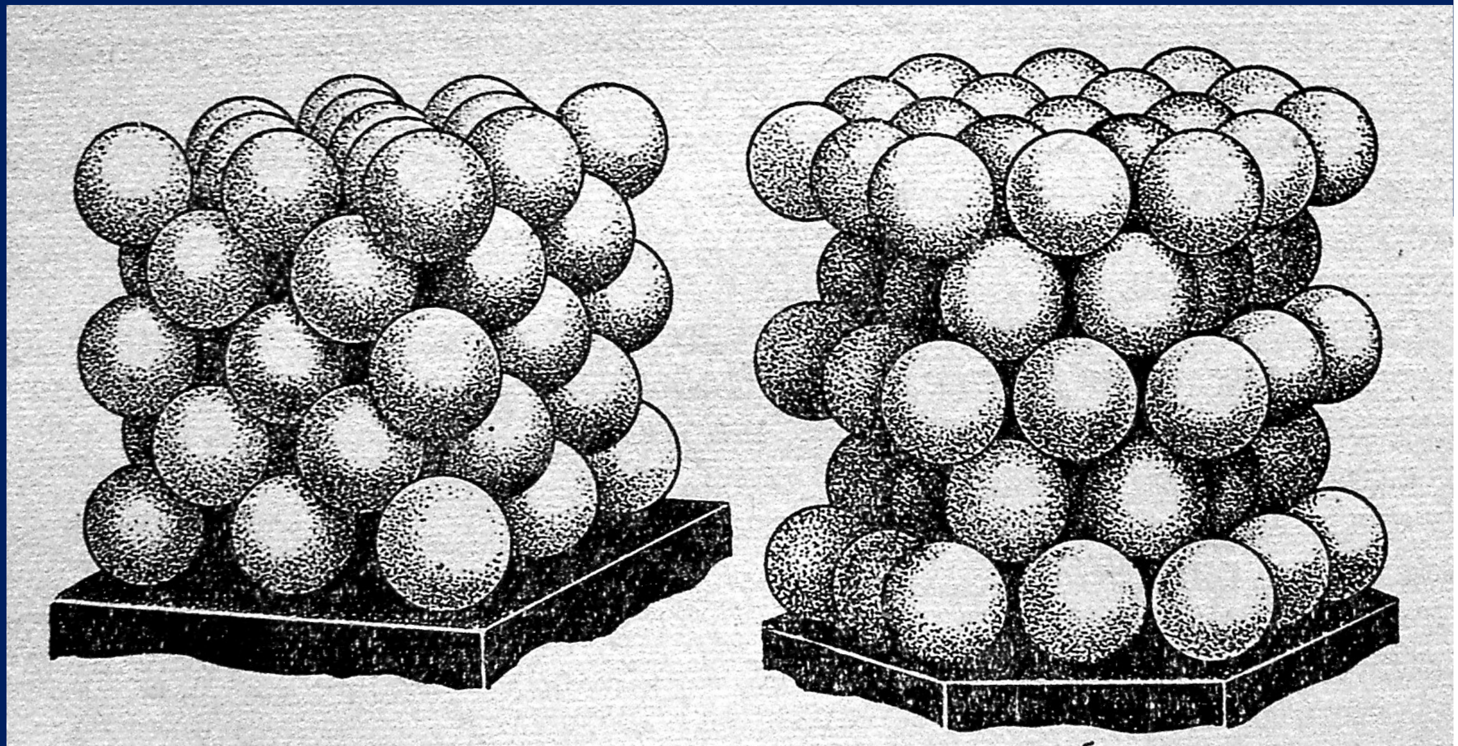
Specific properties of nanoclusters

- dense packing of atoms
- high symmetry
- formation of shell structures

dense packing of atoms



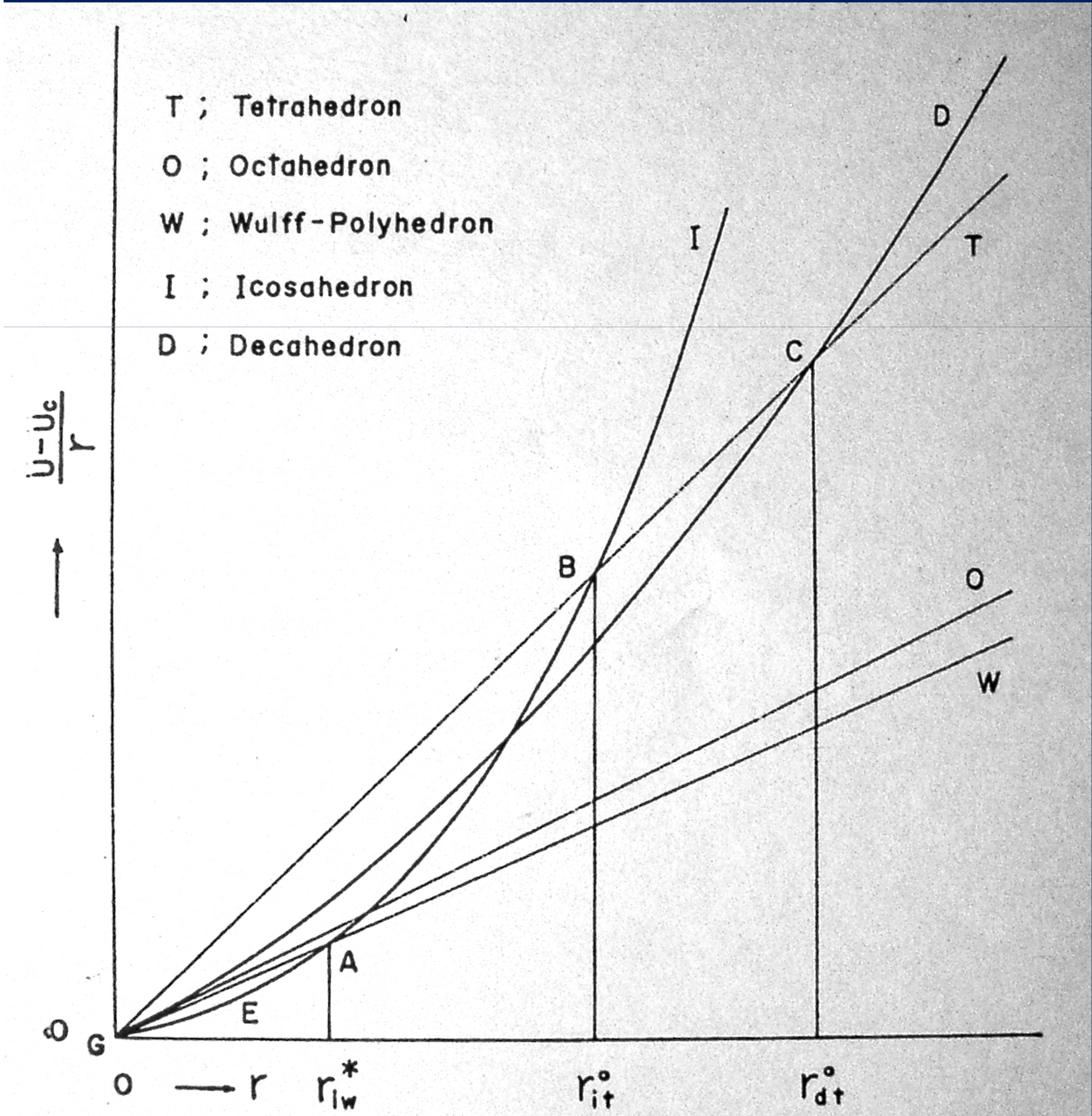




dense packing of atoms

dense packing of atoms

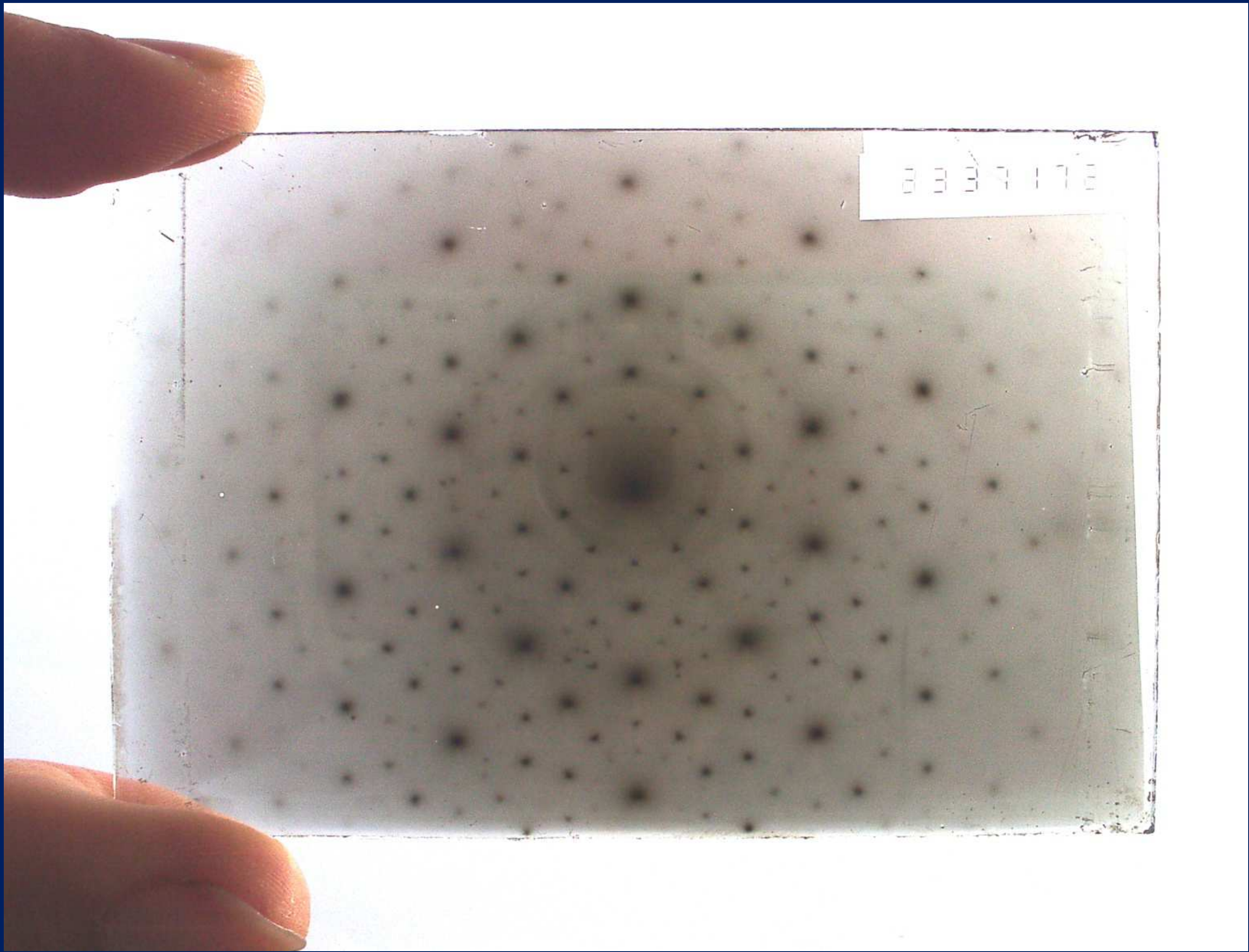
dense packing of atoms



Shozo Ino. Stability of Multiply Twinned Particles.
J. Phys.Soc.Japan 26 (1969)
1559

dense packing of atoms

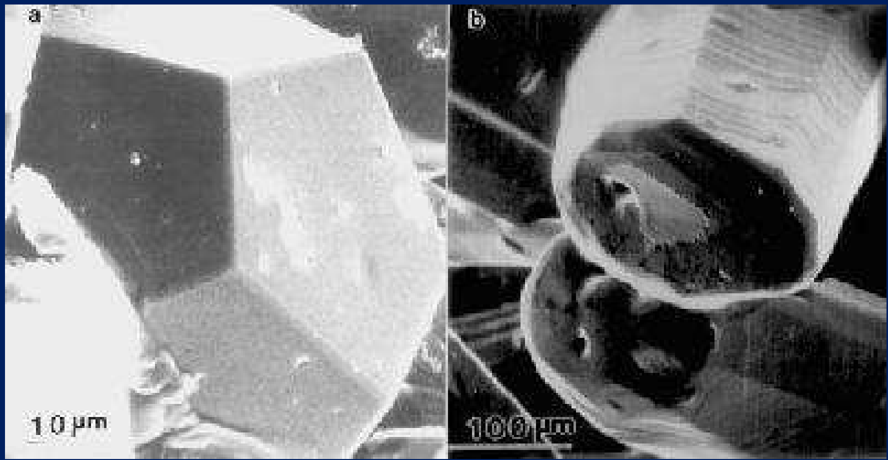
quasicrystals

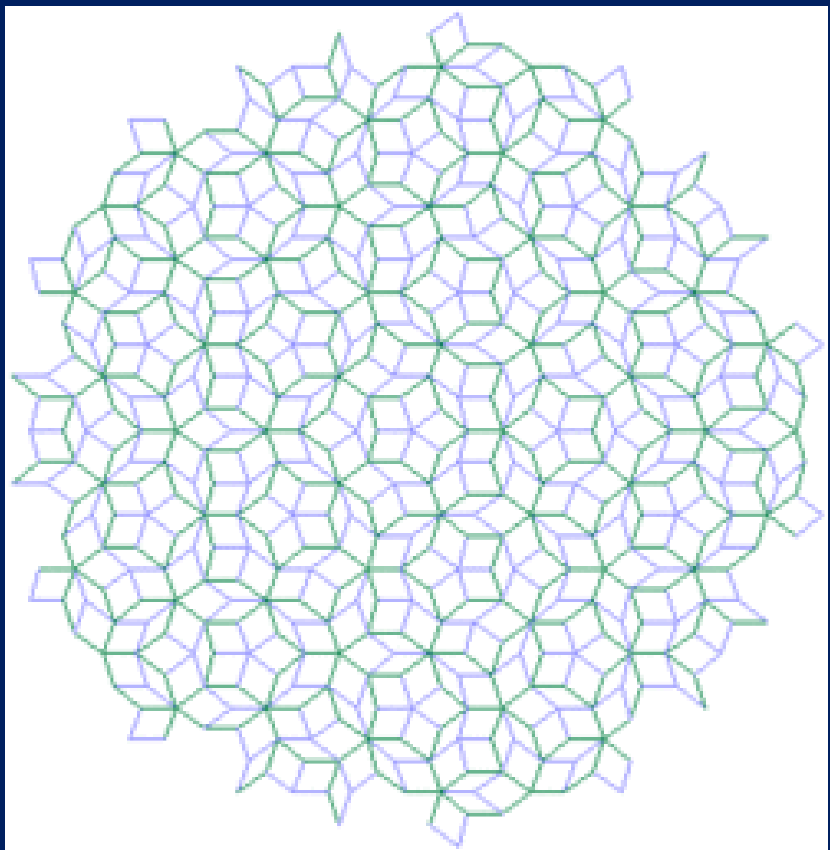


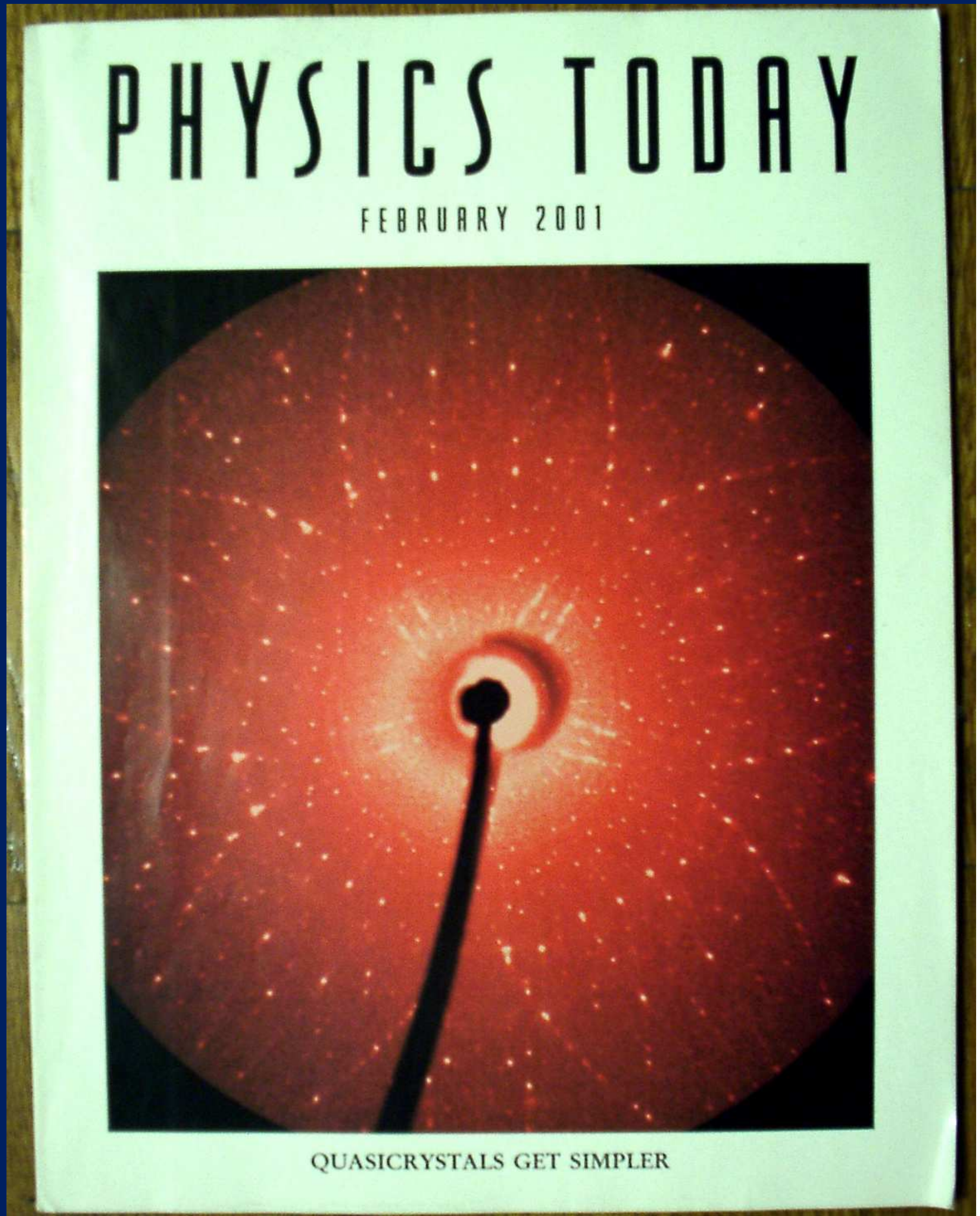
Al_6Mn

dense packing of atoms

quasicrystals







Magic numbers

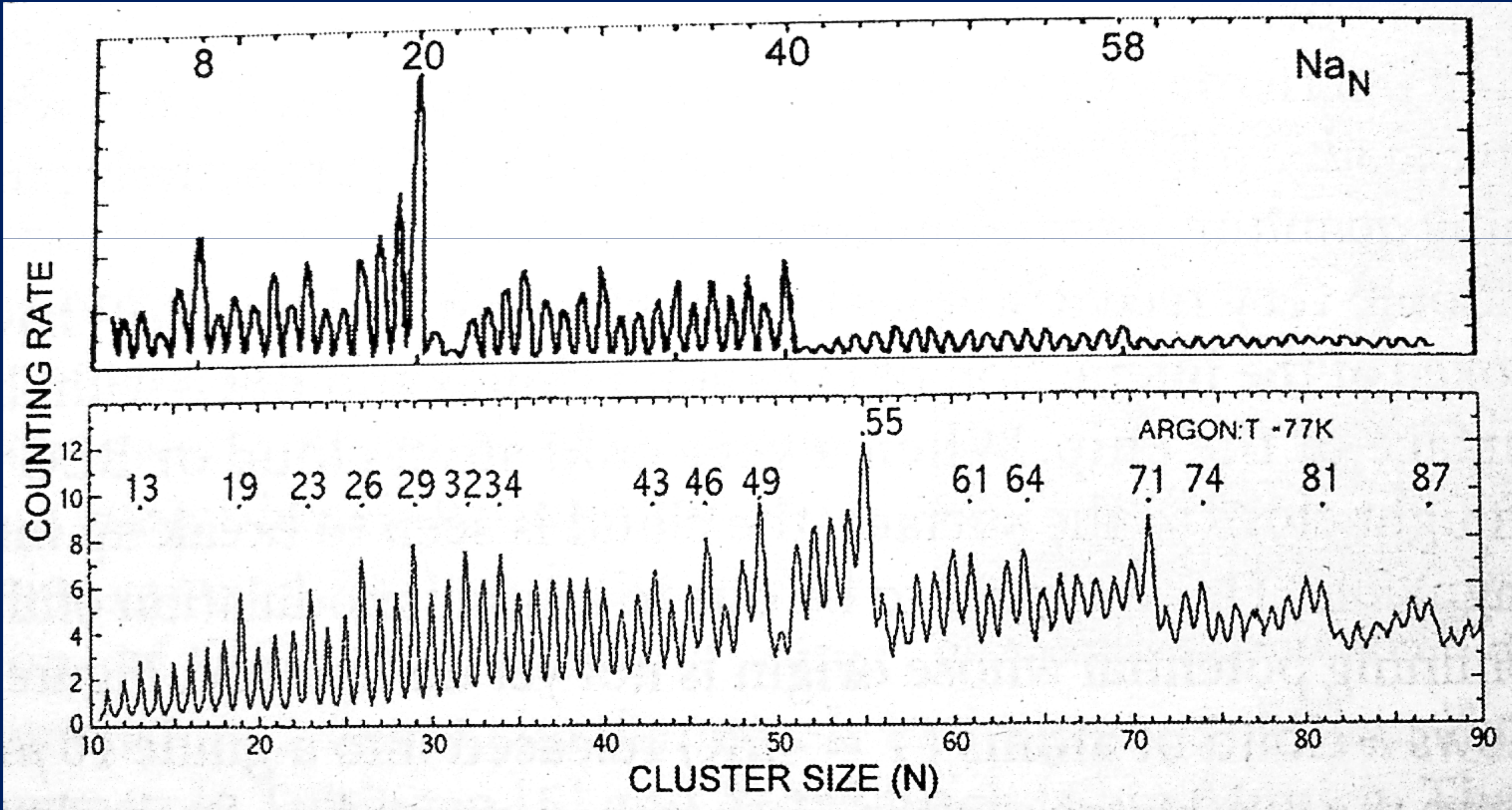
Known examples

- 2, 8, 20, 40, … (electronic shells)
- 4, 13, 55, 147…(shells of atoms)
- 20, 36, 60, 70, … (carbon fullerenes)
- 12, 16, 28, 36, … (binary fullerenes)

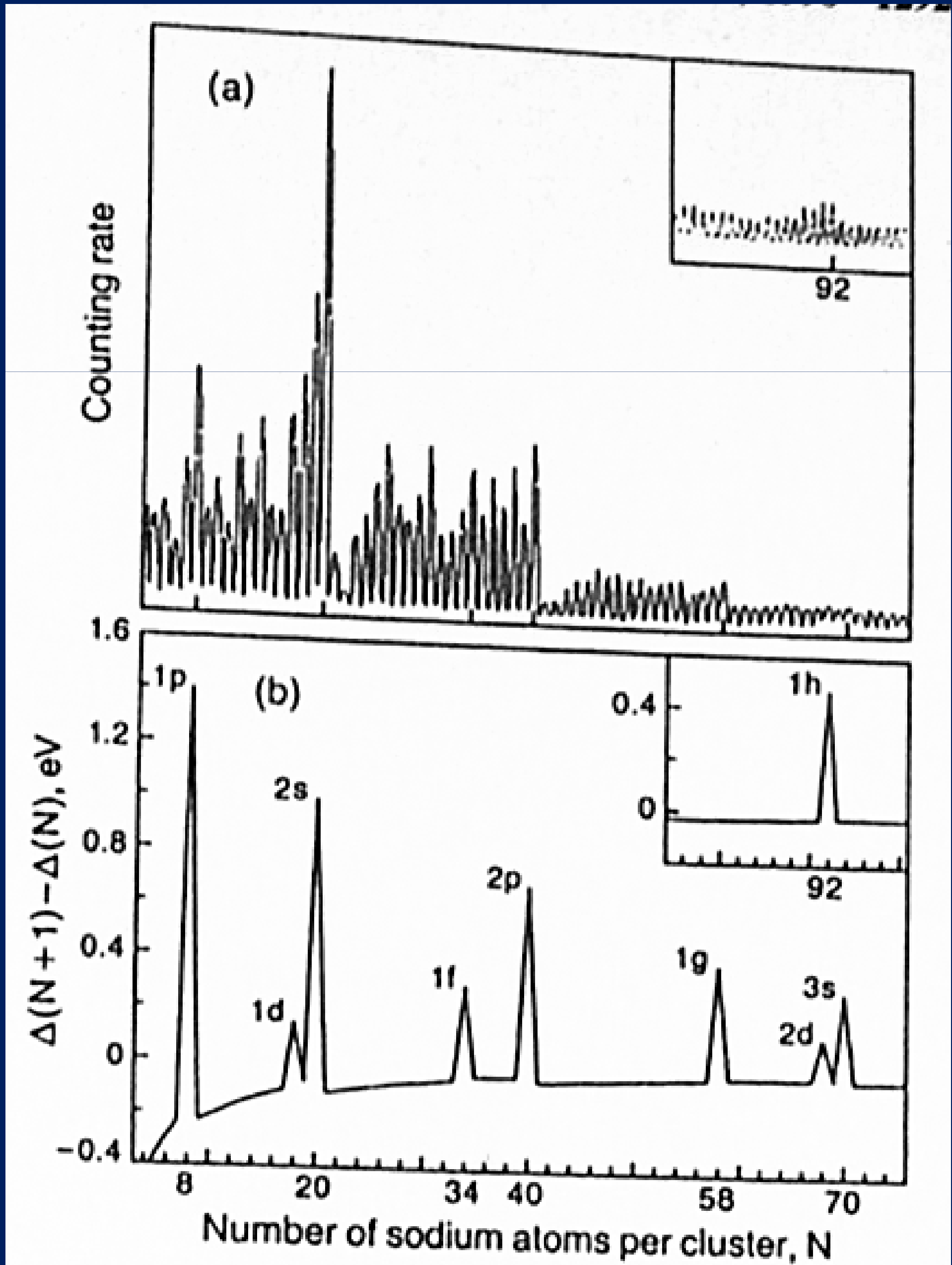
Recently found

- 13, 19, 33, 34, … ($A^{II}B^{VI}$ nested cages)

Magic numbers. Shells.

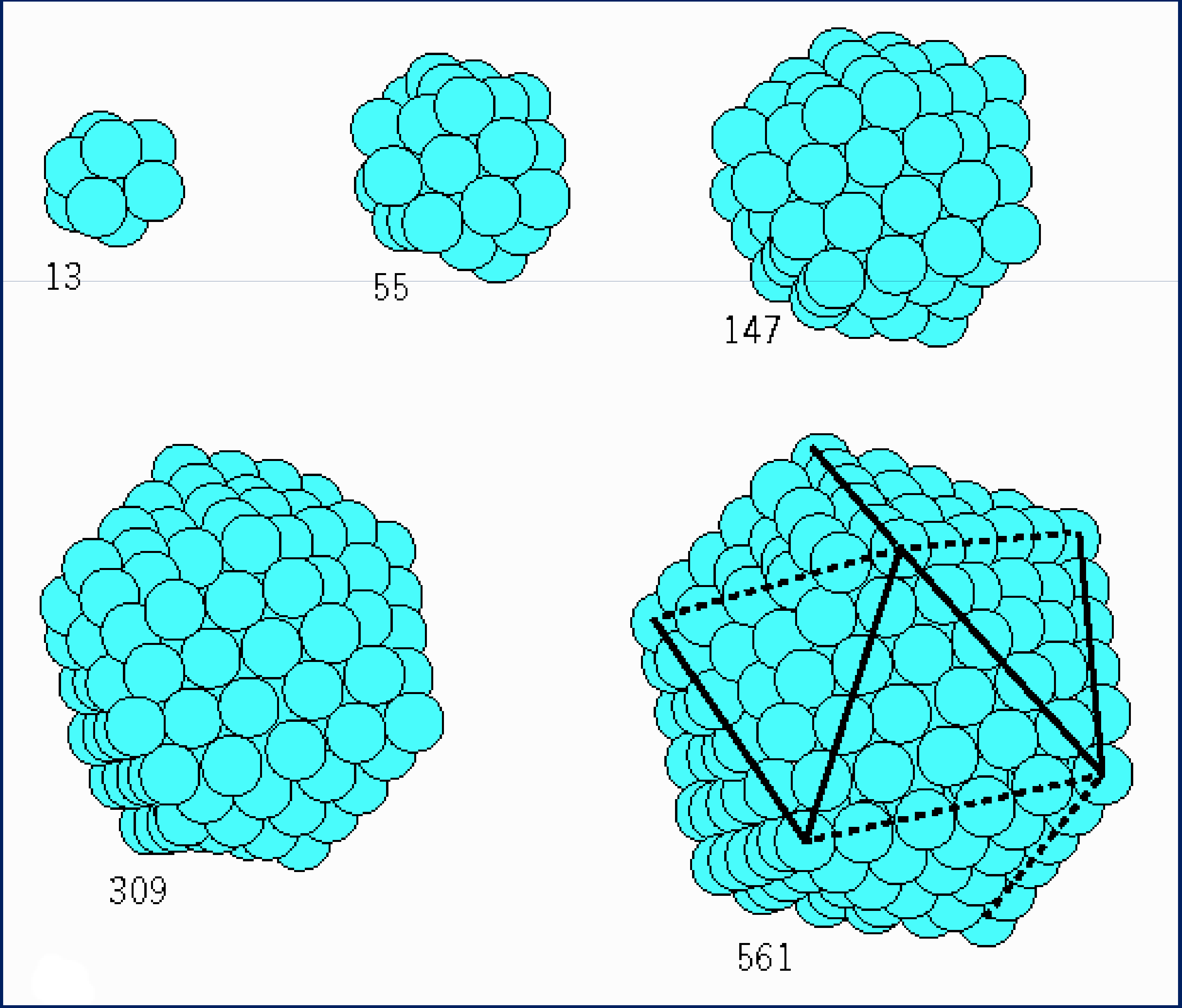


Magic numbers. Shells.



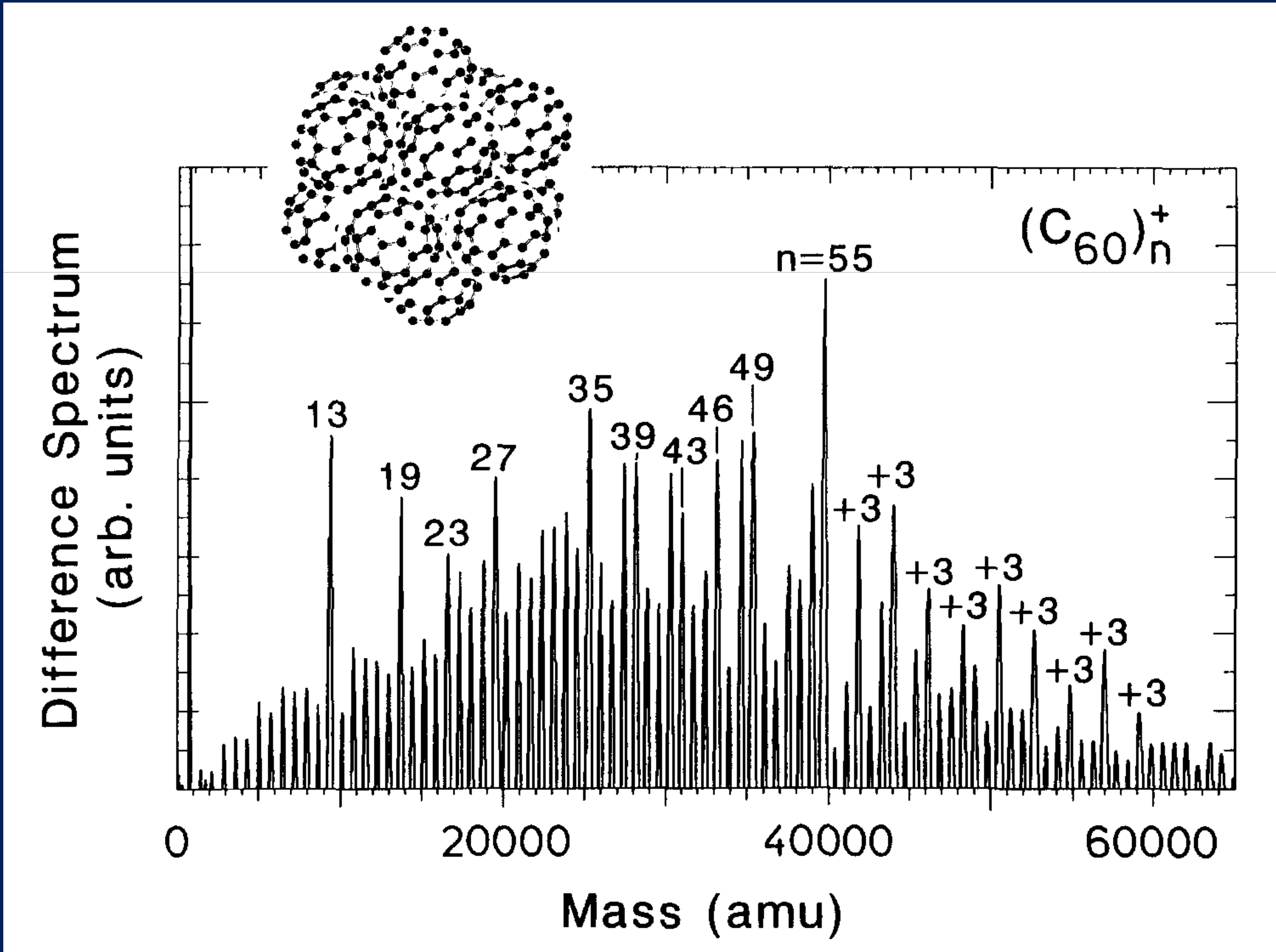
Knight W.D., Clemenger K, de Heer W.A. et al, Phys.Rev.Lett.1984, 52, 2141.

Magic numbers. Shells.



H. Haberland, ed., Clusters of Atoms and Molecules, vol. 1, Springer-Verlag, 1994

Magic numbers. Shells.

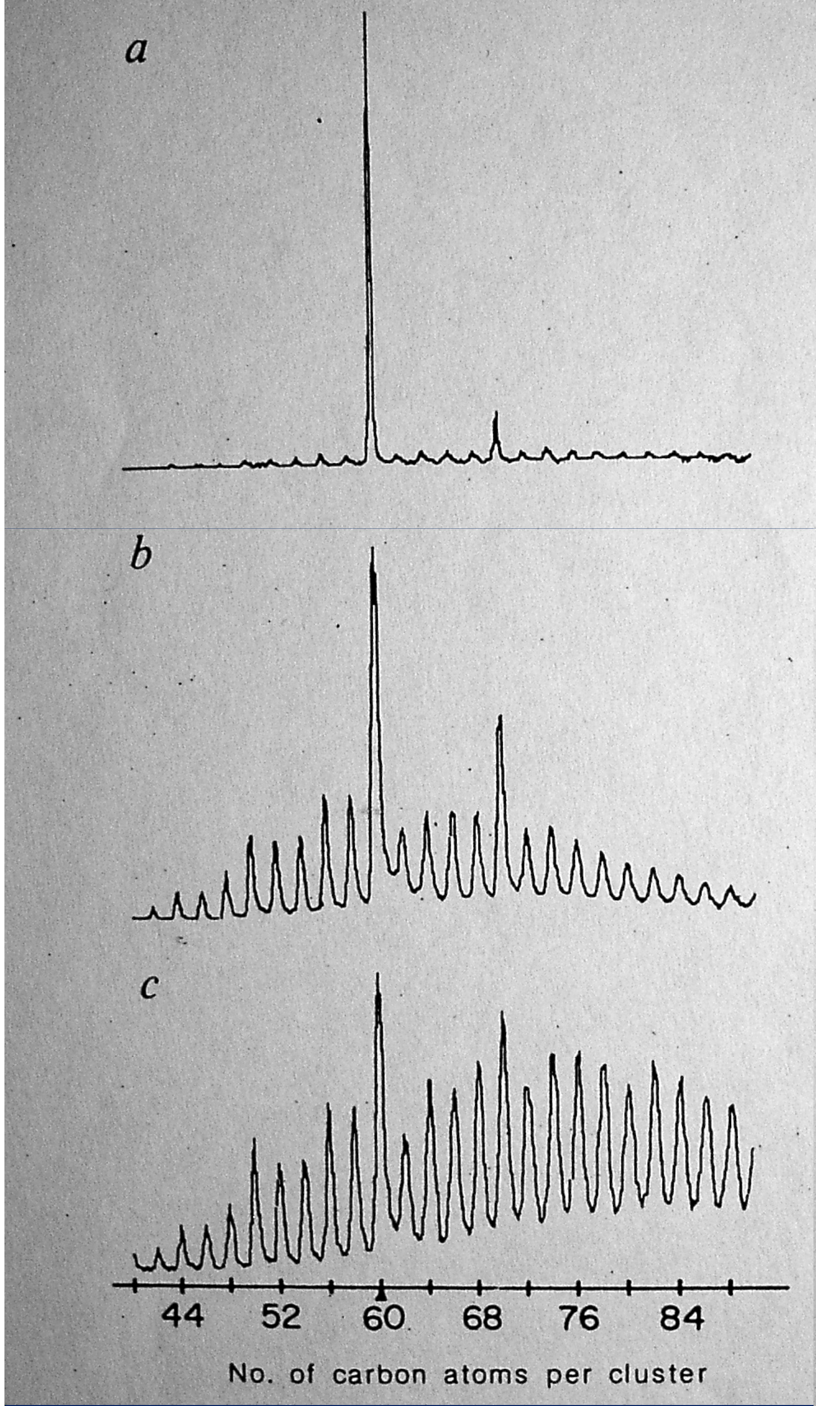


T.P. Martin 1 Physics Reports 273 (1996) 199-241

Examples of nanoclusters

- Carbon fullerenes (C_{20}, C_{60}, C_{70}, C_{84}, …)
- Si, Ge (nanocrystals, polyhedral silicon- and germanium-containing compounds)
- $Cd_{10}S_4(SC_6H_5)_{12}$, $Cd_{32}S_{14}(SC_6H_5)_{36} \cdot DMF_4$
- met-car clusters (Ti_8C_{12} , Zr_8C_{12} , Cr_8C_{12} , Nb_8C_{12} , Fe_8C_{12} , …)
- boron-nitride analogues of fullerenes - $(BN)_{12}$, $(BN)_{16}$, $(BN)_{28}$, $(BN)_{36}$, $(BN)_{52}$, ...

carbon fullerenes



C_{60}: Buckminsterfullerene

H. W. Kroto*, J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley

Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells[1], graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. This object is commonly encountered as the football shown in Fig. 1. The C_{60} molecule which results when a carbon atom is placed at each vertex

carbon fullerenes

TO NATURE

NATURE VOL. 318 14 NOVEMBER 1985

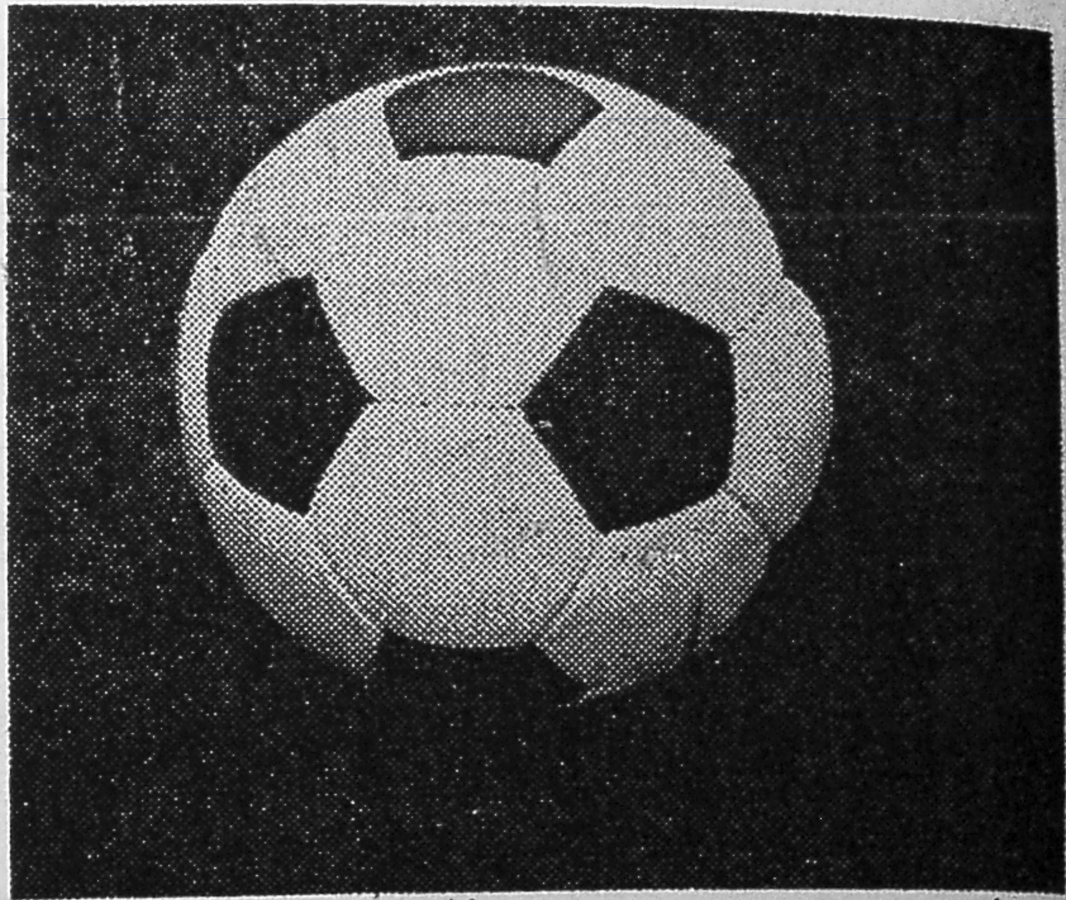


Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.

carbon fullerenes

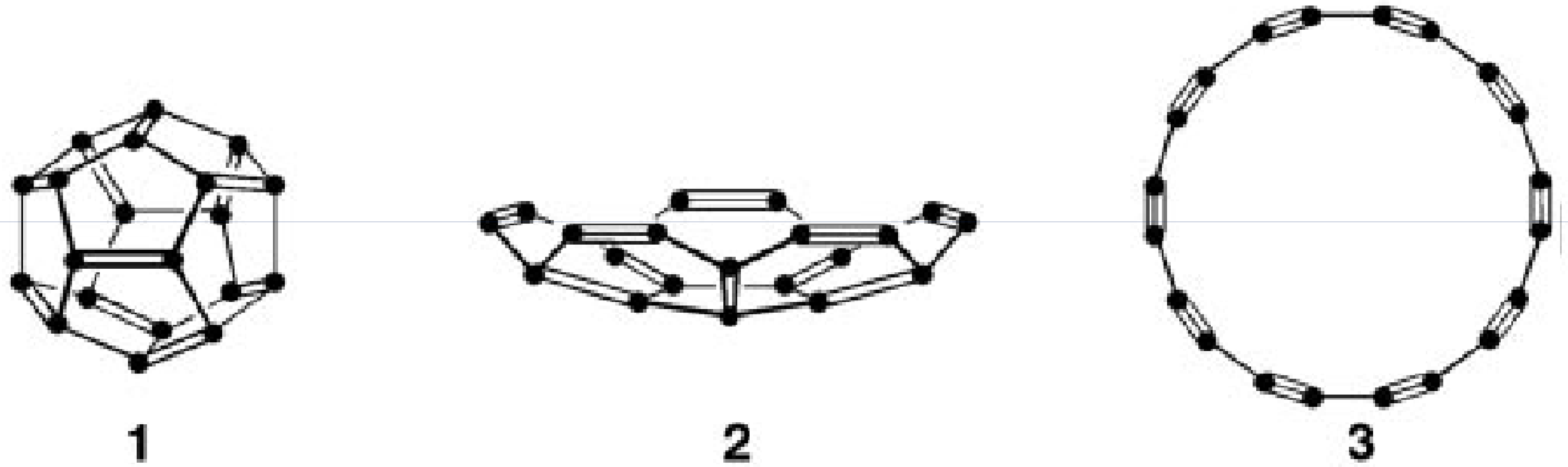
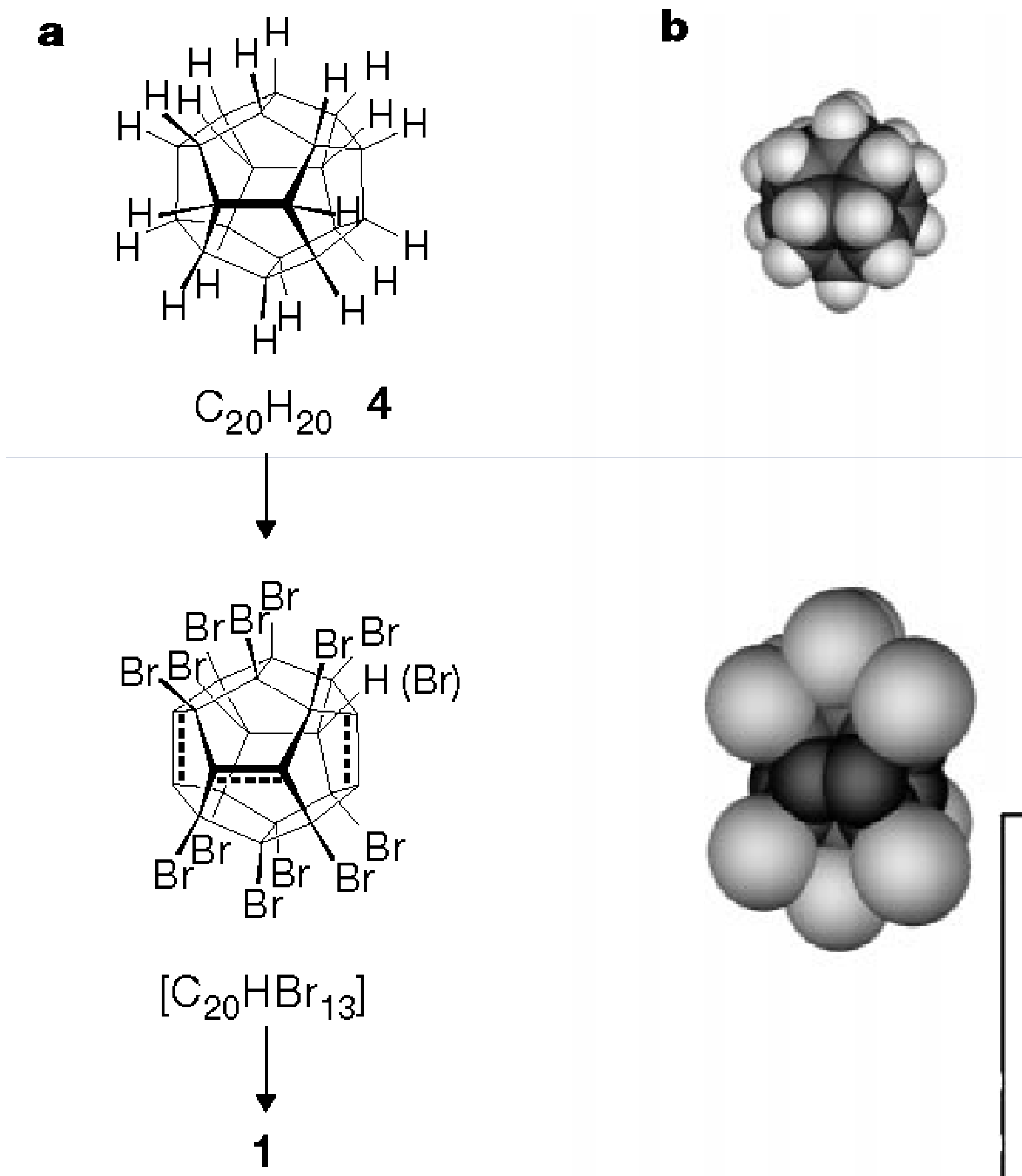
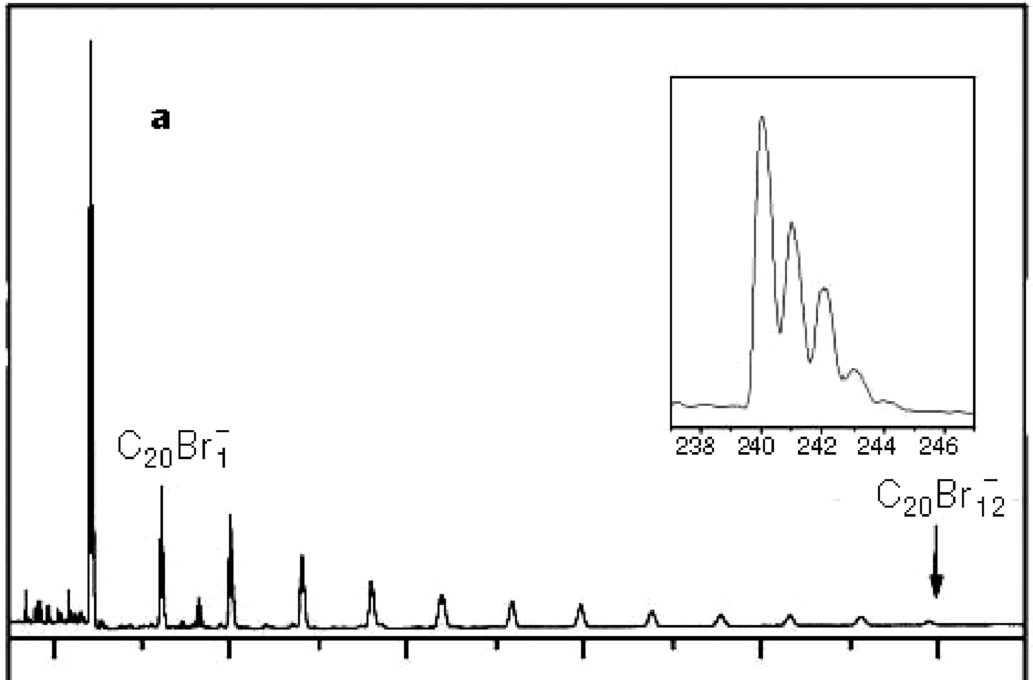


Figure 1 Isomers of C_{20}. **1**, cage; **2**, bowl; **3**, ring.

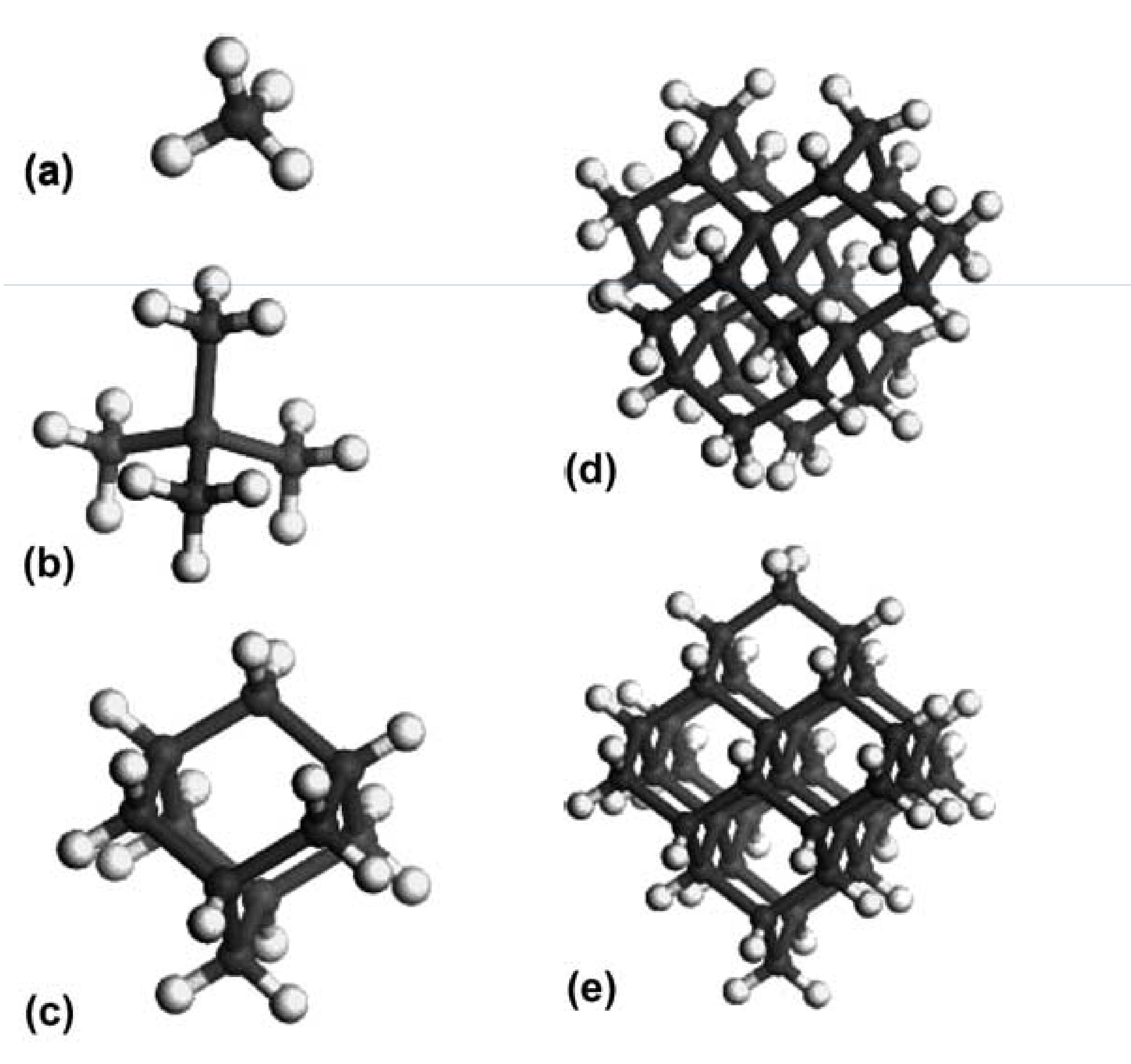
Gas-phase production and photoelectron spectroscopy of the smallest fullerene,C20.
Horst Prinzbach, Andreas Weiler, PeterLandenberger, FabianWahl et al.
NATURE | VOL407 | 7SEPTEMBER2000

carbon fullerenes





nanocrystals

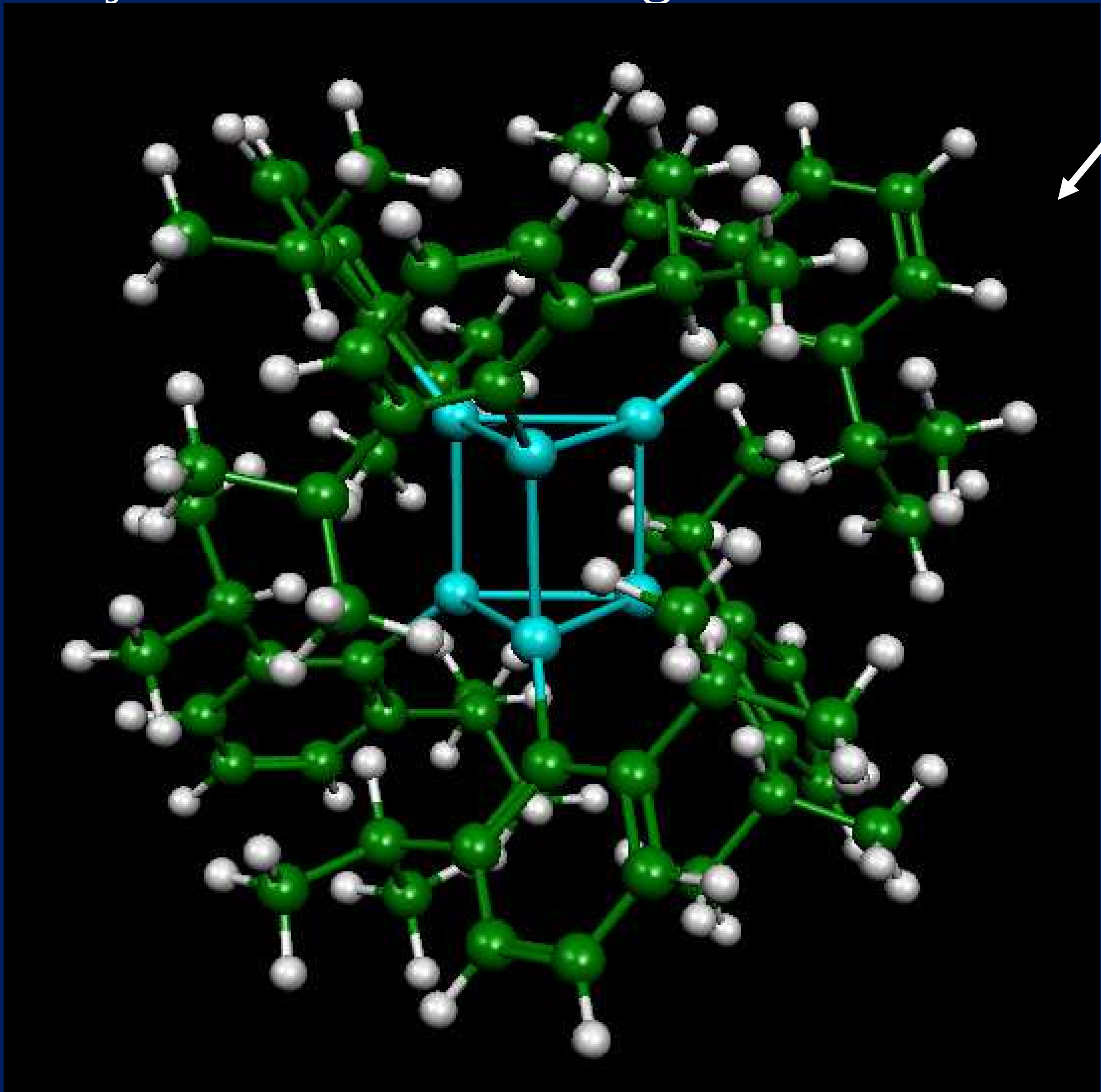


SiH_4, Si_5H_{12}, $Si_{10}H_{16}$, $Si_{29}H_{36}$, $Si_{35}H_{36}$

The electronic and optical properties of silicon nanoclusters: absorption and emission.
E.Luppi, E.Degoli, et al, Optical Materials, 2004

Si, Ge

Polyhedral silicon- and germanium-containing compounds



$Ge_6(C_6H_3(CH_3)_2)_6$

$Si_6(C_6H_3(CH_3)_2)_6$

$Ge_8(R)_8$

$Si_8(R)_8$

$Cd_{10}S_4(SC_6H_5)_{12}$,
$Cd_{32}S_{14}(SC_6H_5)_{36} \cdot DMF_4$

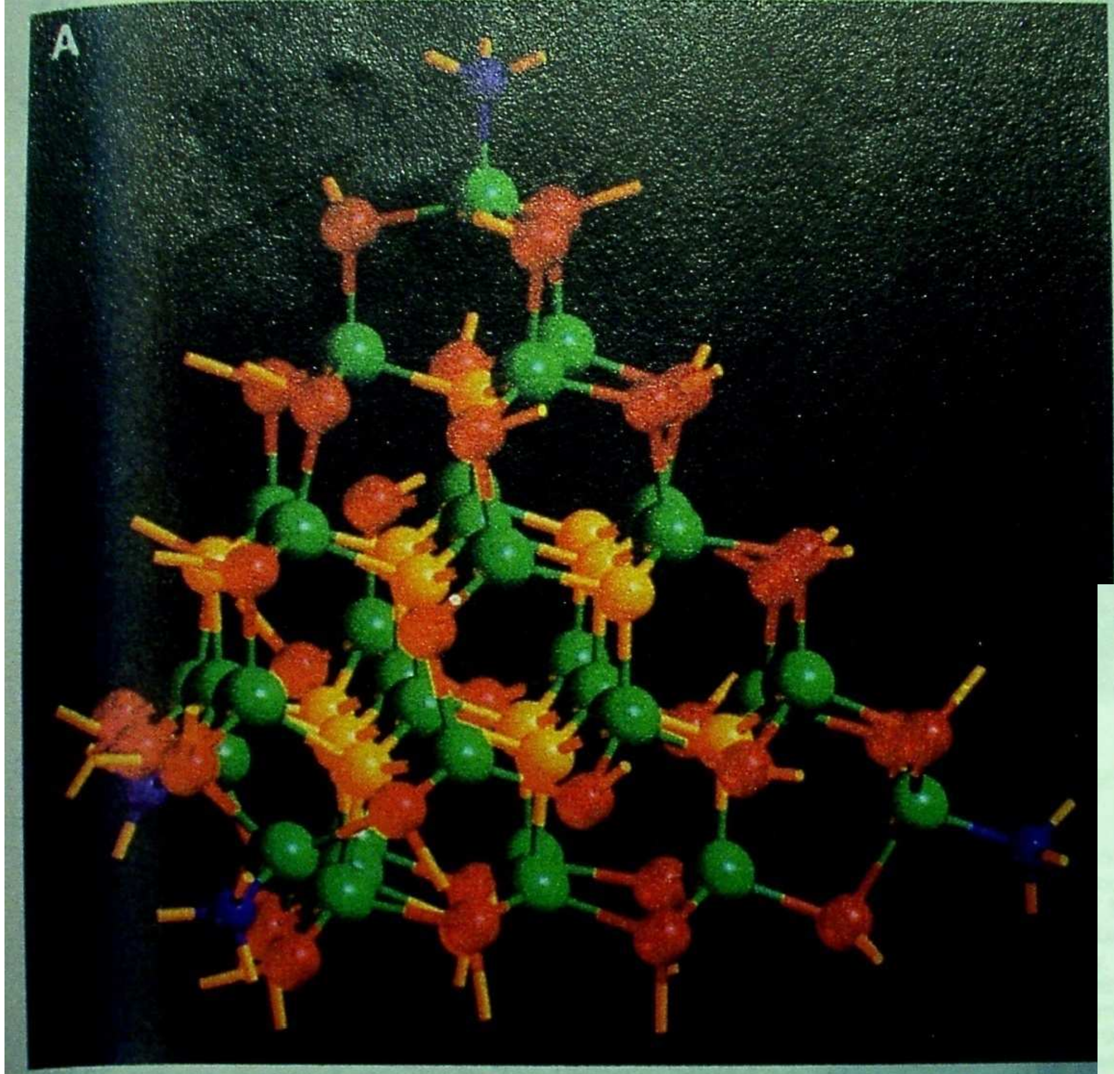
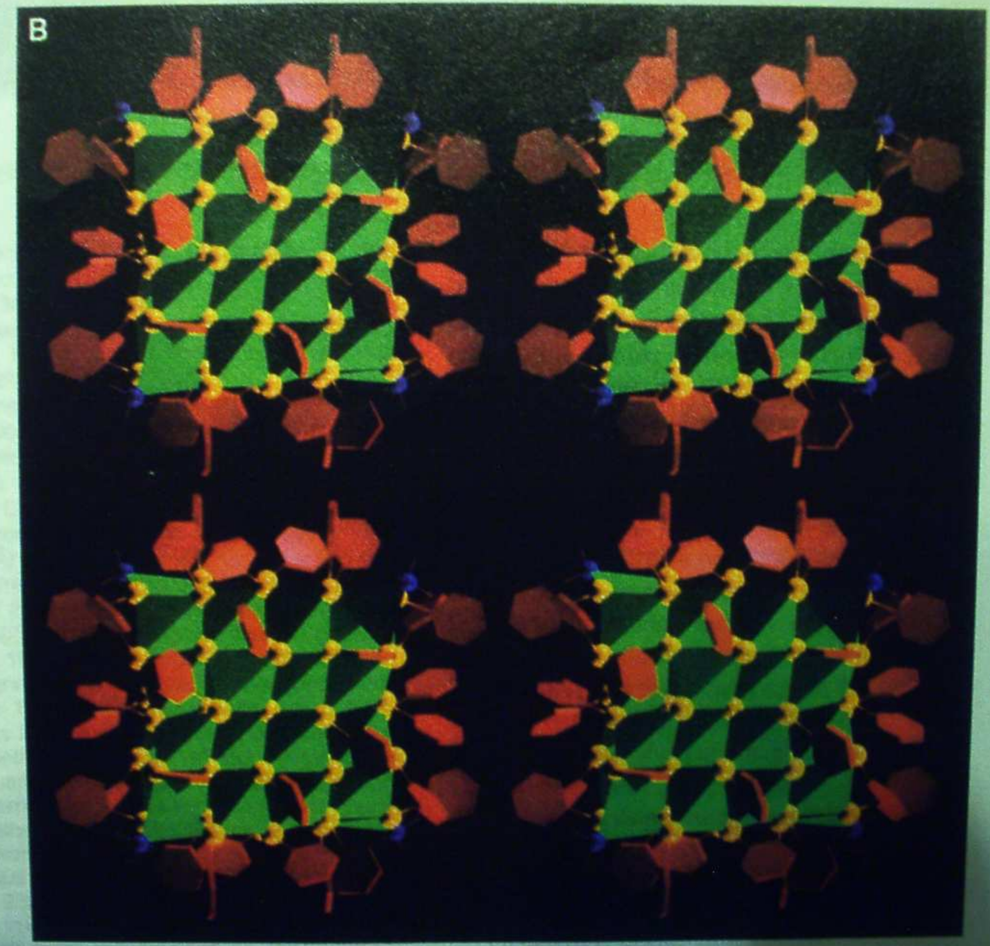


Fig. 1. (**A**) Crystal structure of $Cd_{32}S_{14}(SC_6H_5)_{36} \cdot DMF_4$ core.

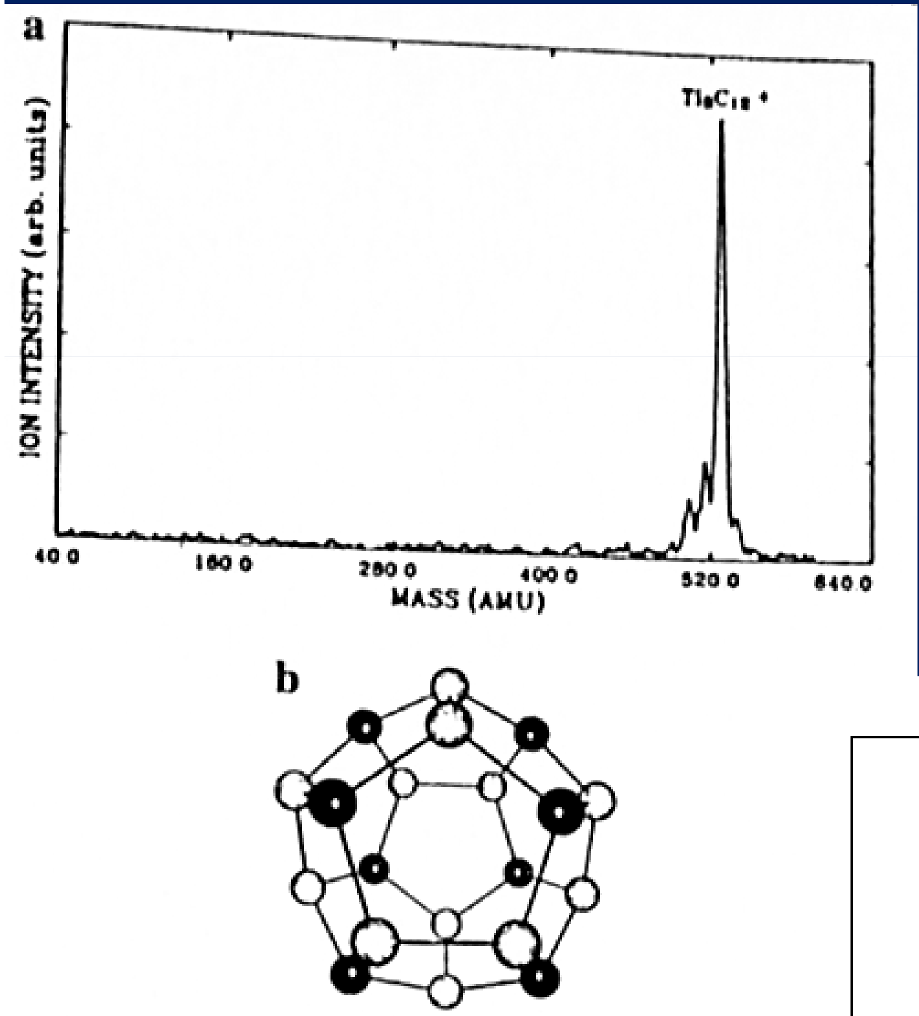


N.Herron et al. Science, 259 (1993) 1426

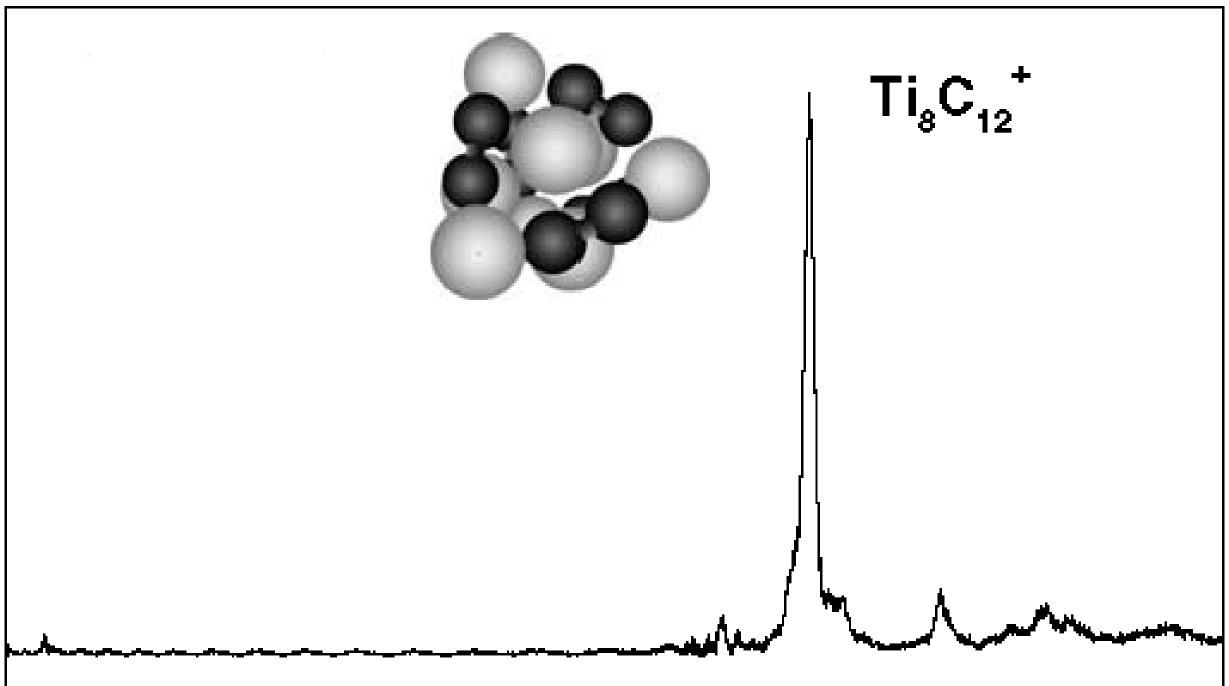
Met-car clusters

(Metallo-carbohedrenes)

Ti_8C_{12}, Zr_8C_{12}, Cr_8C_{12}, Nb_8C_{12}, Fe_8C_{12}, V_8C_{12}…



Guo B.C., Kerns K.P., Castleman A.W. Science 255 (1992) 1411

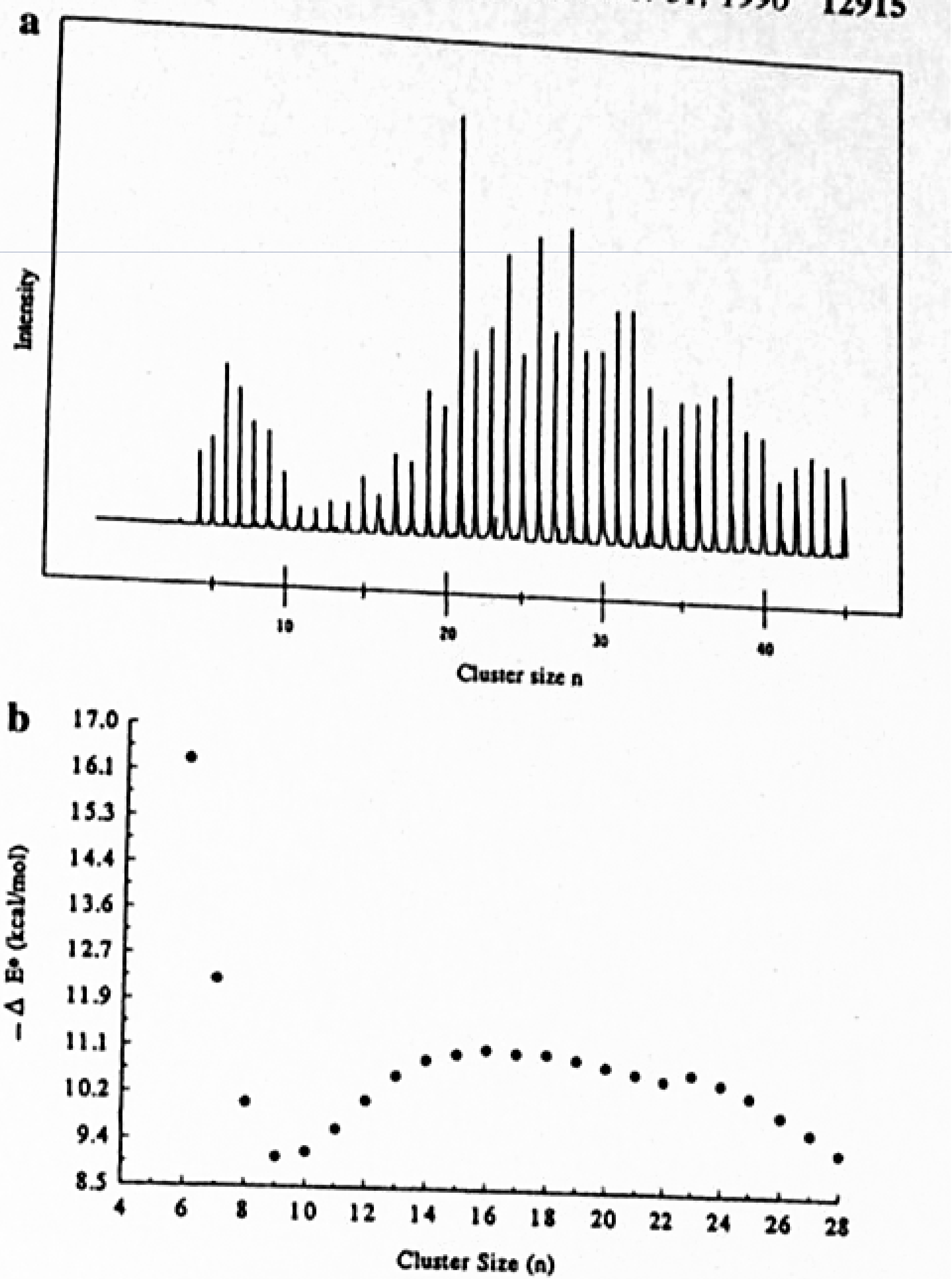


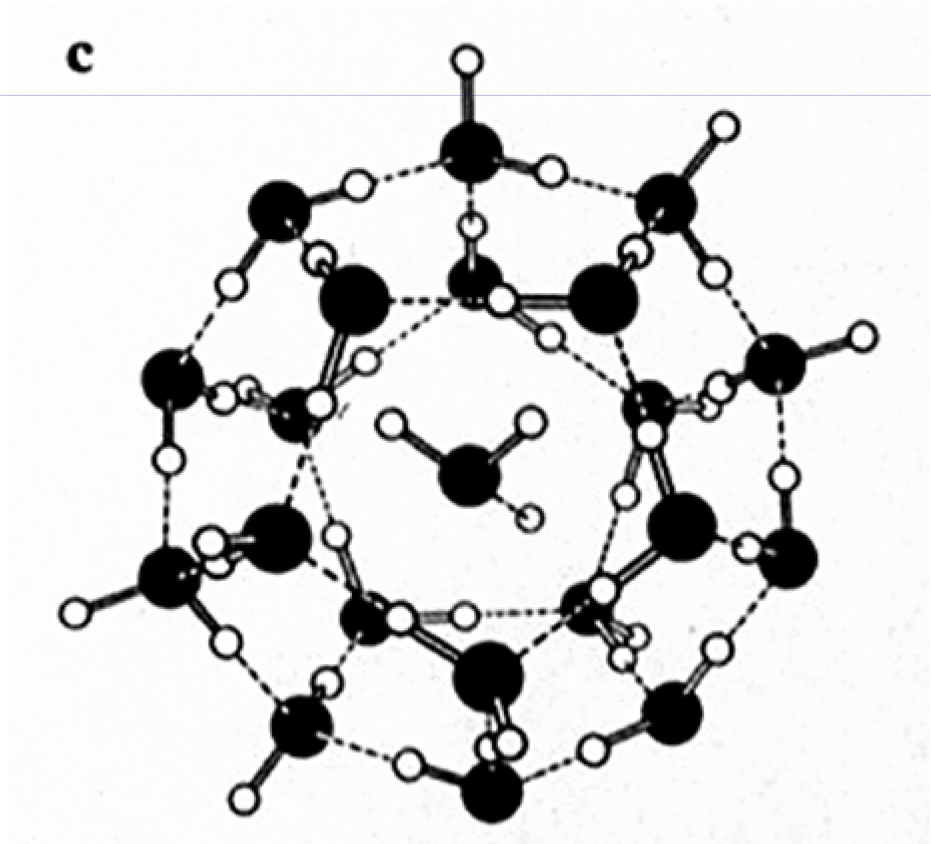
D. van Heijnsbergen et al Chem.Phys.Lett. 349 (2001) 220-226

Examples of nanoclusters

H_2O

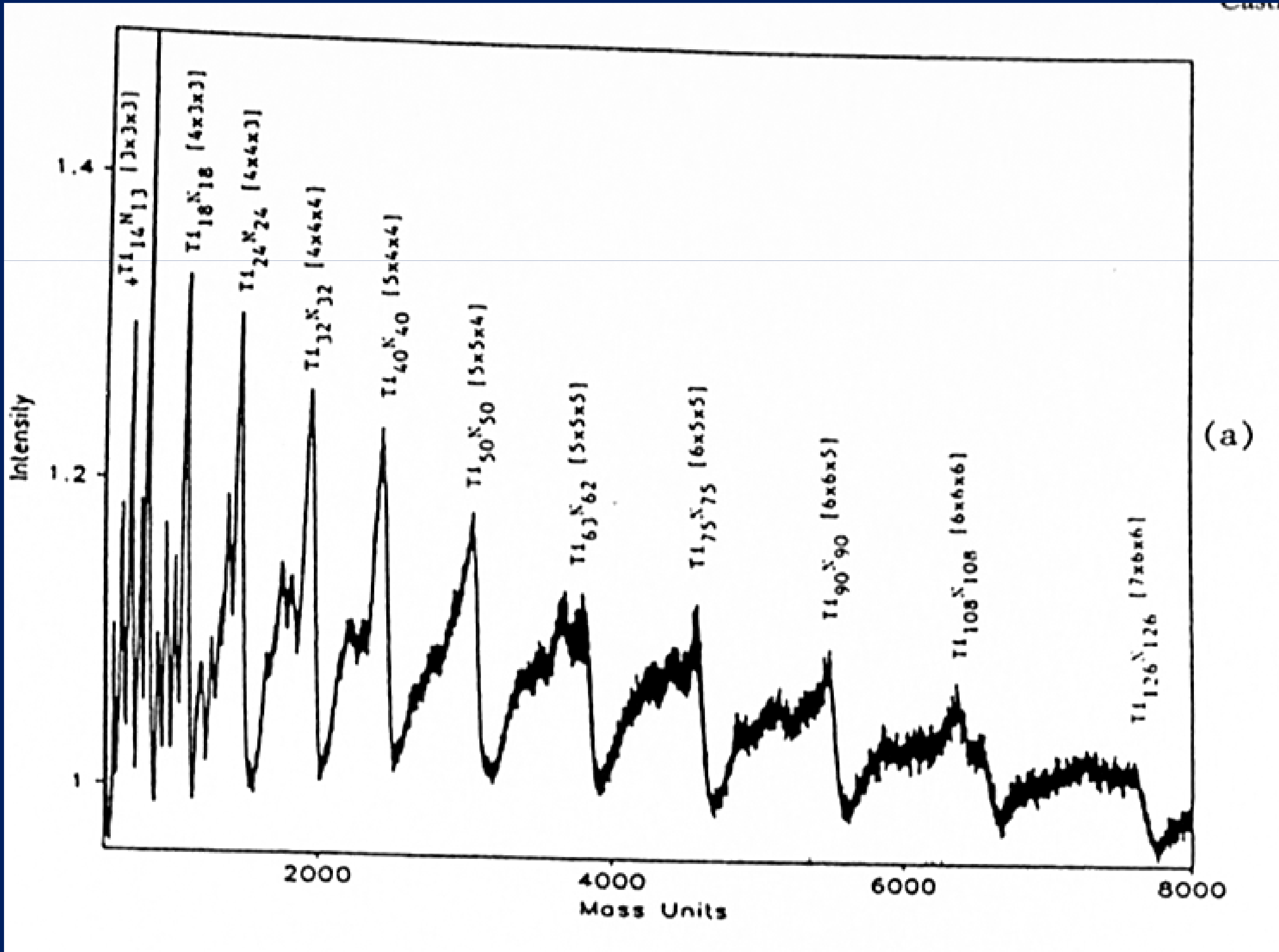
J. Phys. Chem., Vol. 100, No. 31, 1996 12915





Examples of nanoclusters

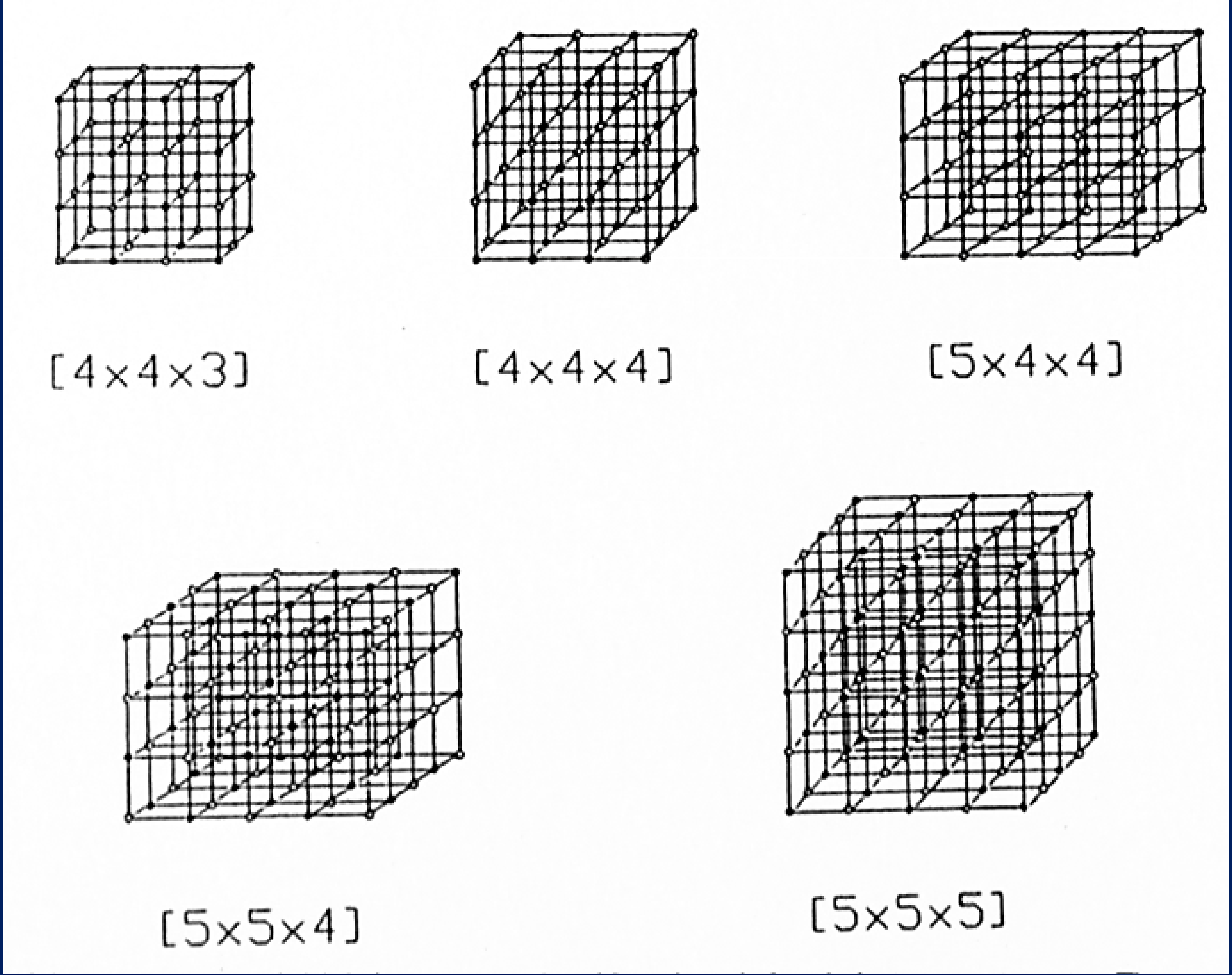
TiN



Chen Z.Y., Castleman A.W. J. Chem. Phys. 1993, 98, 231

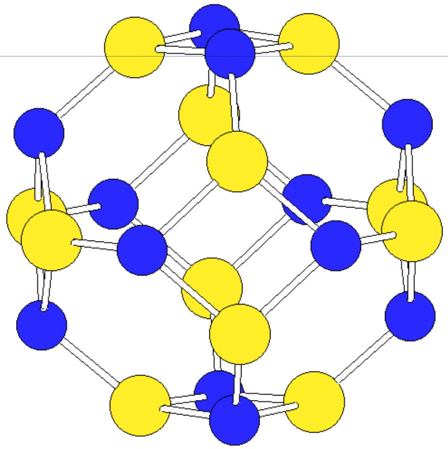
Examples of nanoclusters

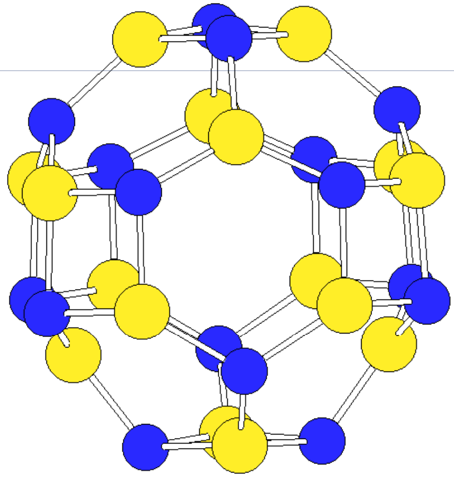
TiN

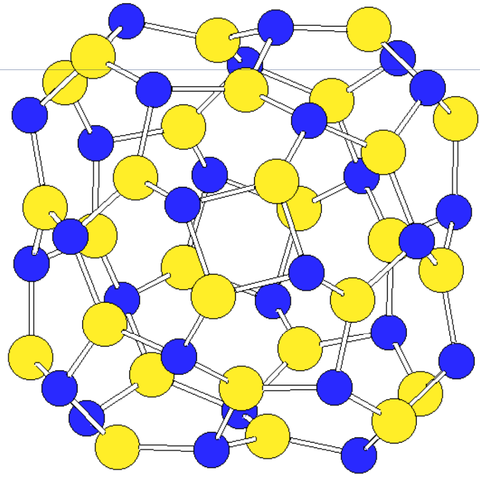


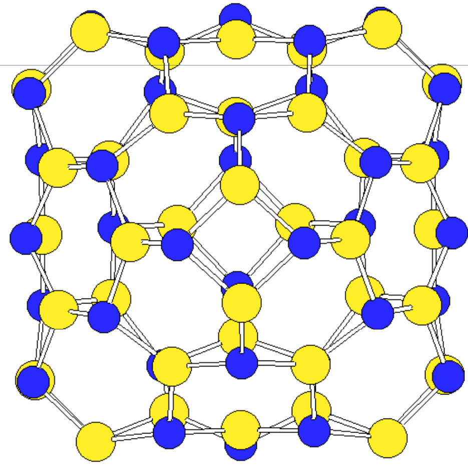
Chen Z.Y., Castleman A.W. J. Chem. Phys. 1993, 98, 231

boron-nitride anagues of fullerenes





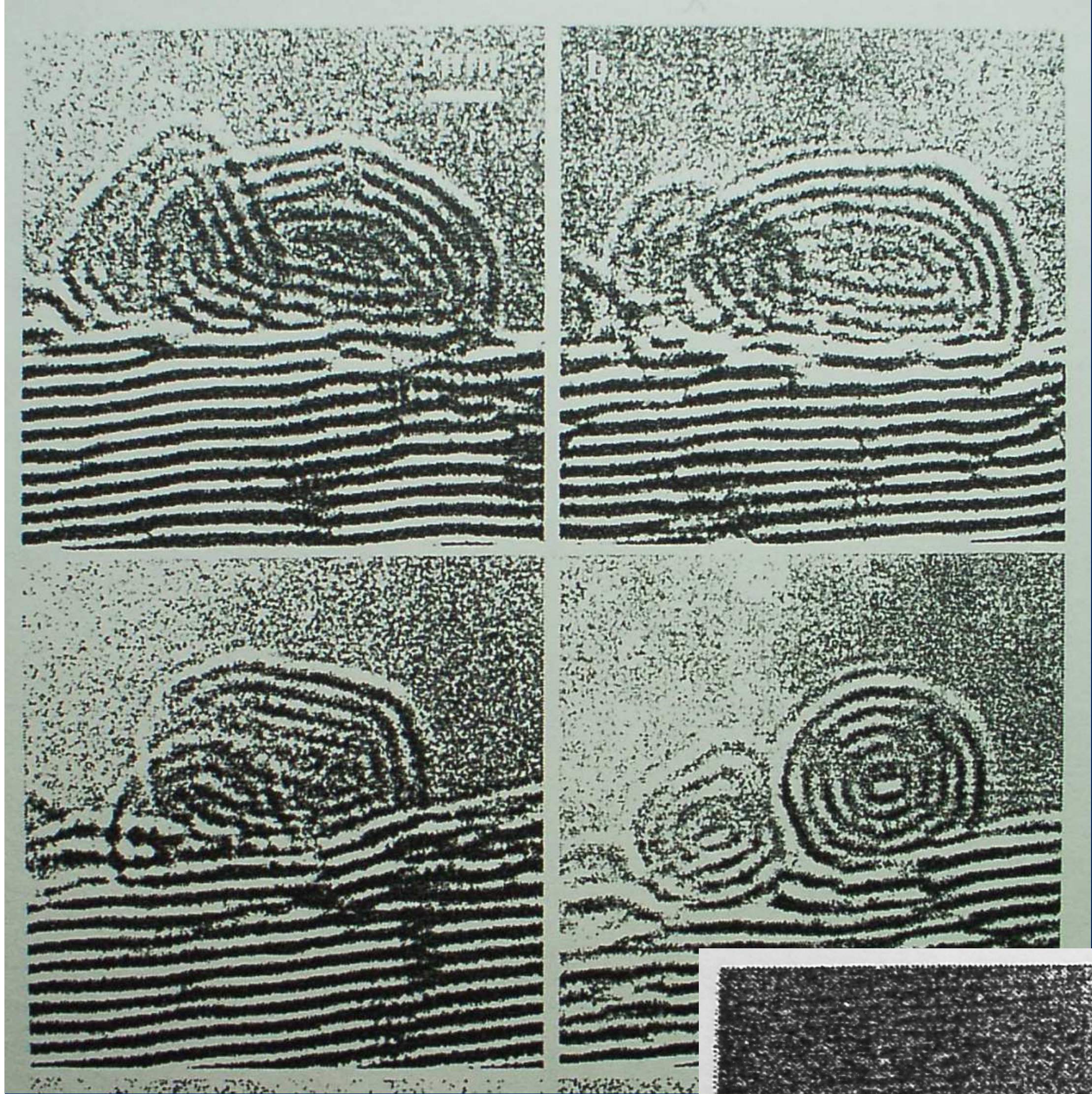


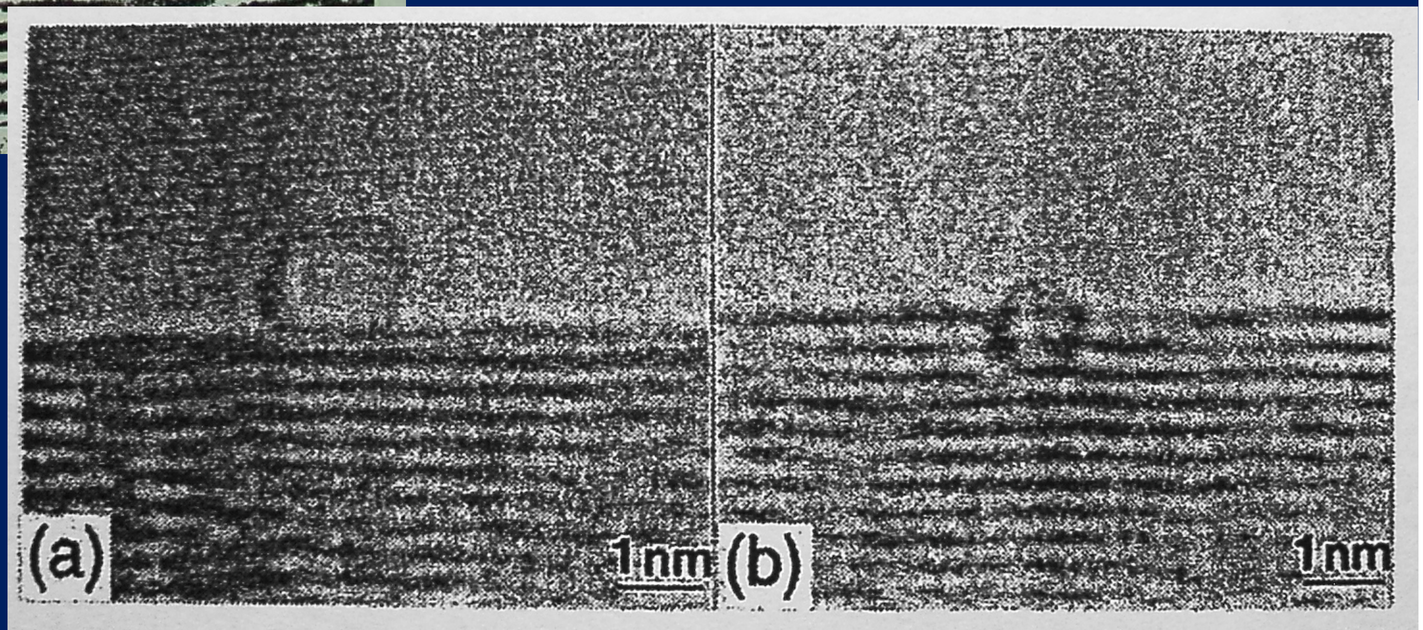


$(BN)_{12}$ $(BN)_{16}$ $(BN)_{28}$ $(BN)_{36}$

boron-nitride
anagues of fullerenes

Goldberg D., Bando Y., Stephan O., Kurashima K. Octahedral boron nitride fullerenes formed by electron beam irradiation. Appl.Phys.Lett. 1998, V.73, P.2441-2443.





boron-nitride analogues of fullerenes

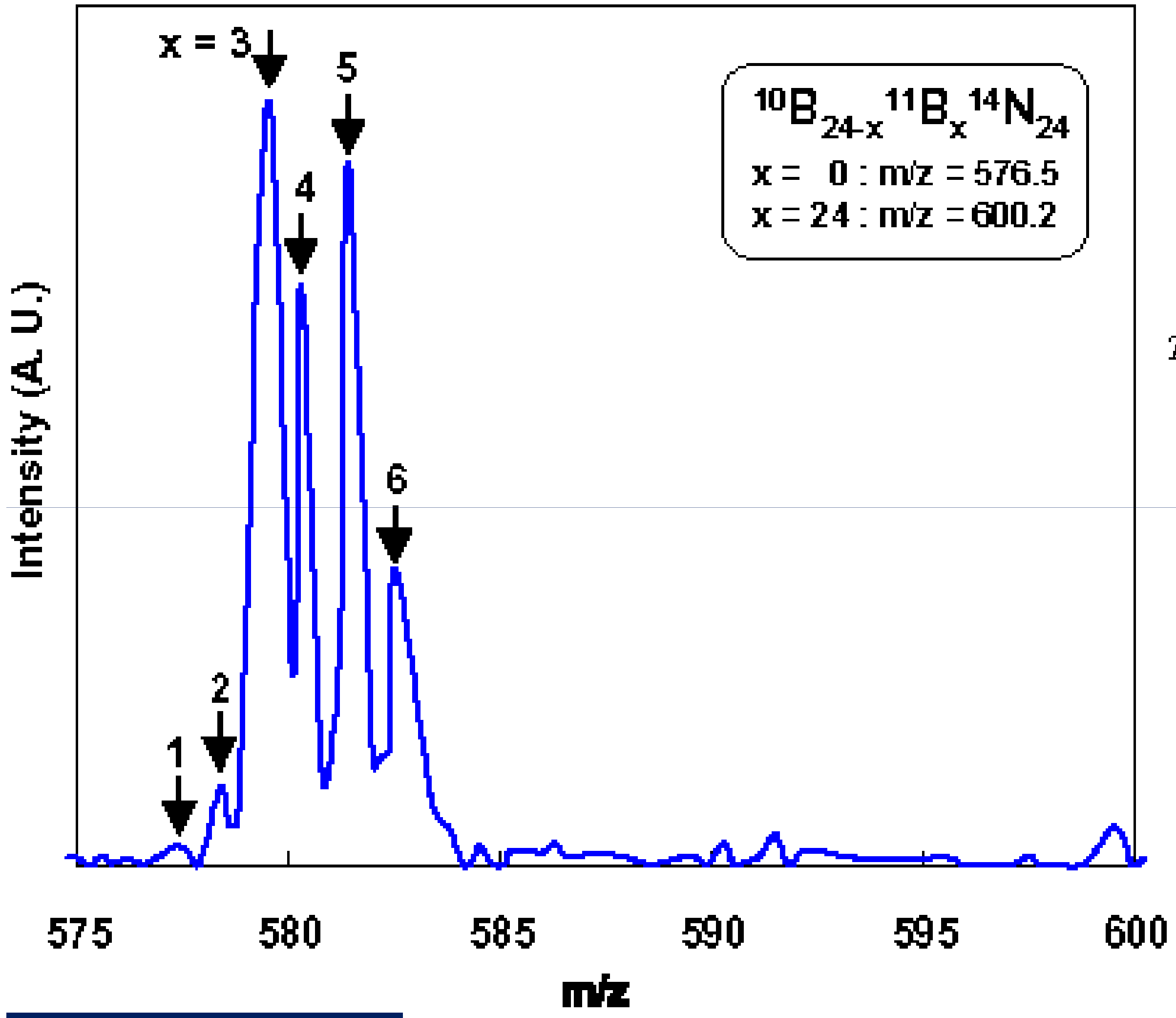
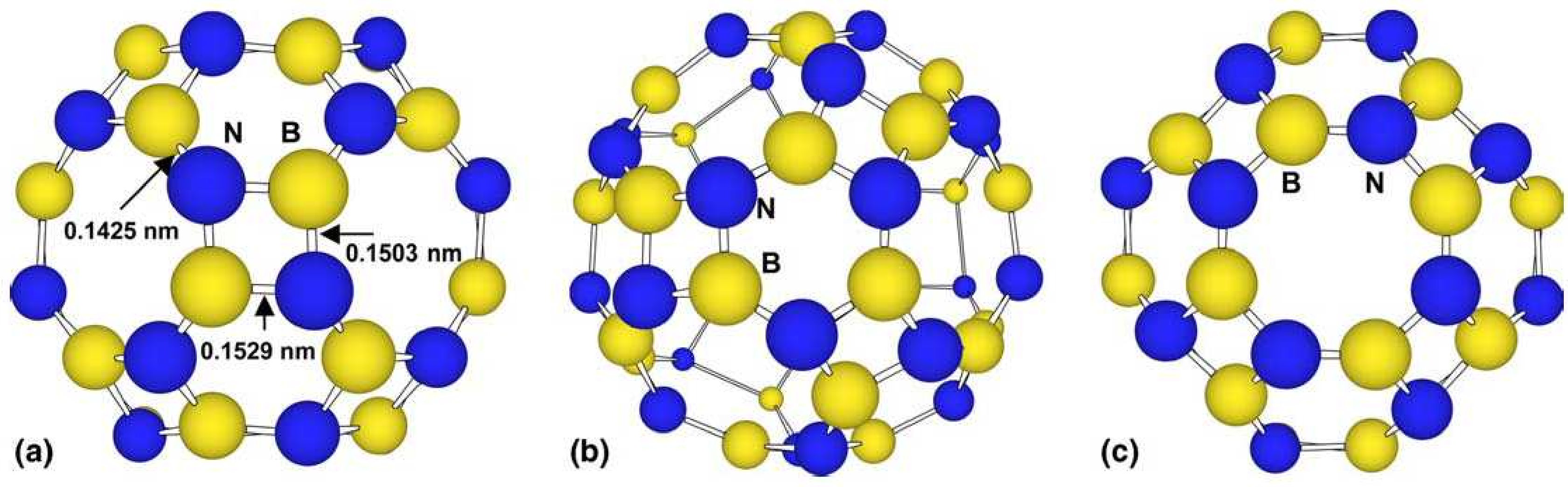


Fig. 1. LD-TOF mass spectrum for BN clusters.

T. Oku et al. / Chemical Physics Letters 380 (2003) 620–623

V.V. Pokropivny, V.V. Skorokhod, G.S. Oleinik, A.V. Kurdyumov, T.S. Bartnitskaya, A.V. Pokropivny, A.G. Sisonyuk, D.M.Sheichenko. Boron nitride analogues of fullerenes (the fulborenes), nanotubes, and fullerites (the fulborenites)// J. Solid State Chemistry 54, 212-224 (2000)



New kind of nanoclusters of $A^{II}B^{VI}$ compounds: $(AB)_{13}$, $(AB)_{19}$, $(AB)_{33}$, $(AB)_{34}$

- Preparation
- Optical and photochemical properties
- Mass-spectroscopy
- Structure
- Claster crystals
- Application

New kind of nanoclusters of $A^{II}B^{VI}$ compounds

Ultra-stable nanoparticles of CdSe revealed from mass spectrometry

ATSUO KASUYA*[1], RAJARATNAM SIVAMOHAN[1], YURII A. BARNAKOV[1], IGOR M. DMITRUK[1], TAKASHI NIRASAWA[2,3], VOLODYMYR R. ROMANYUK[1], VIJAY KUMAR[1,4,5], SERGIY V. MAMYKIN[1], KAZUYUKI TOHJI[2], BALACHANDRAN JEYADEVAN[2], KOZO SHINODA[2], TOSHIJI KUDO[3], OSAMU TERASAKI[6], ZHENG LIU[6], RODION V. BELOSLUDOV[4], VIJAYARAGHAVAN SUNDARARAJAN[1,7] AND YOSHIYUKI KAWAZOE[4]

[1]Center for Interdisciplinary Research, Tohoku University, Sendai, 980-8578, Japan
[2]Graduate School of Environmental Studies, Tohoku University, Sendai, 980-8579, Japan
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[4]Institute for Materials Research, Tohoku University, Sendai, 980-8577, Japan
[5]Dr Vijay Kumar Foundation, Chennai, 600 078, India
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*e-mail: kasuya@cir.tohoku.ac.jp

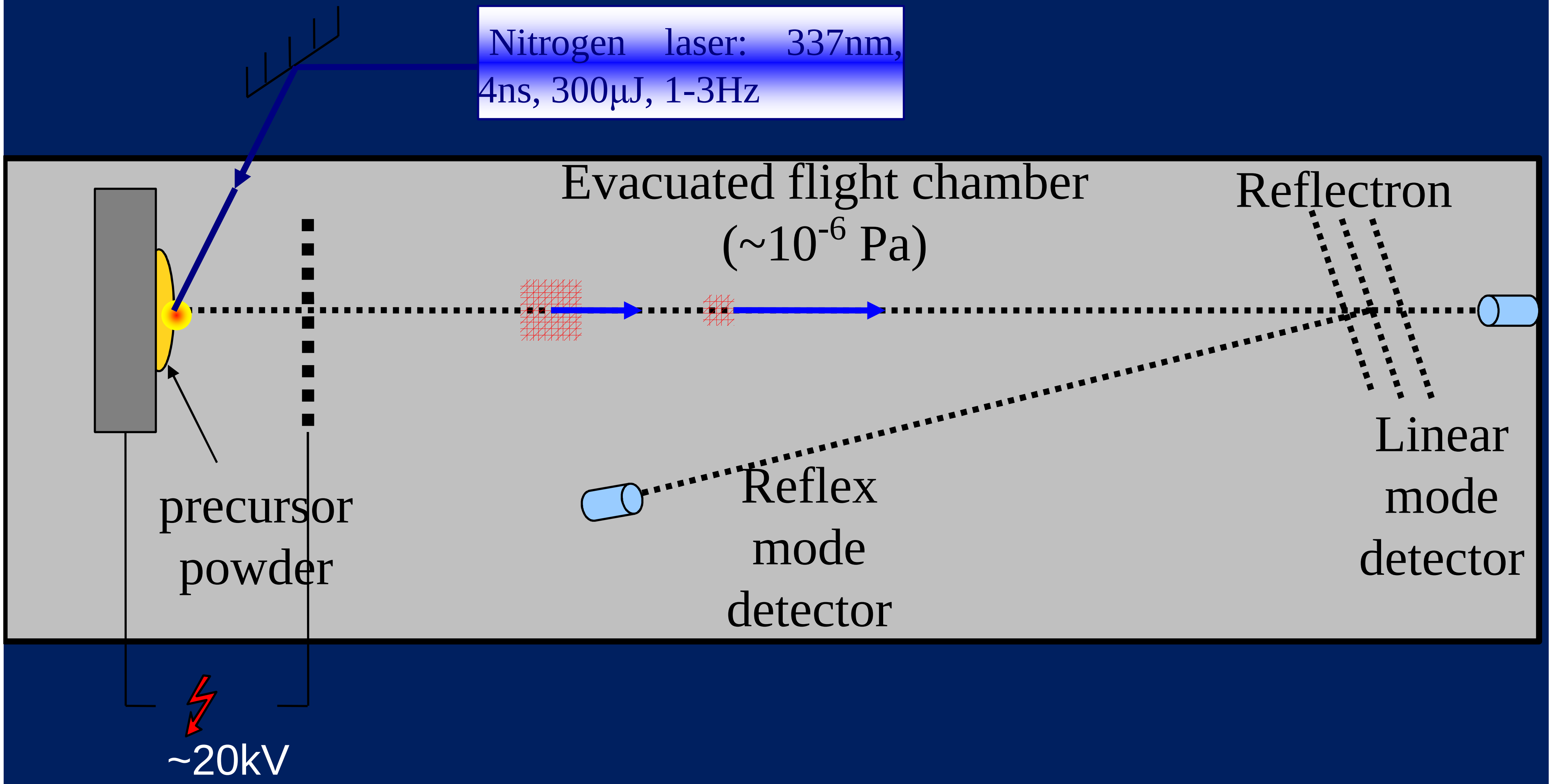
Published online: 25 January 2004; doi:10.1038/nmat1056

Nanoparticles under a few nanometres in size have structures and material functions that differ from the bulk because of their distinct geometrical shapes and strong quantum confinement. These qualities could lead to unique device

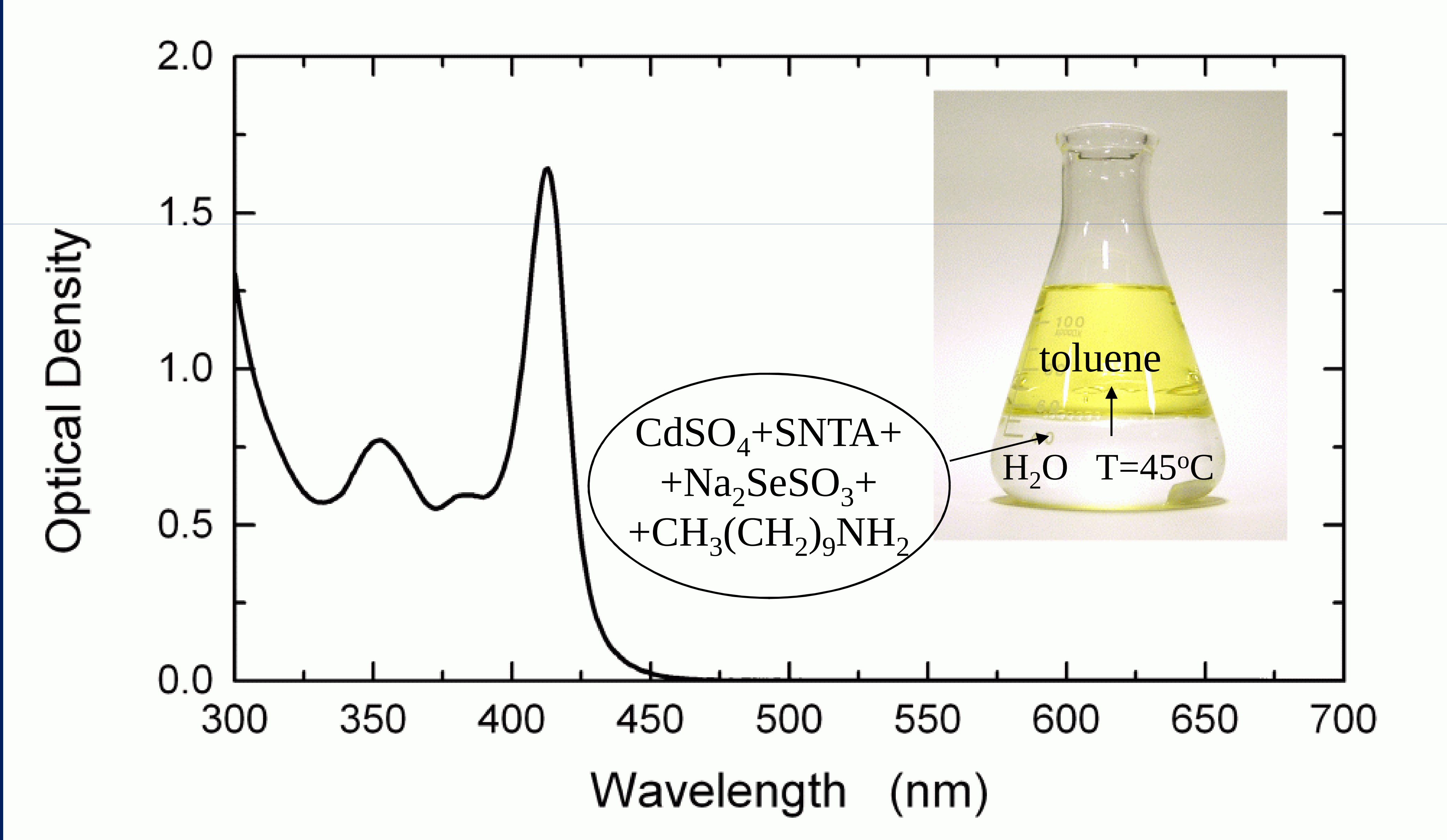
of mass-selected $(CdSe)_{33}$ and $(CdSe)_{34}$ nanoparticles in solution. These constitute the first compound nanoparticles that are stable and macroscopically produced at precisely specified numbers of constituent atoms with their stoichiometric composition identical to the bulk solids.

Bruker Reflex III-T time-of-flight mass spectrometer

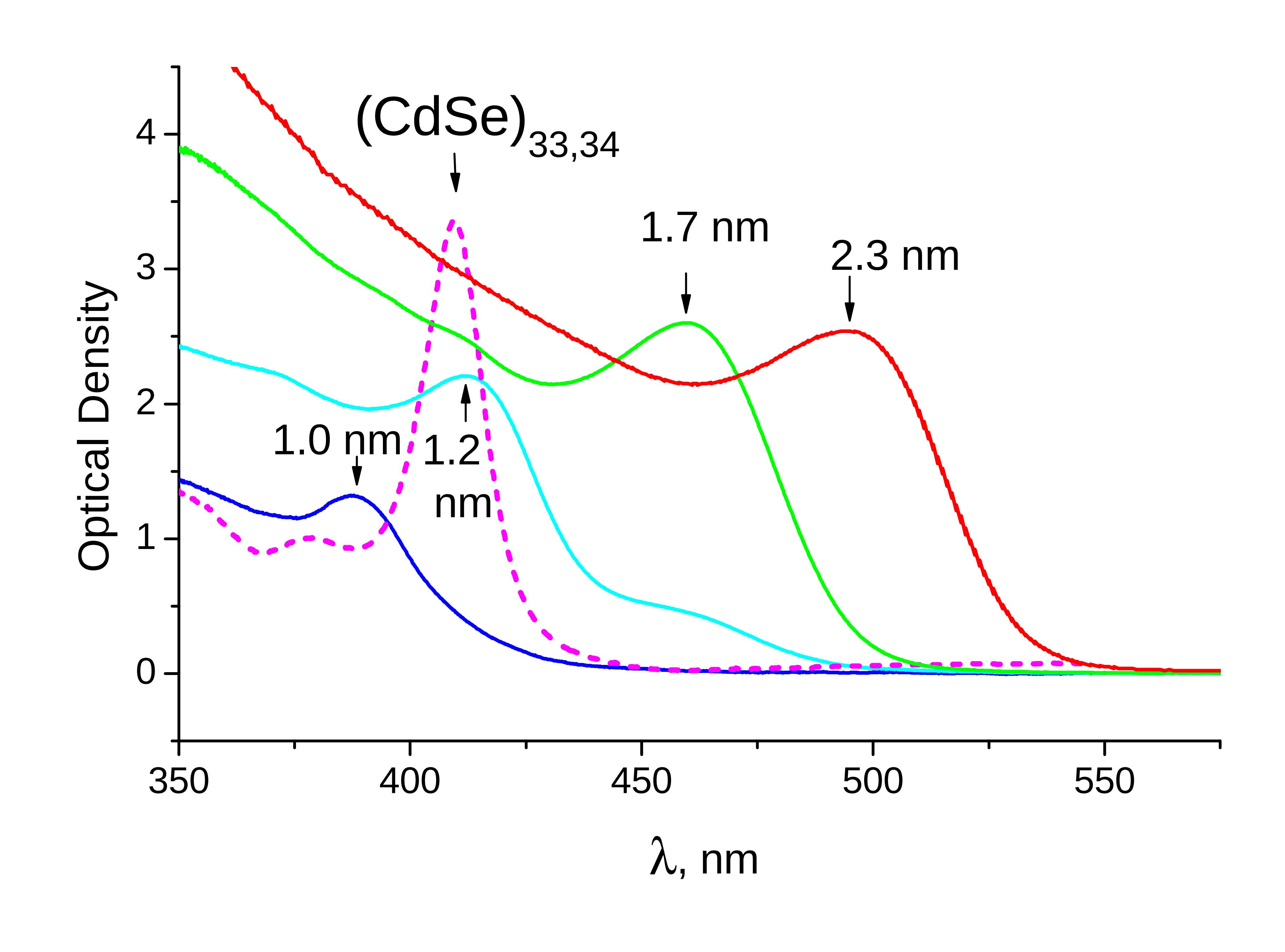
Laser ablation and mas-spectroscopy



Preparation



Absorption

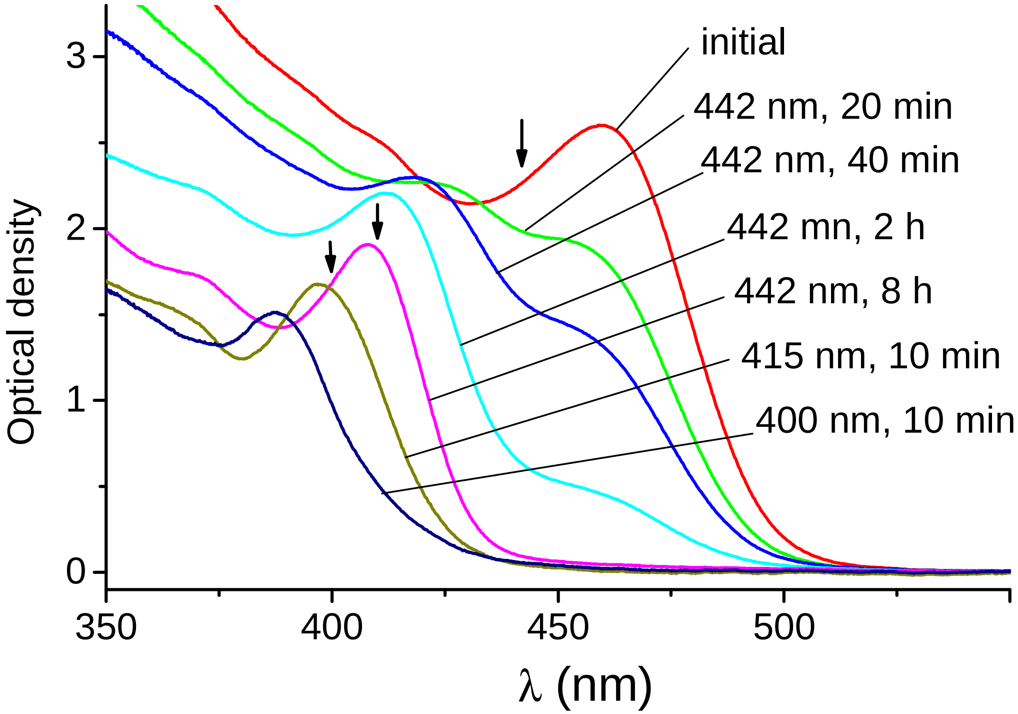


(CdSe)33,34
1.7 nm
2.3 nm
1.0 nm
1.2
nm
Optical Density
0
1
2
3
4
350
400
450
500
550
λ, nm

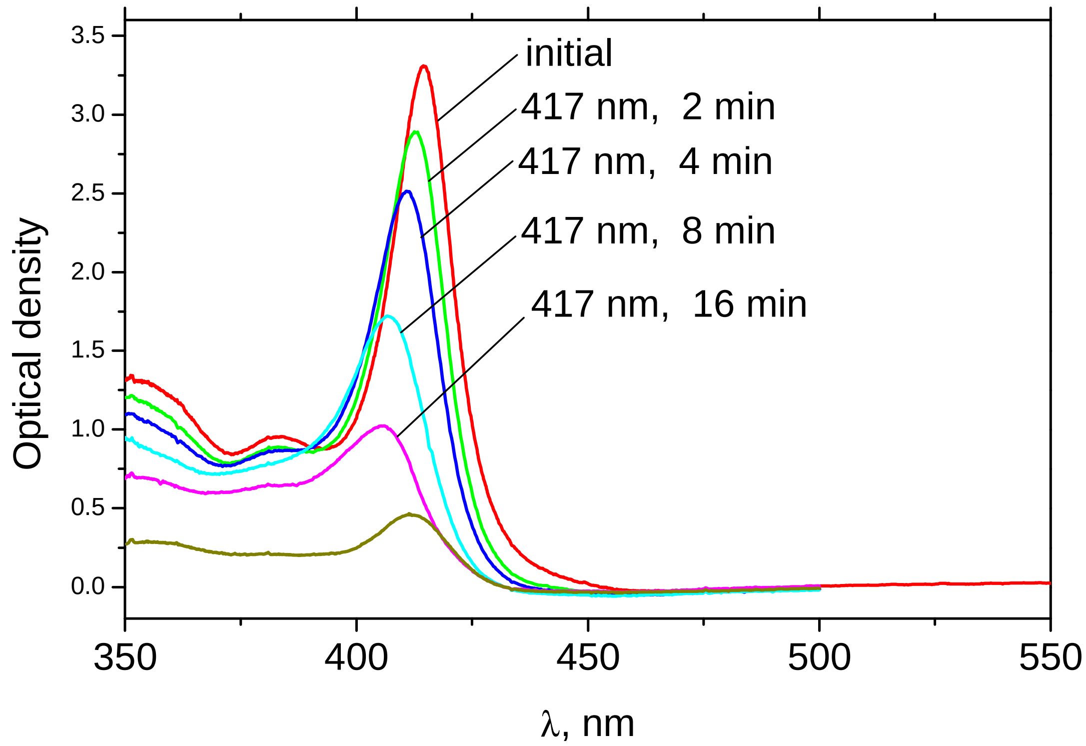
Photoetching

$CdSe + 2O_2 + light \longrightarrow Cd^{2+} + SeO_4^{2-}$

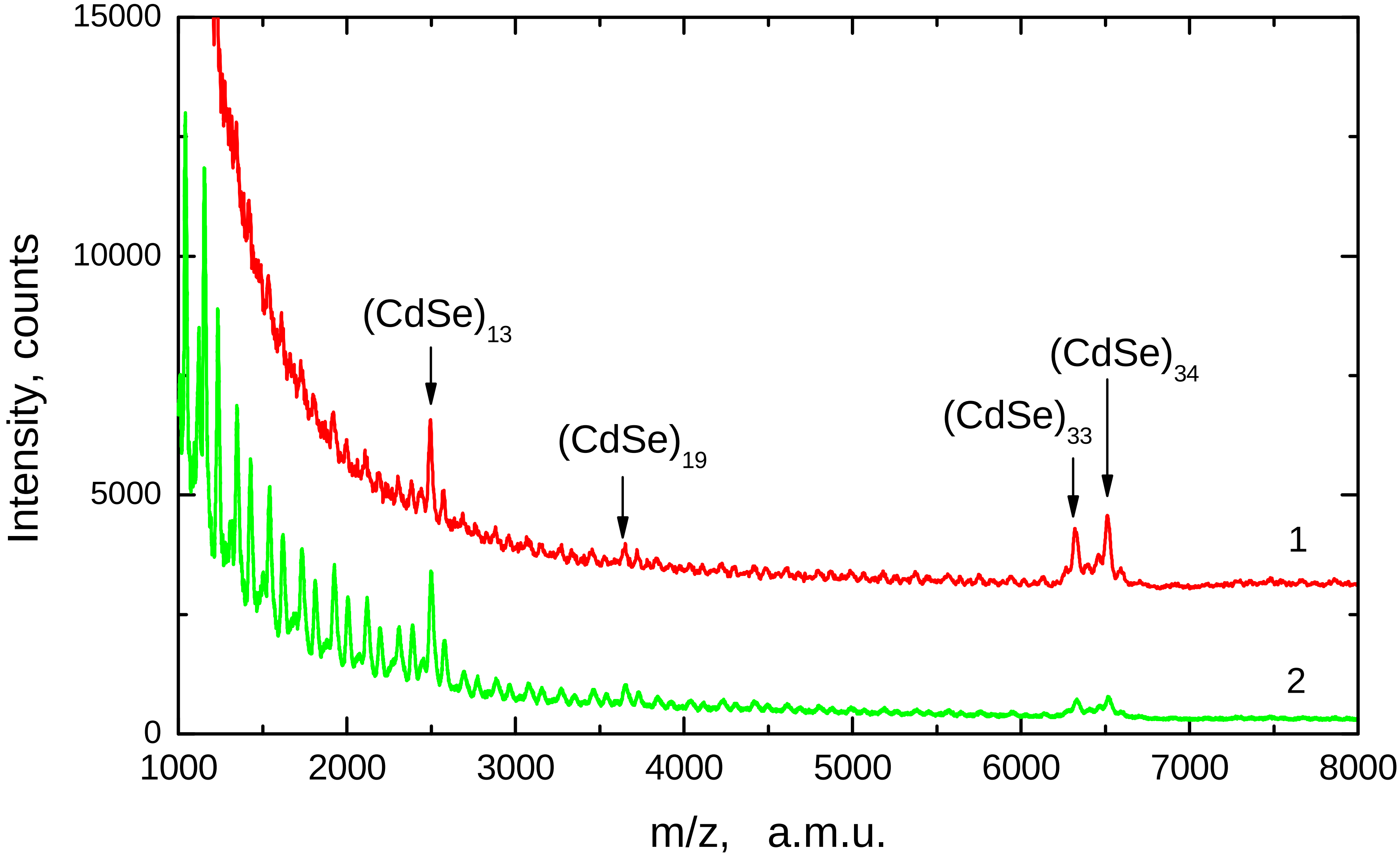
crystalline CdSe nanoparticles



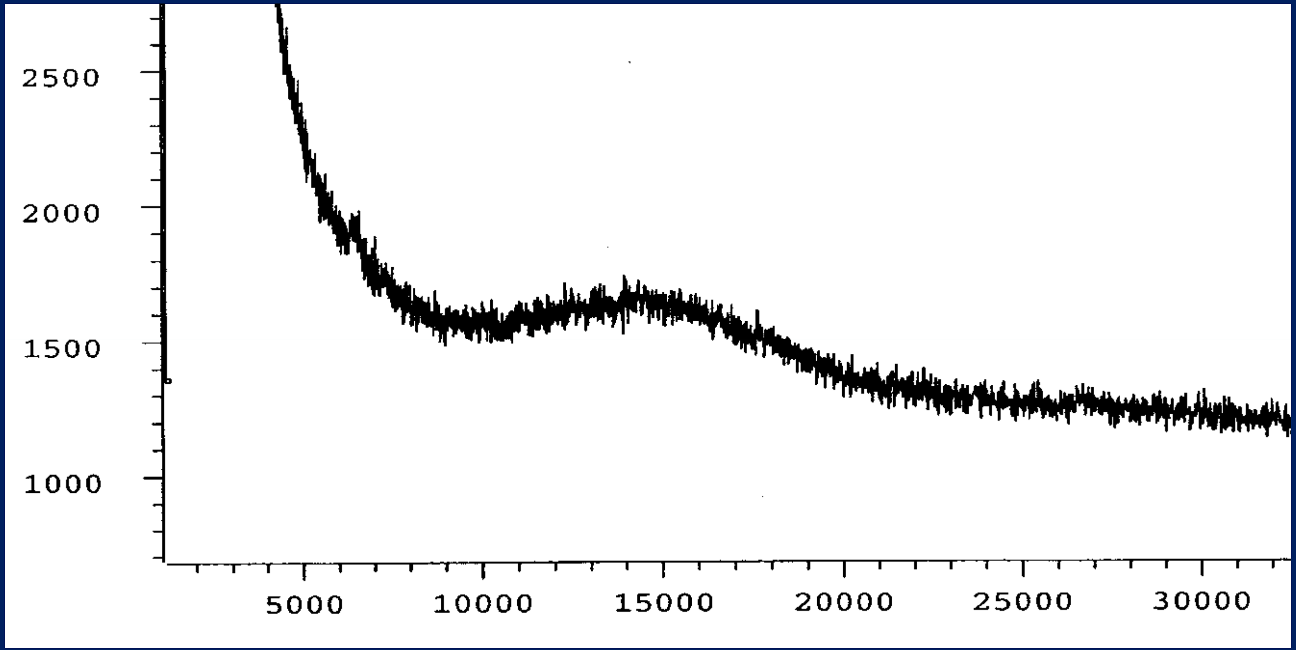
$(CdSe)_{33}$, $(CdSe)_{34}$

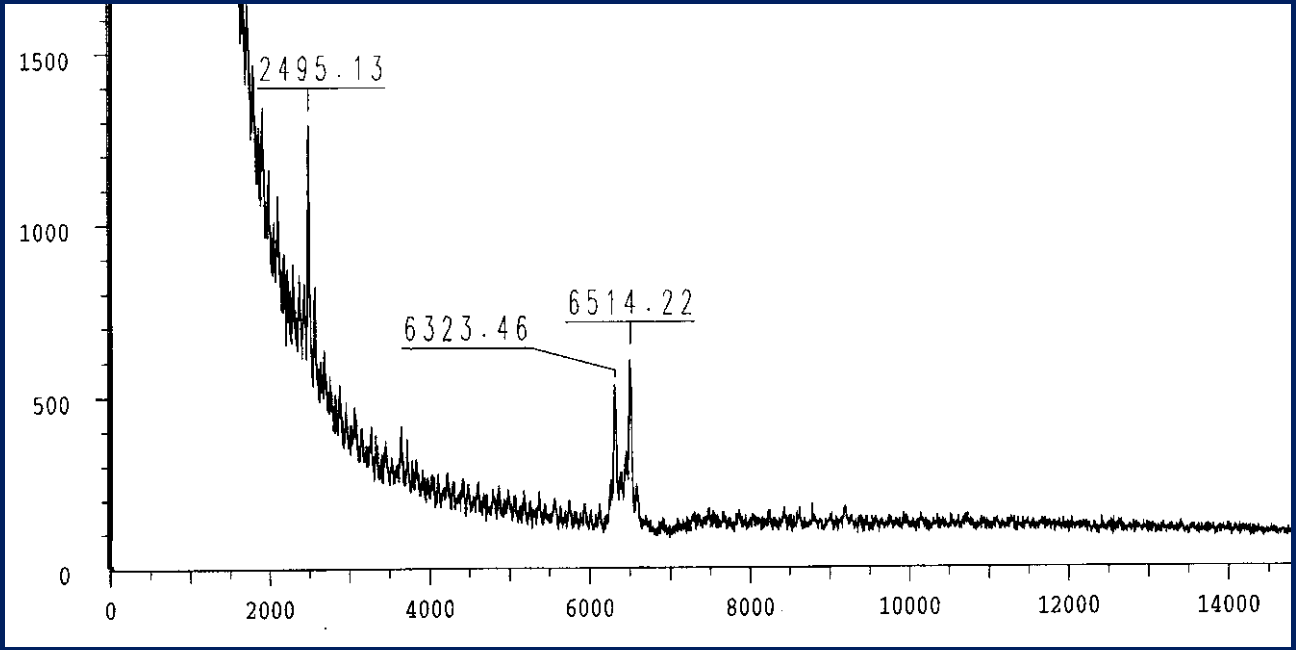


Mass-spectroscopy

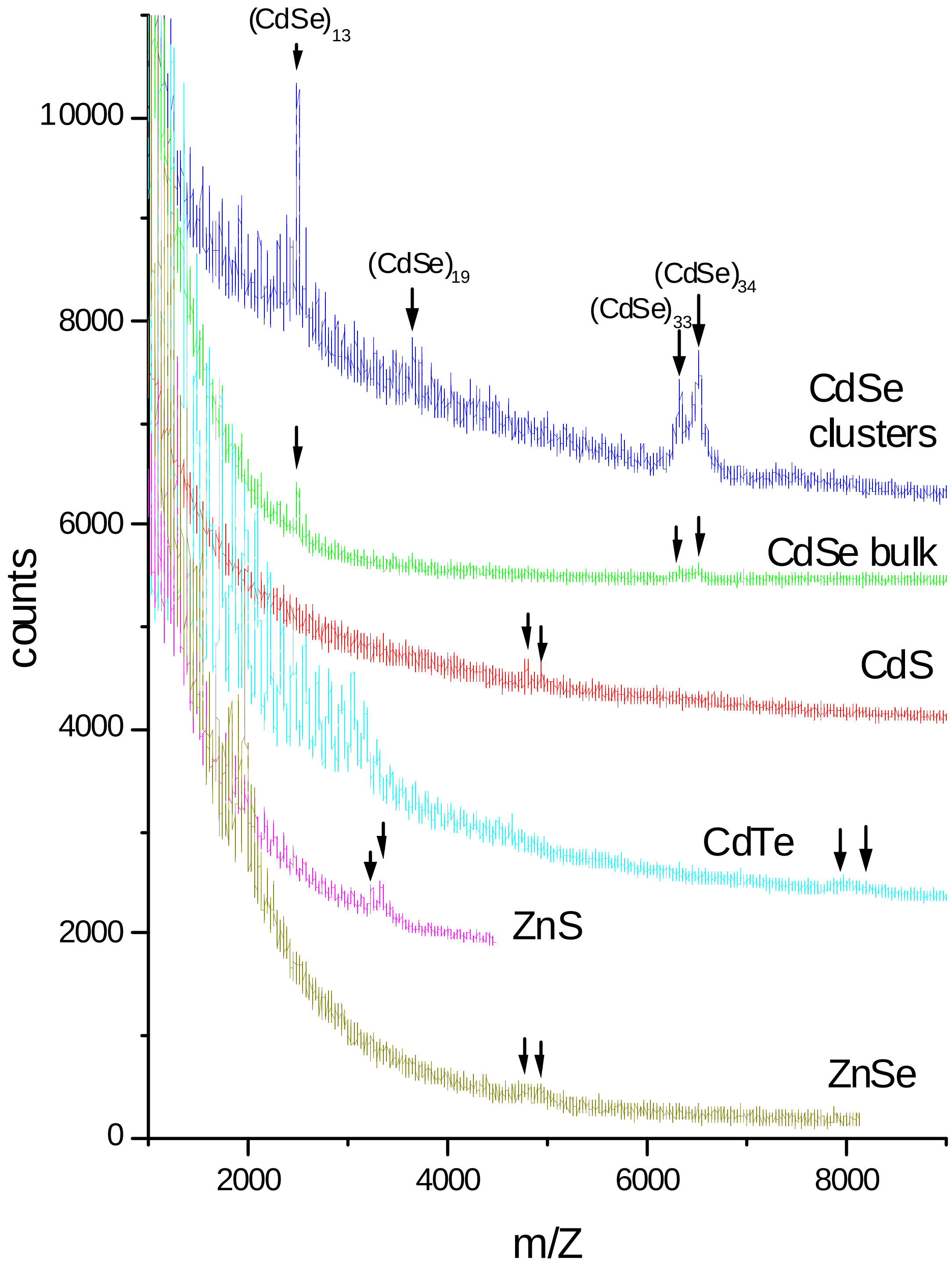


Mass-spectroscopy

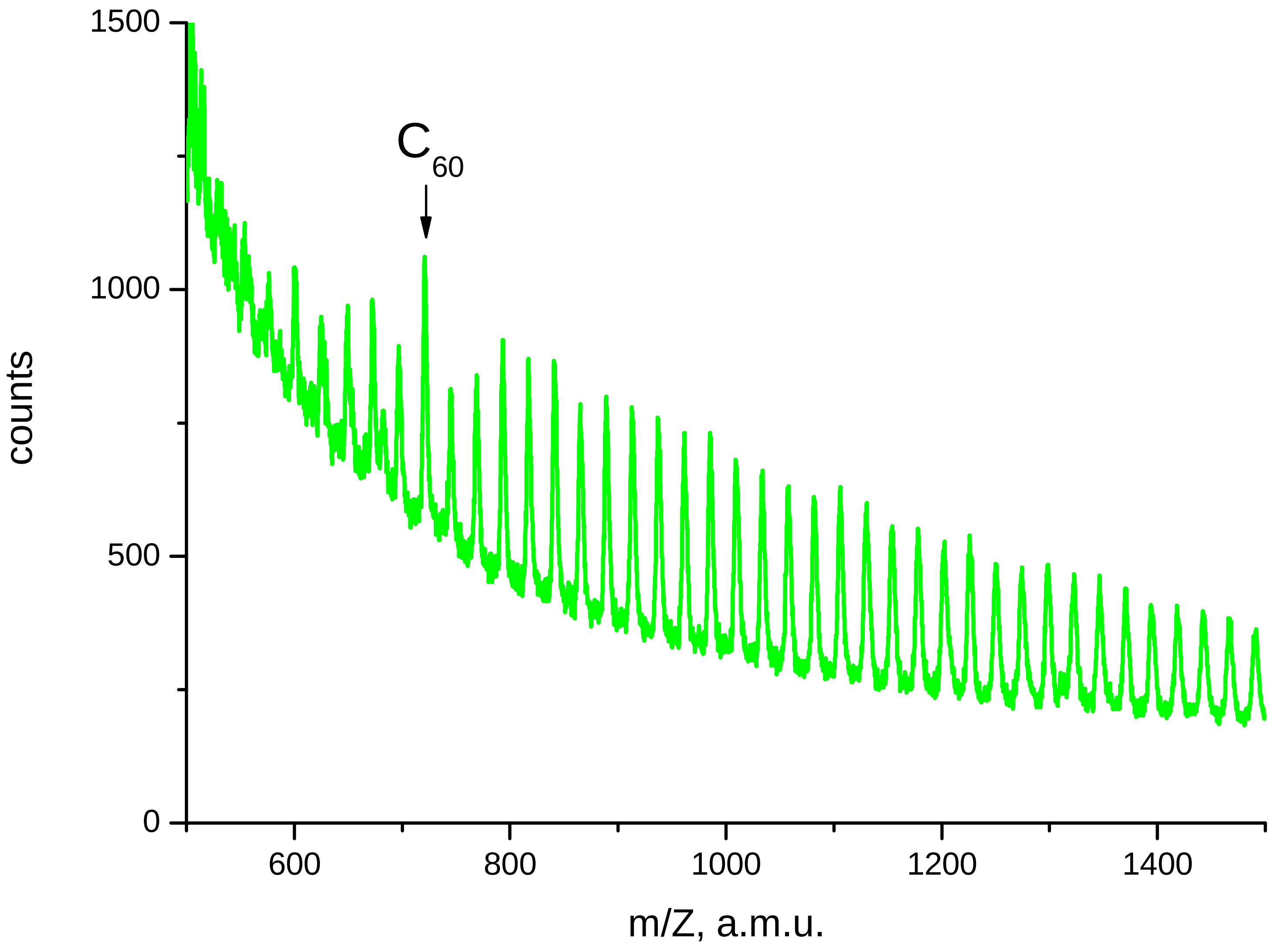




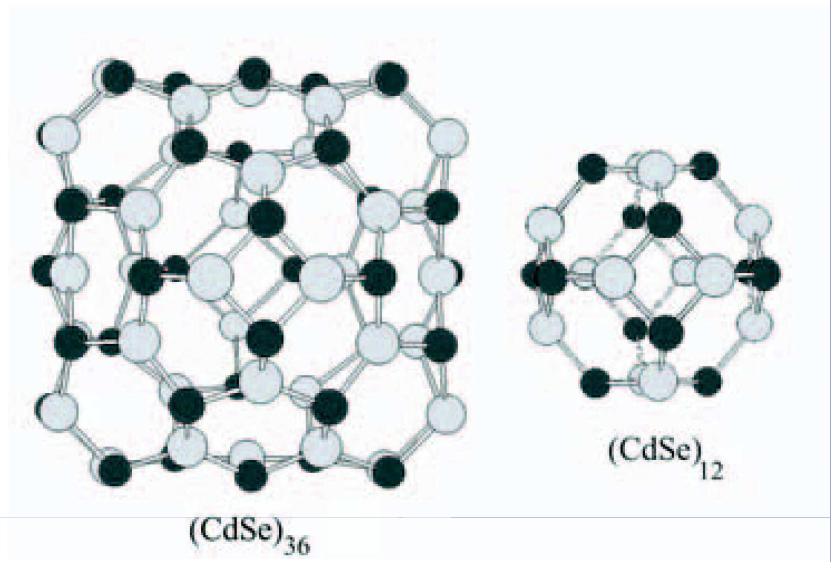
Mass-spectroscopy

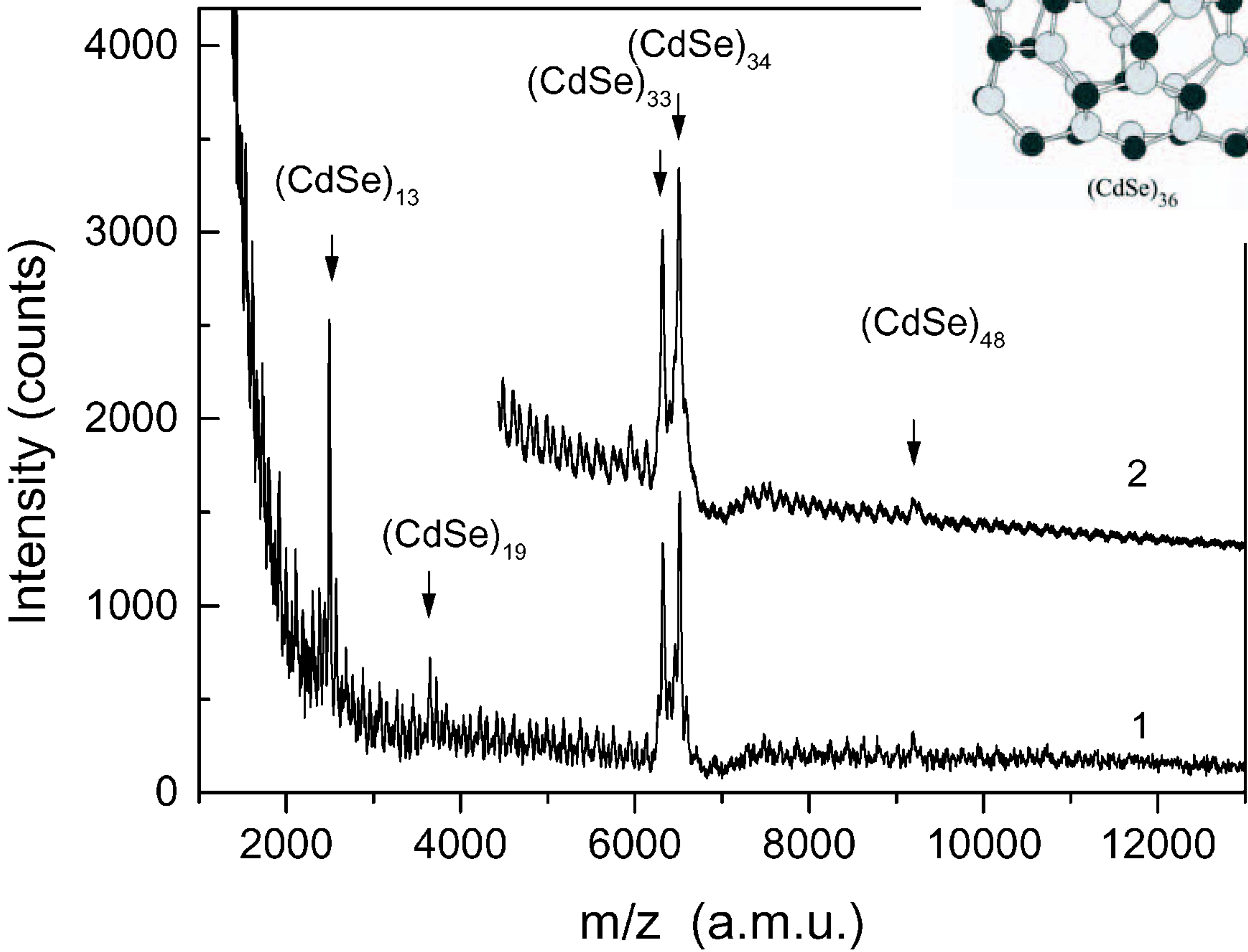


Mass-spectroscopy

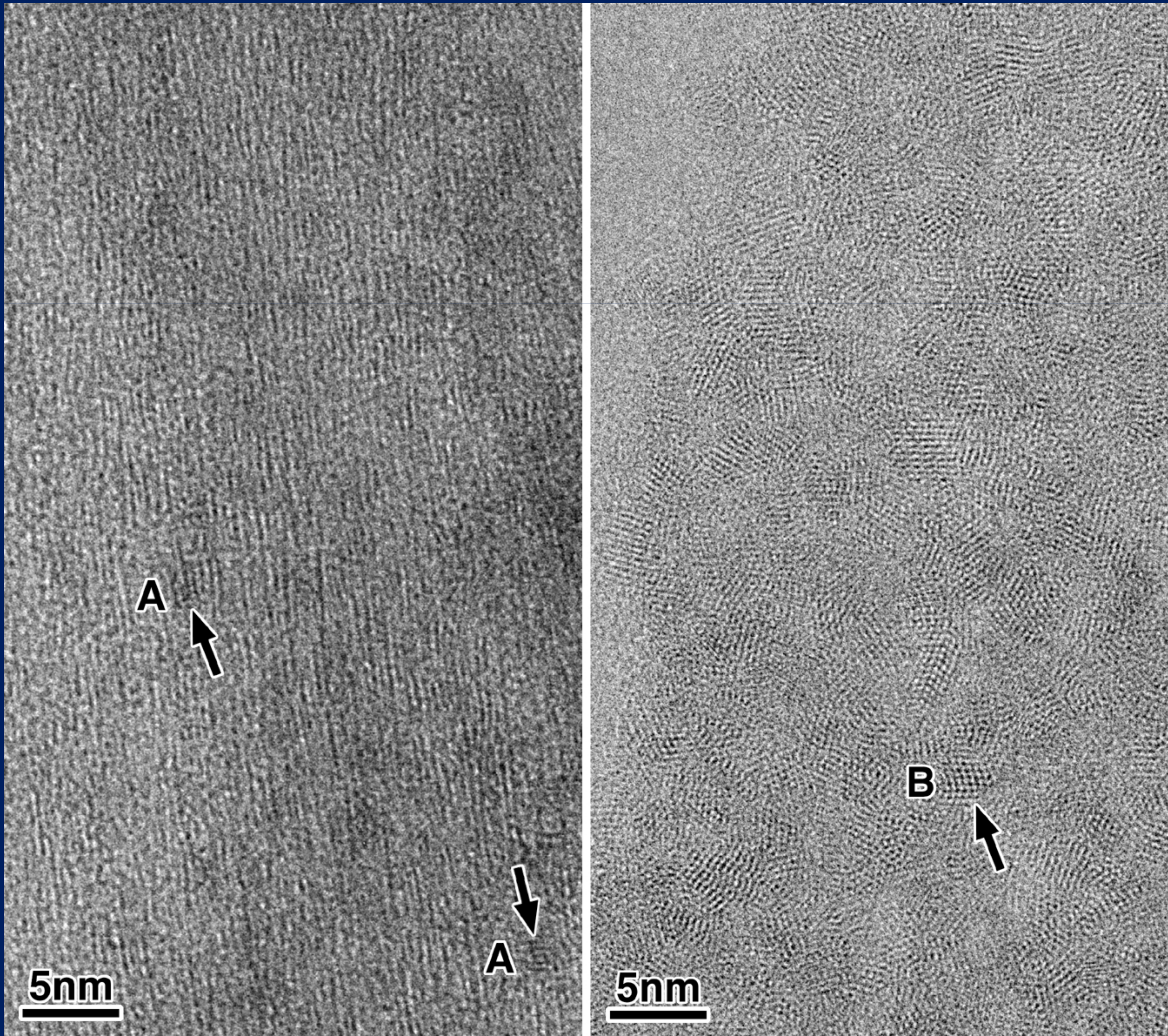


Next magic cluster

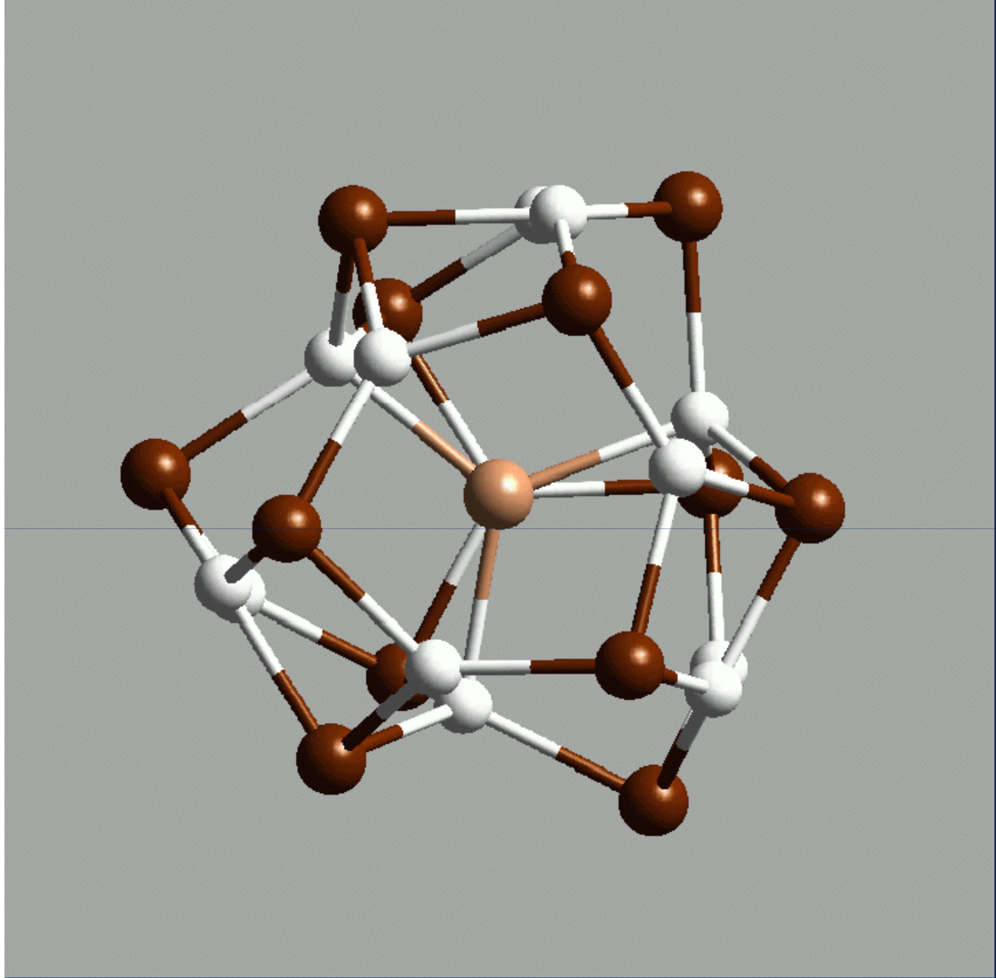


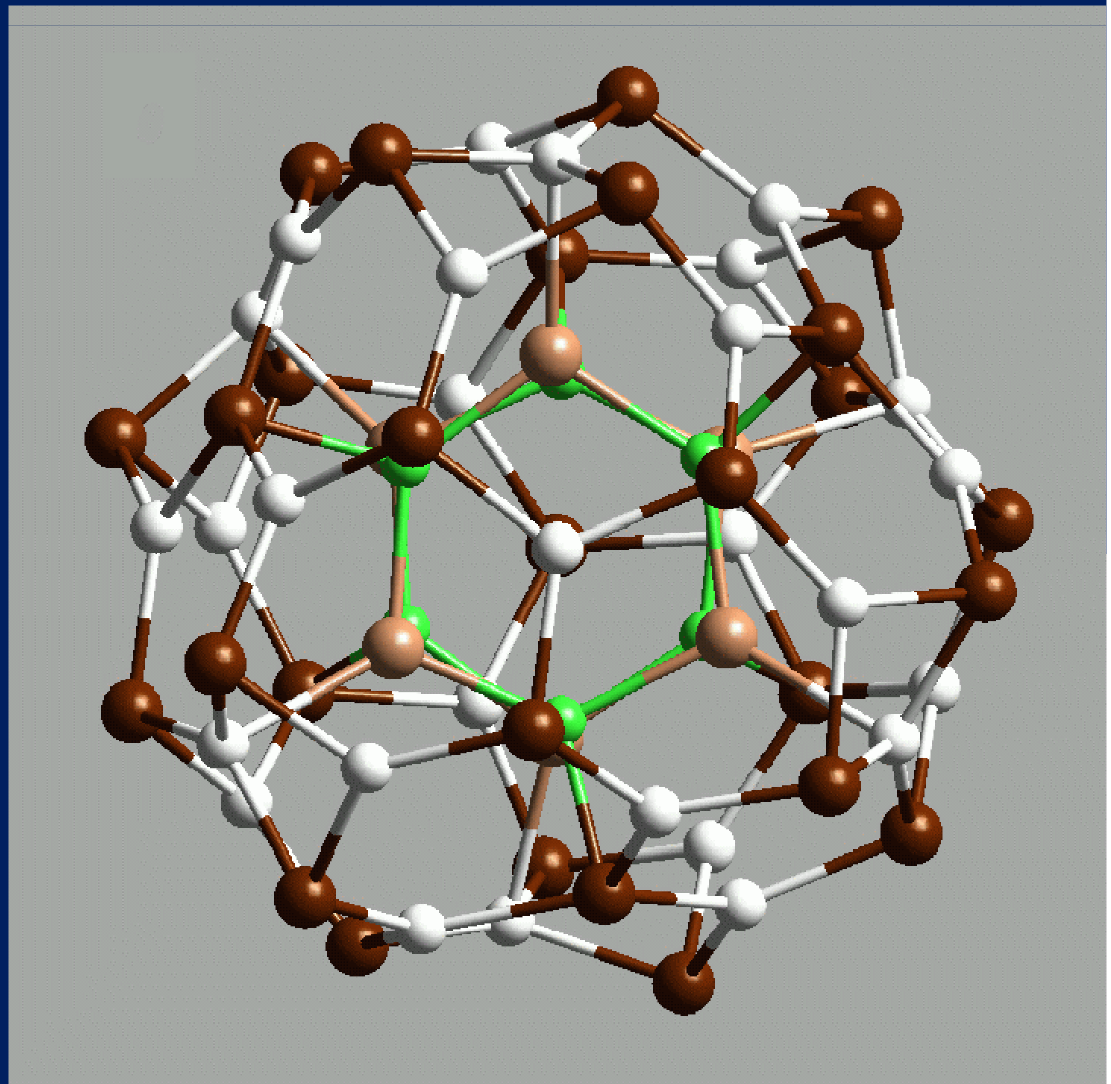


Structure

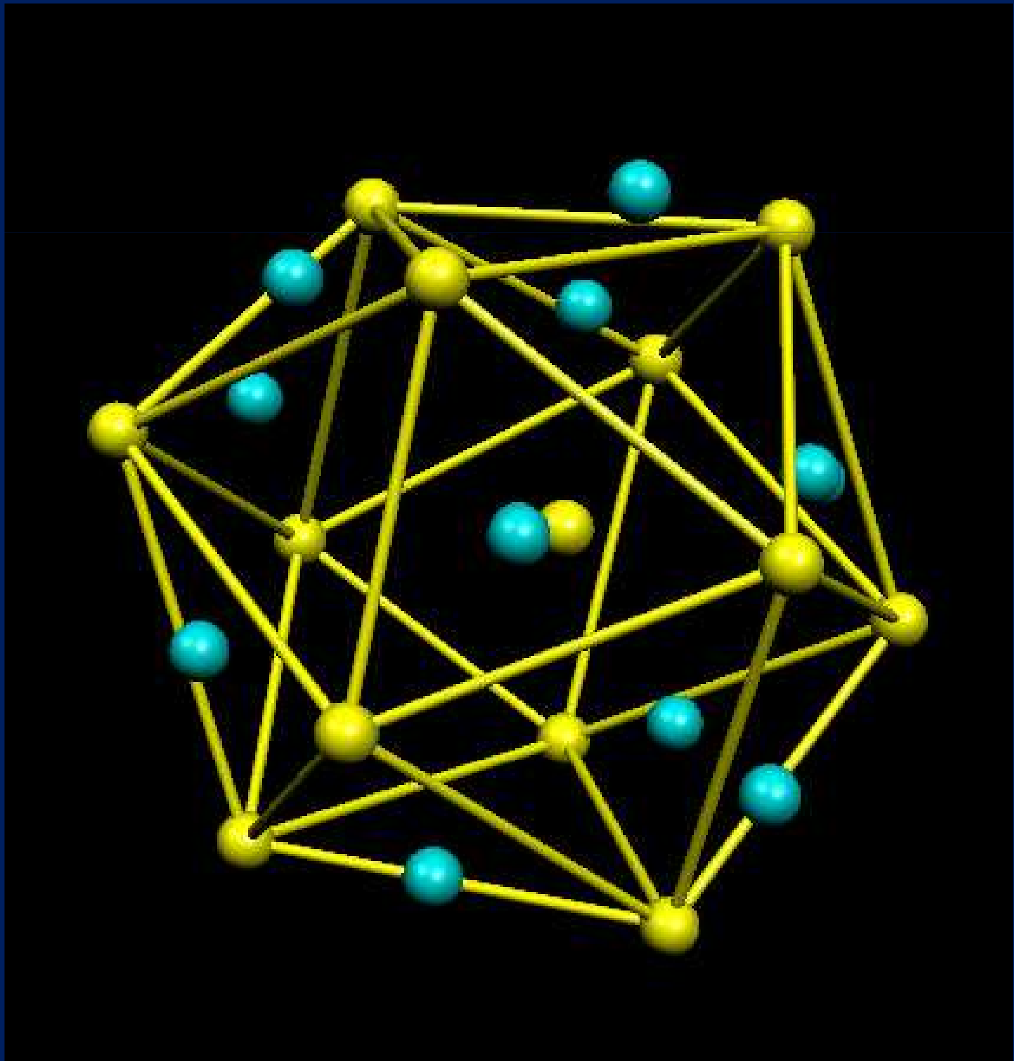


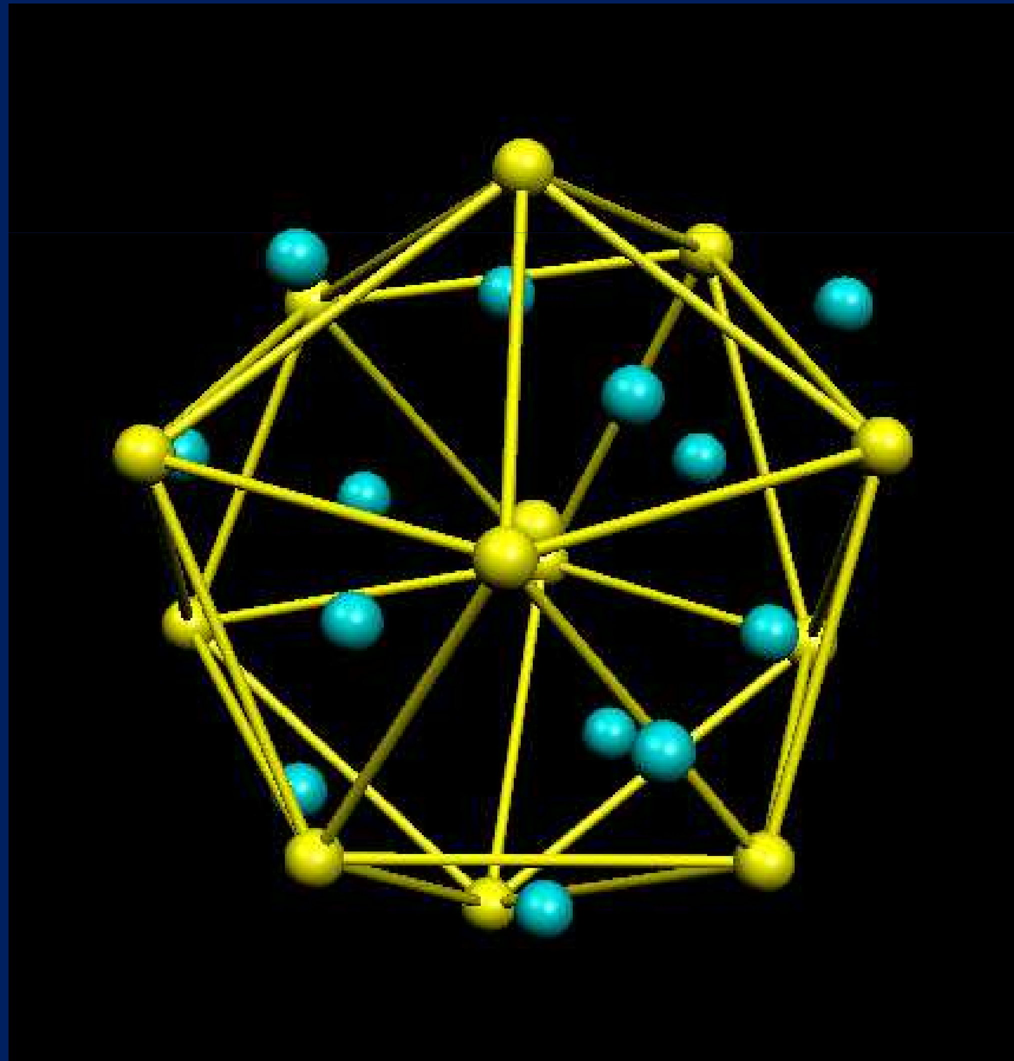
Structure



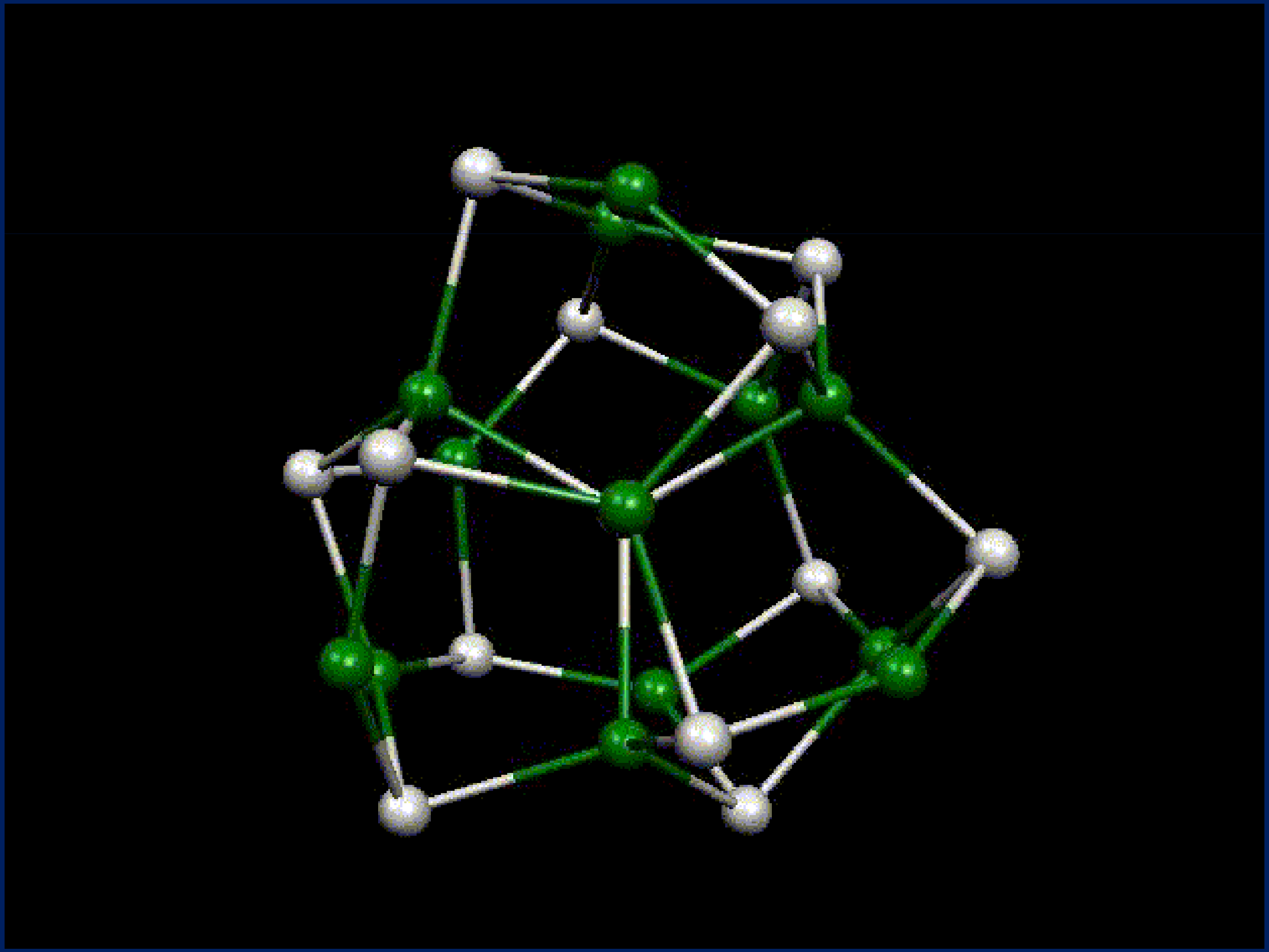


Structure

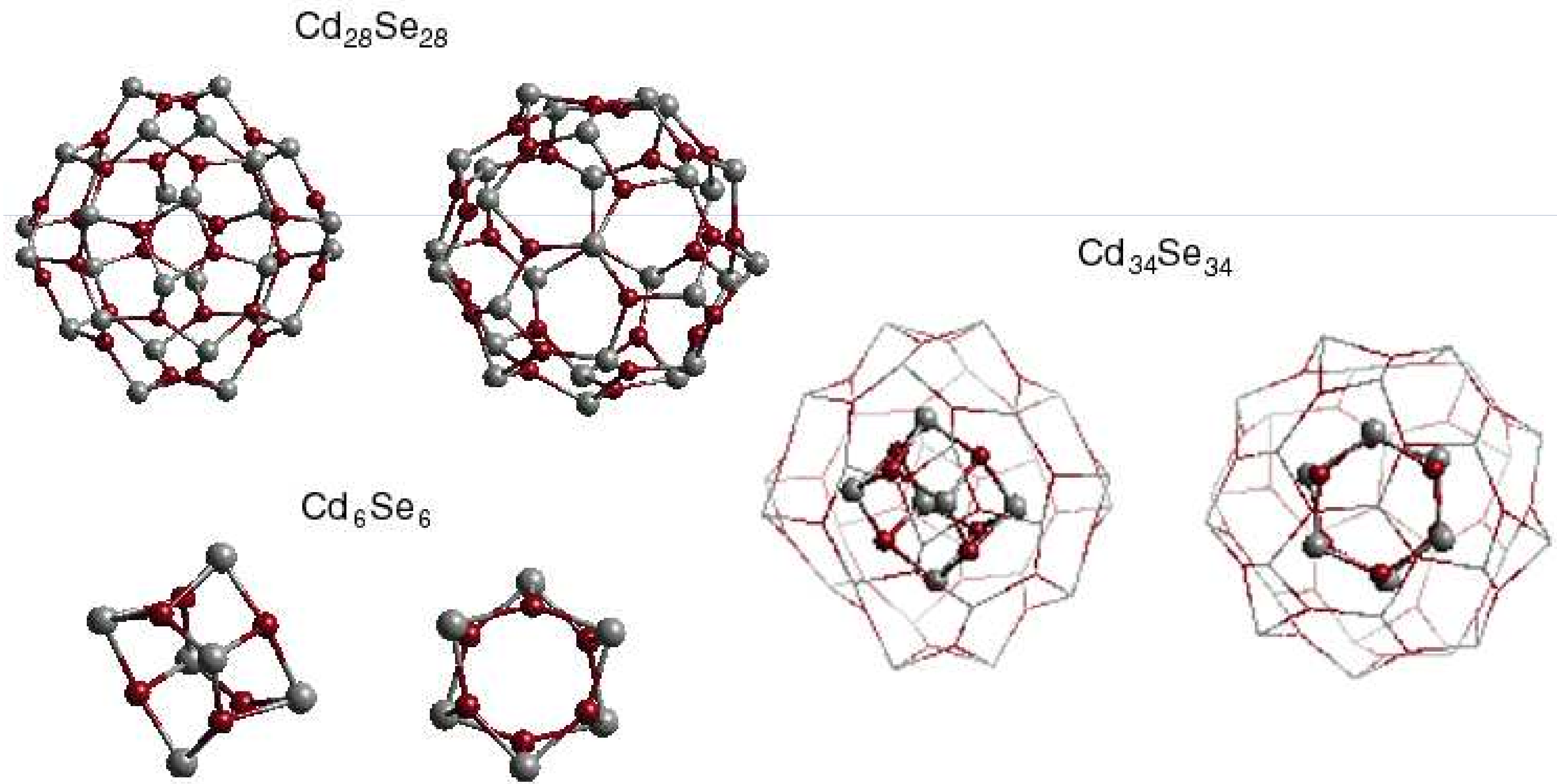




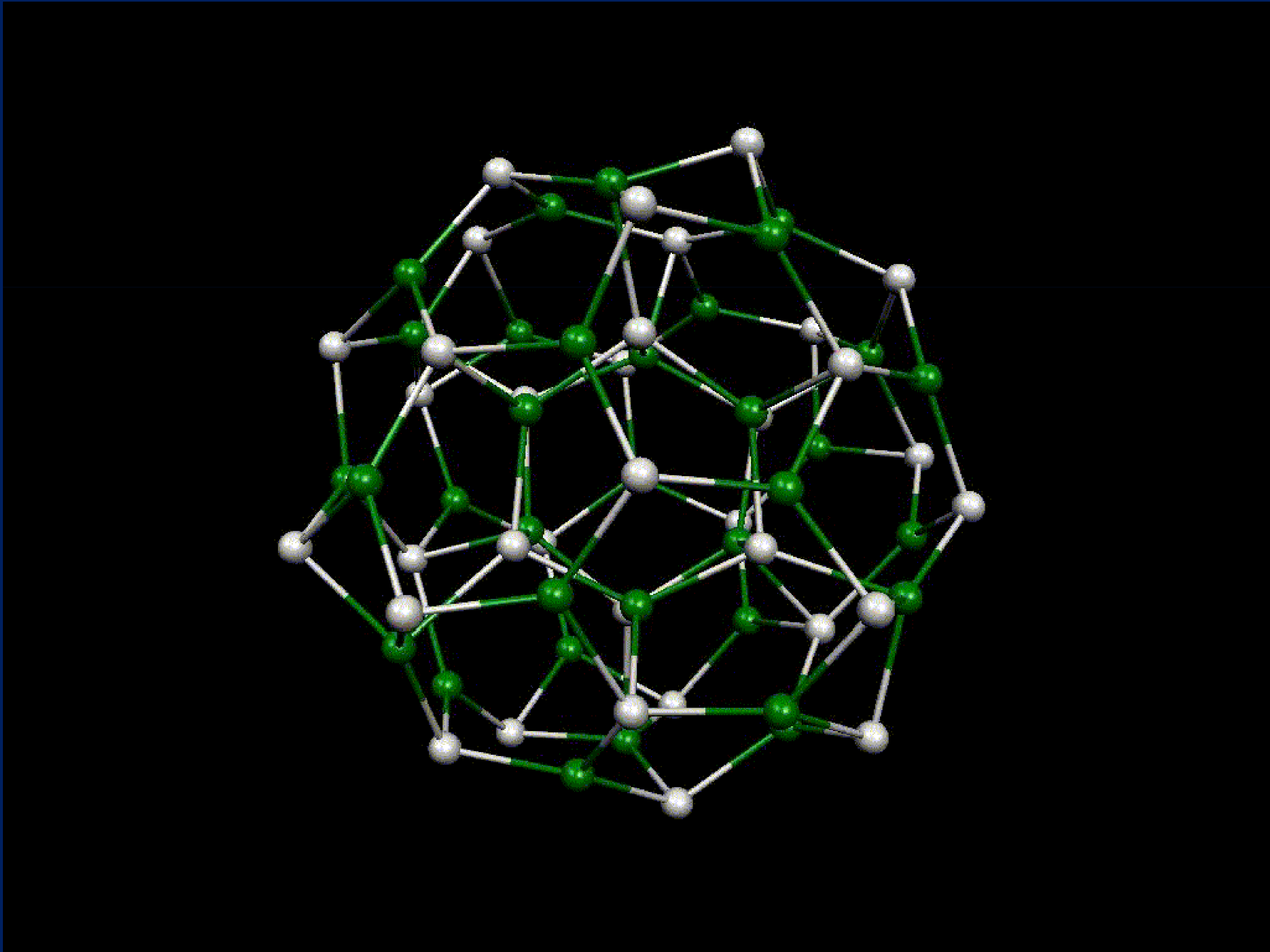
Structure

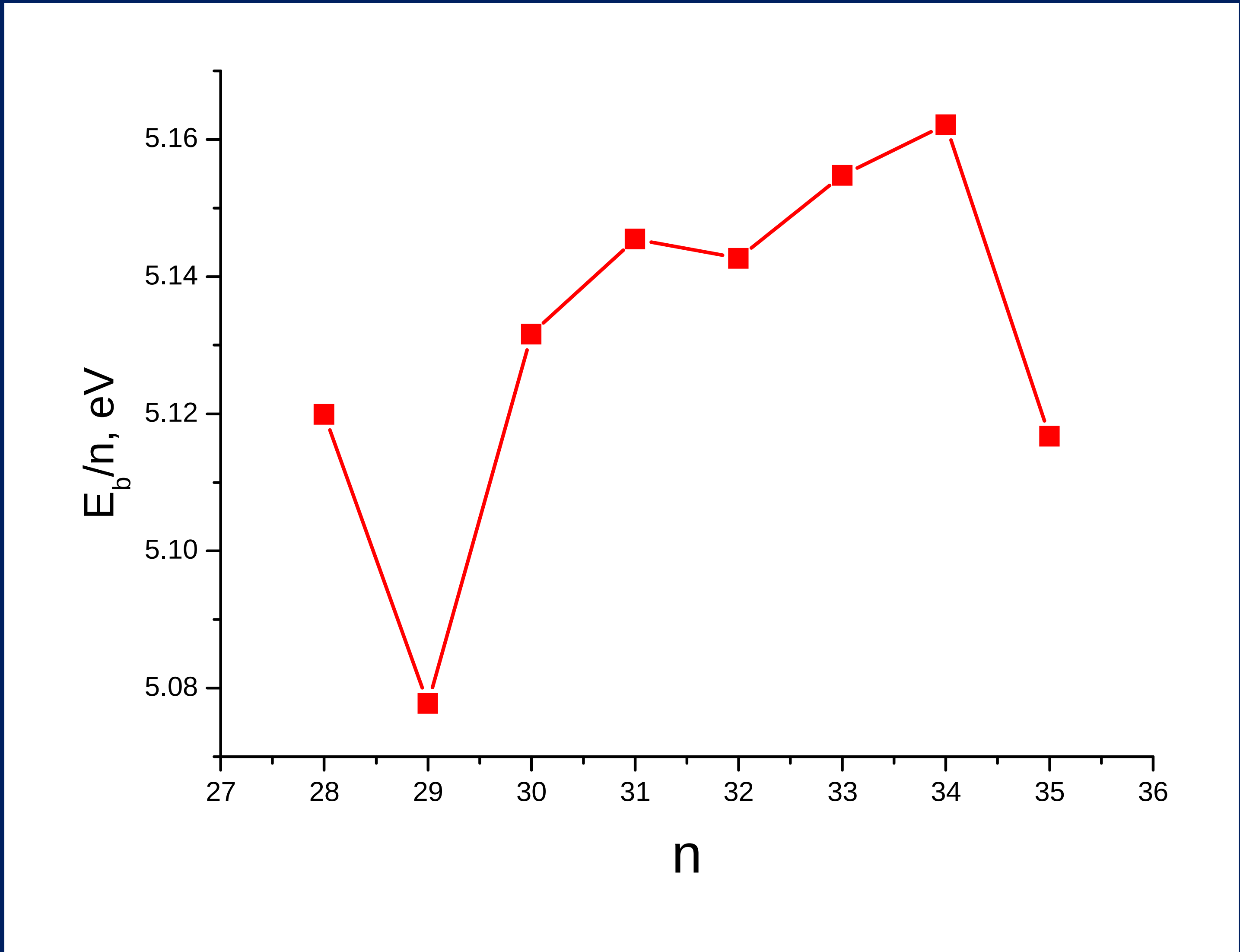


Structure



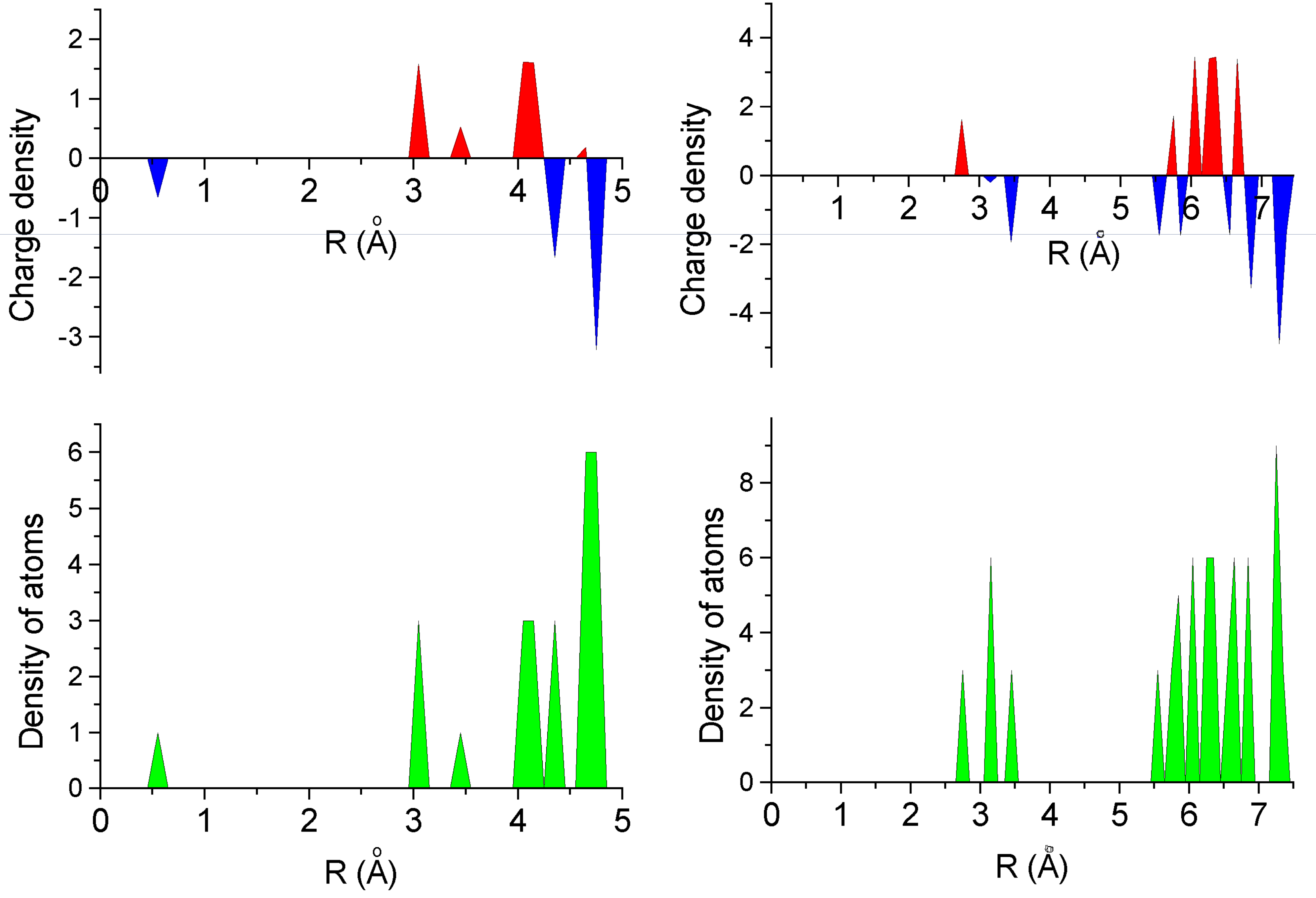
Structure





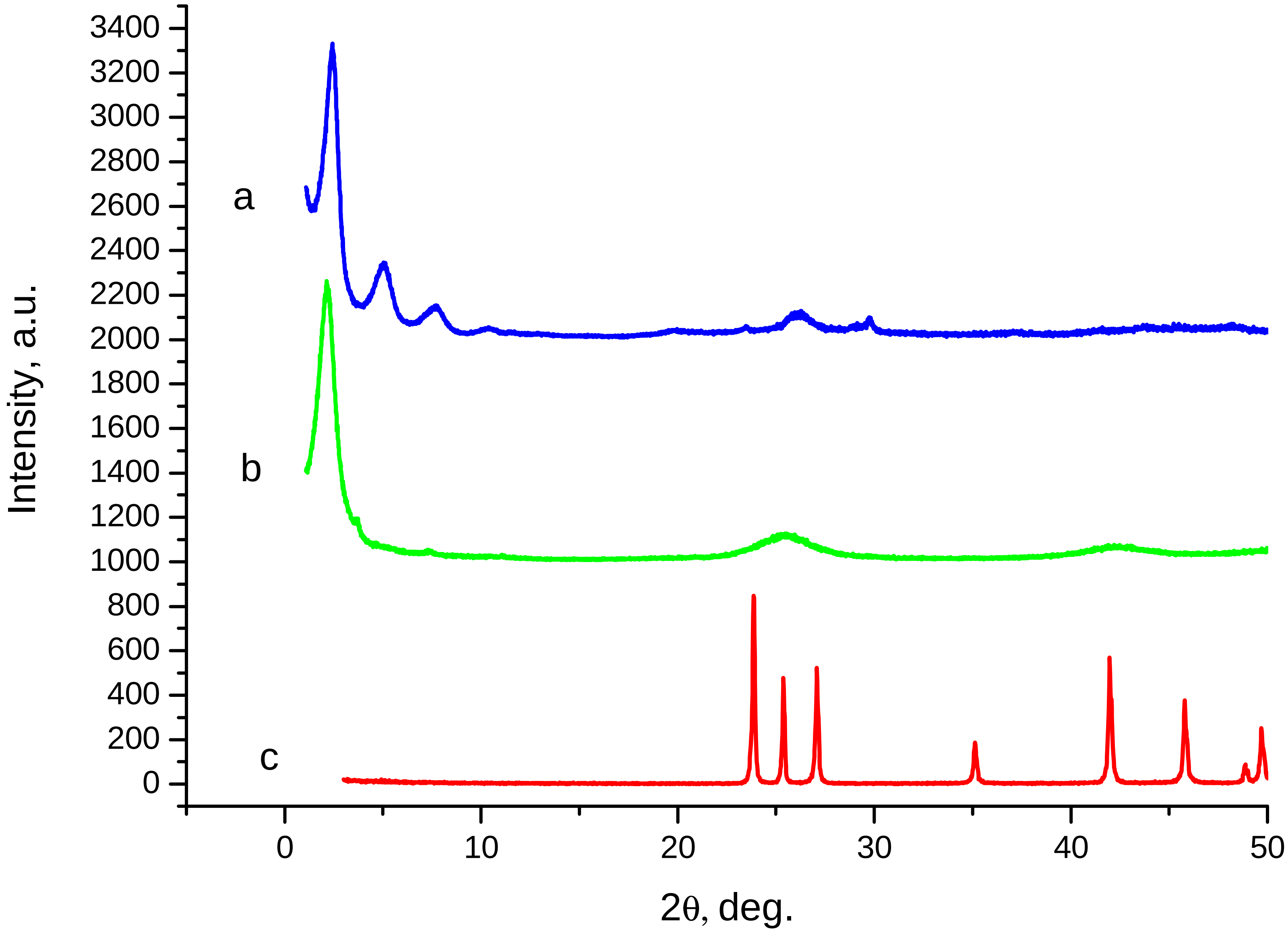
Calculated binding energies per molecule of the clusters $(CdSe)_n$, consisting of $(CdSe)_{28}$ shell and $(CdSe)_m$ core (n=28+m, m=0,1,…,7)

Structure

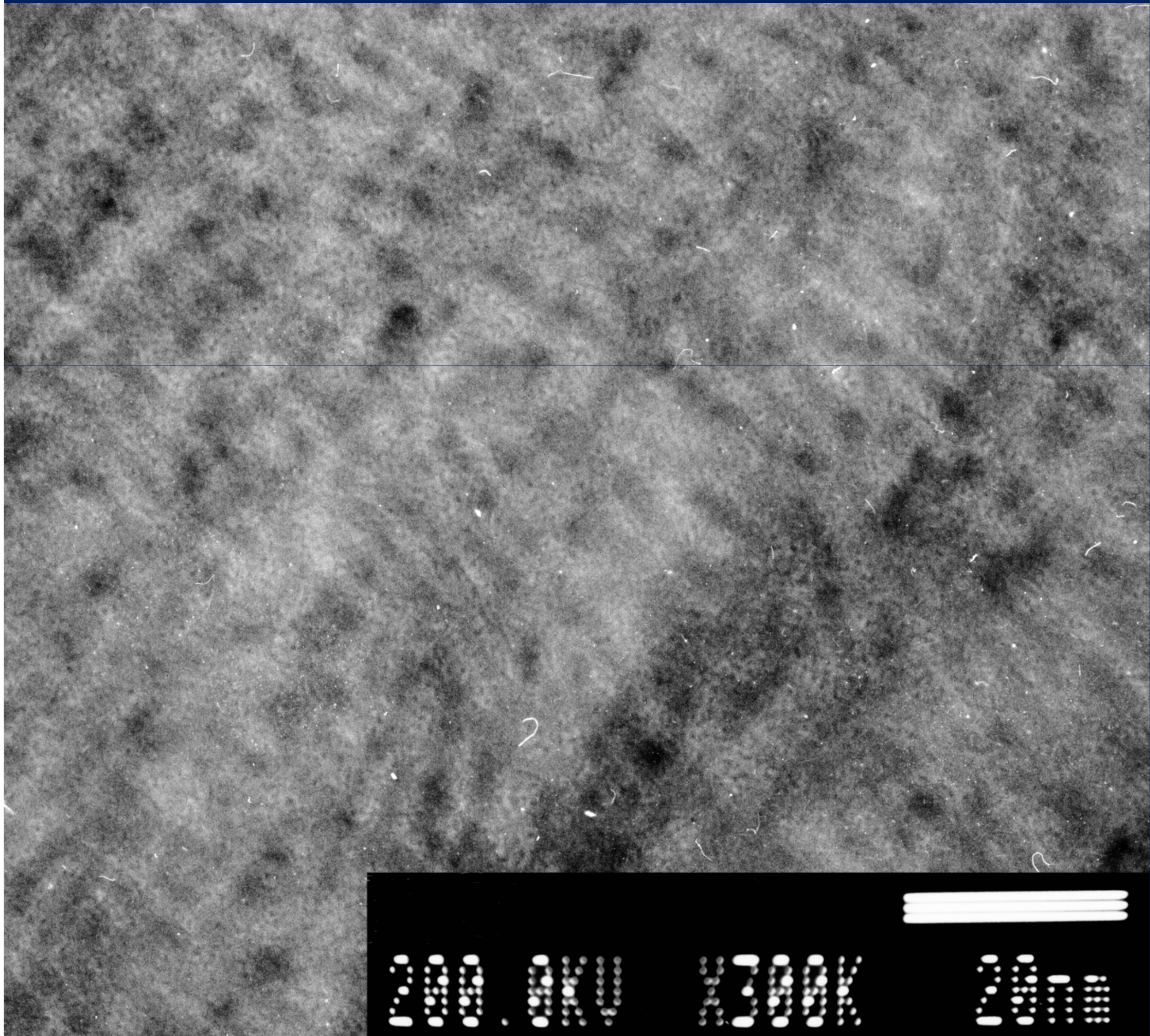


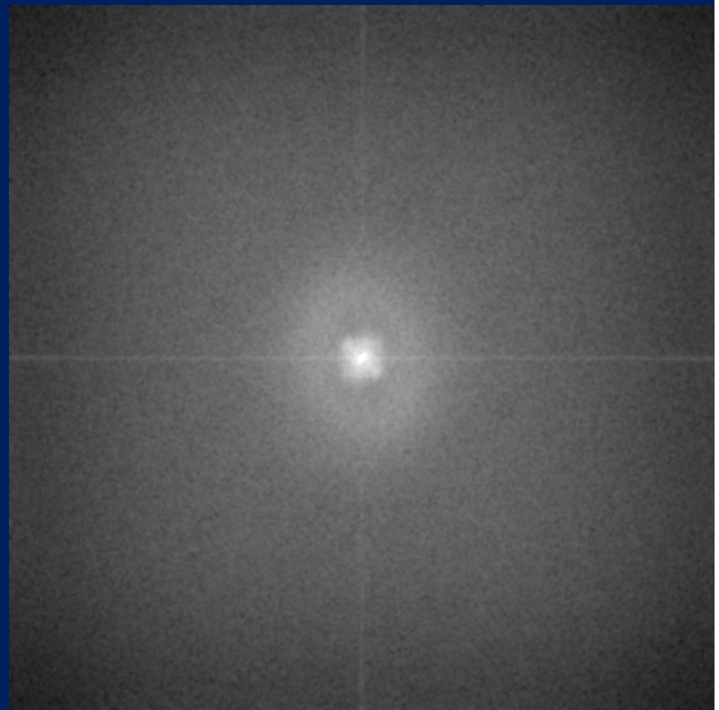
Charge density
R (Å)
Charge density
R (Å)
Density of atoms
R (Å)
Density of atoms
R (Å)

Cluster crystals

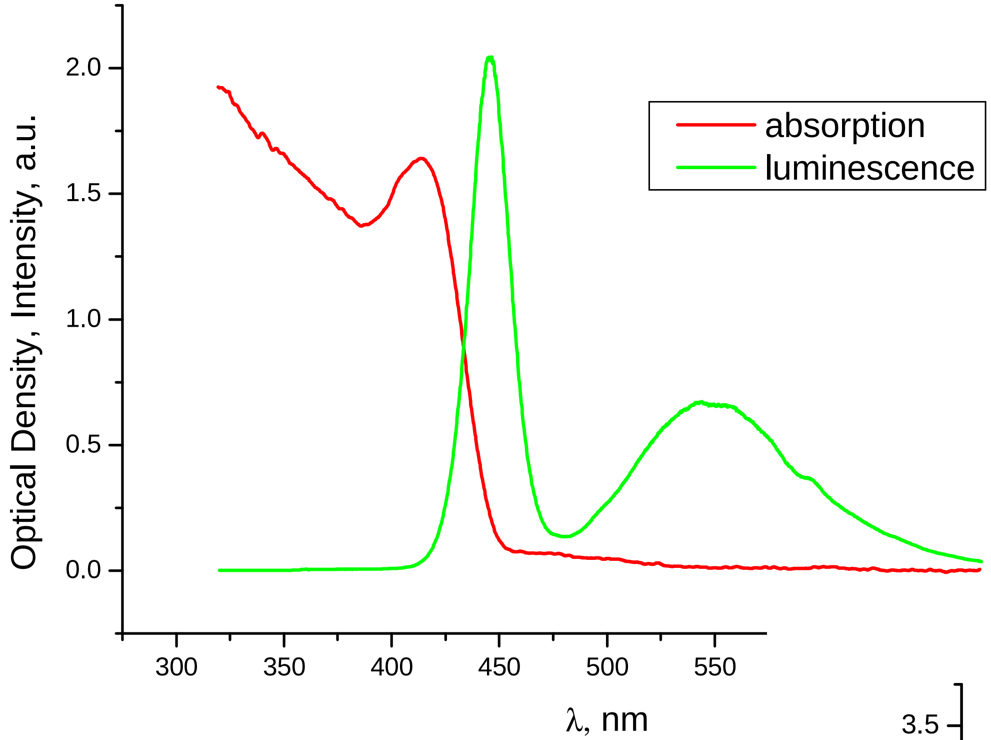


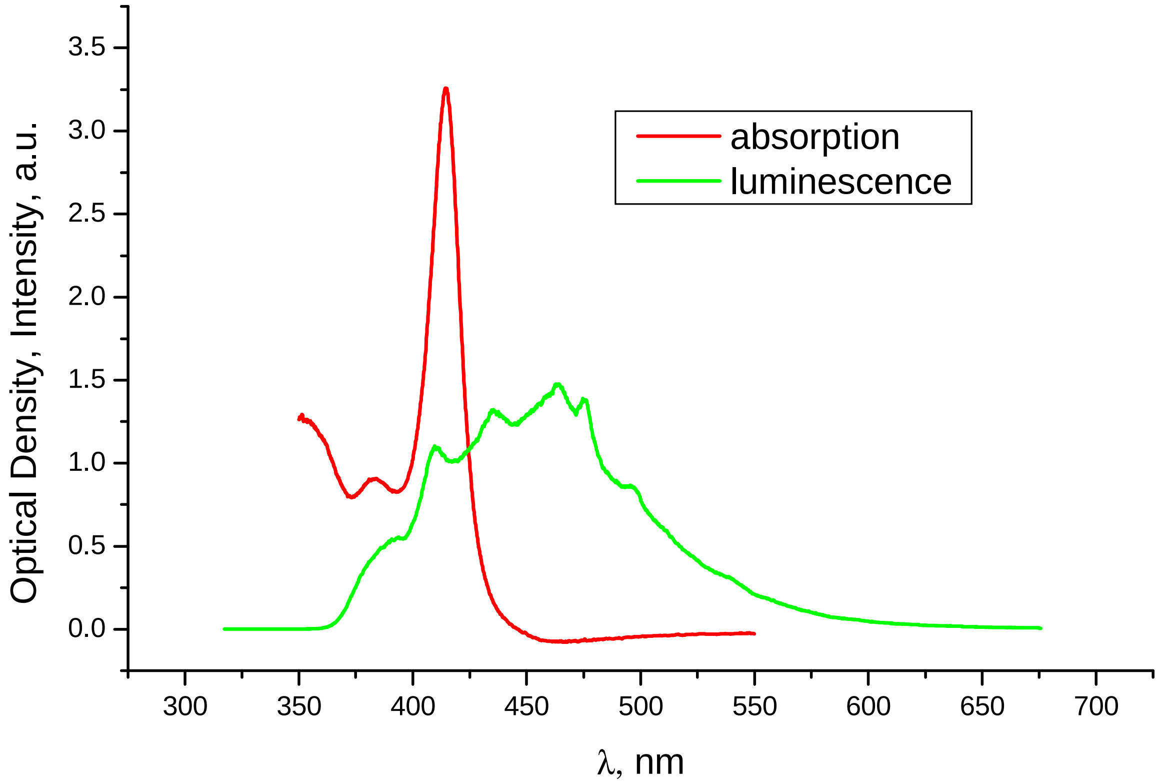
Cluster crystals



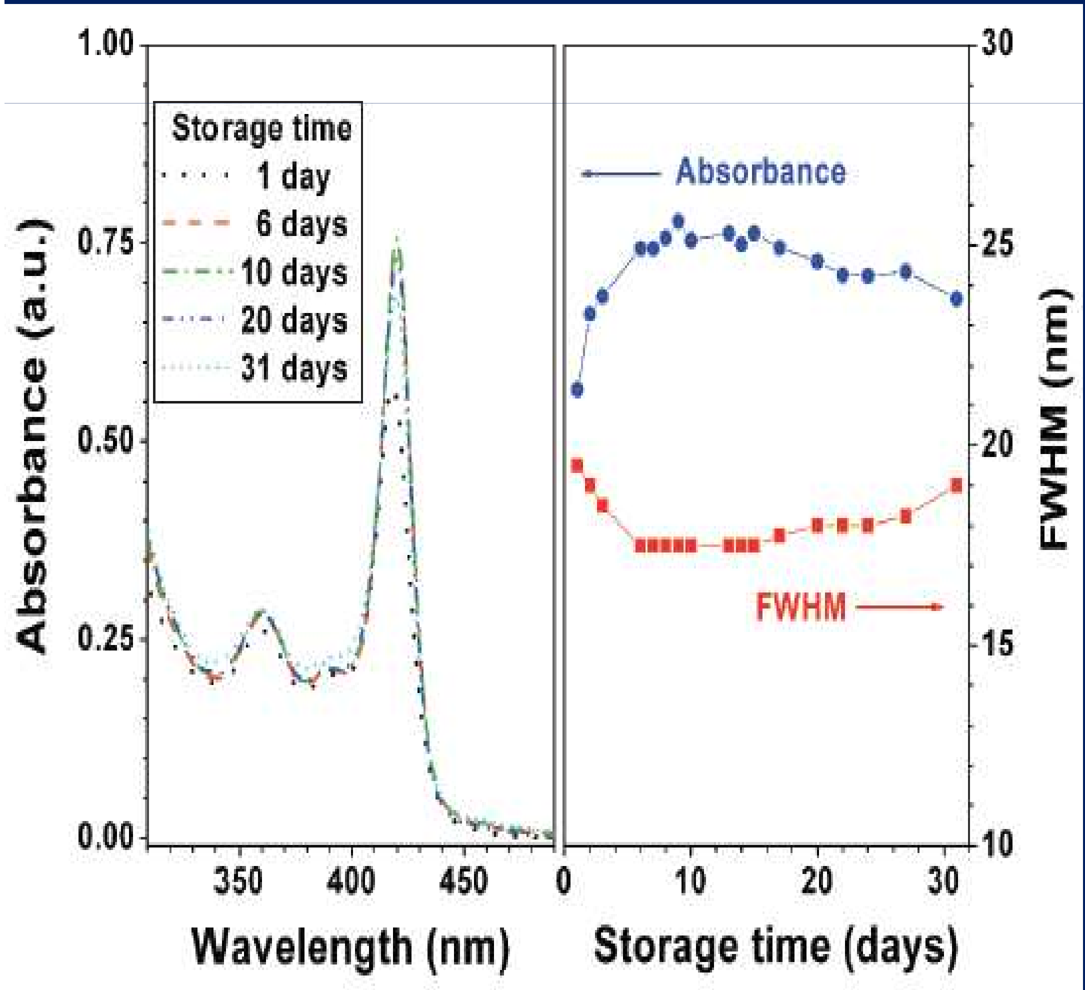


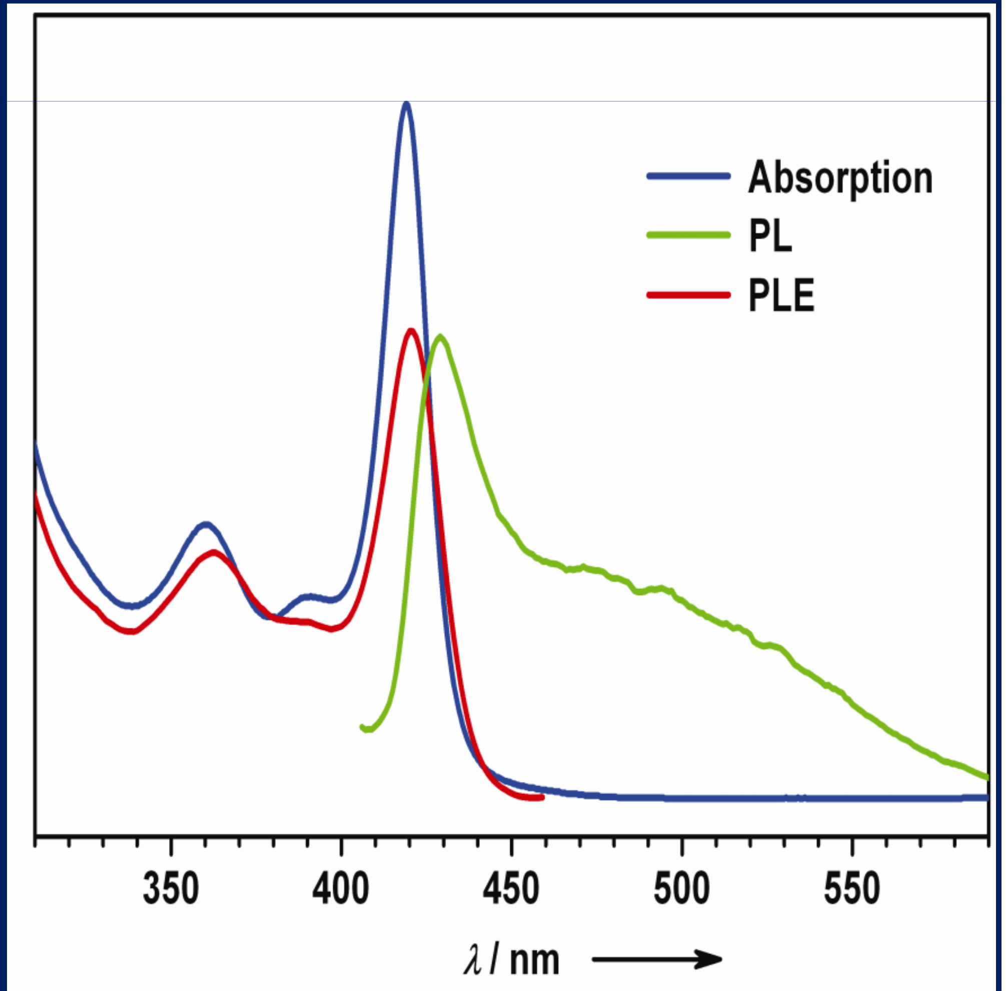
Luminescence



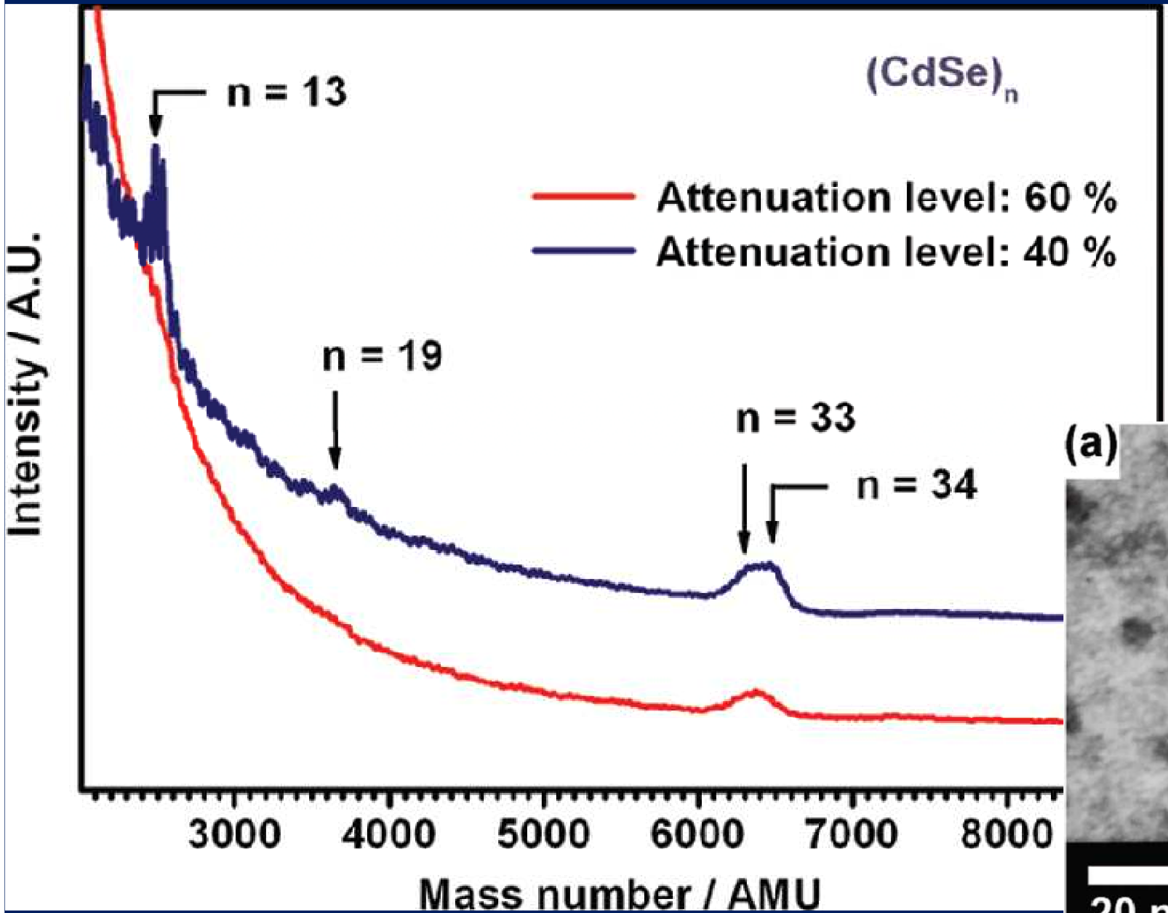


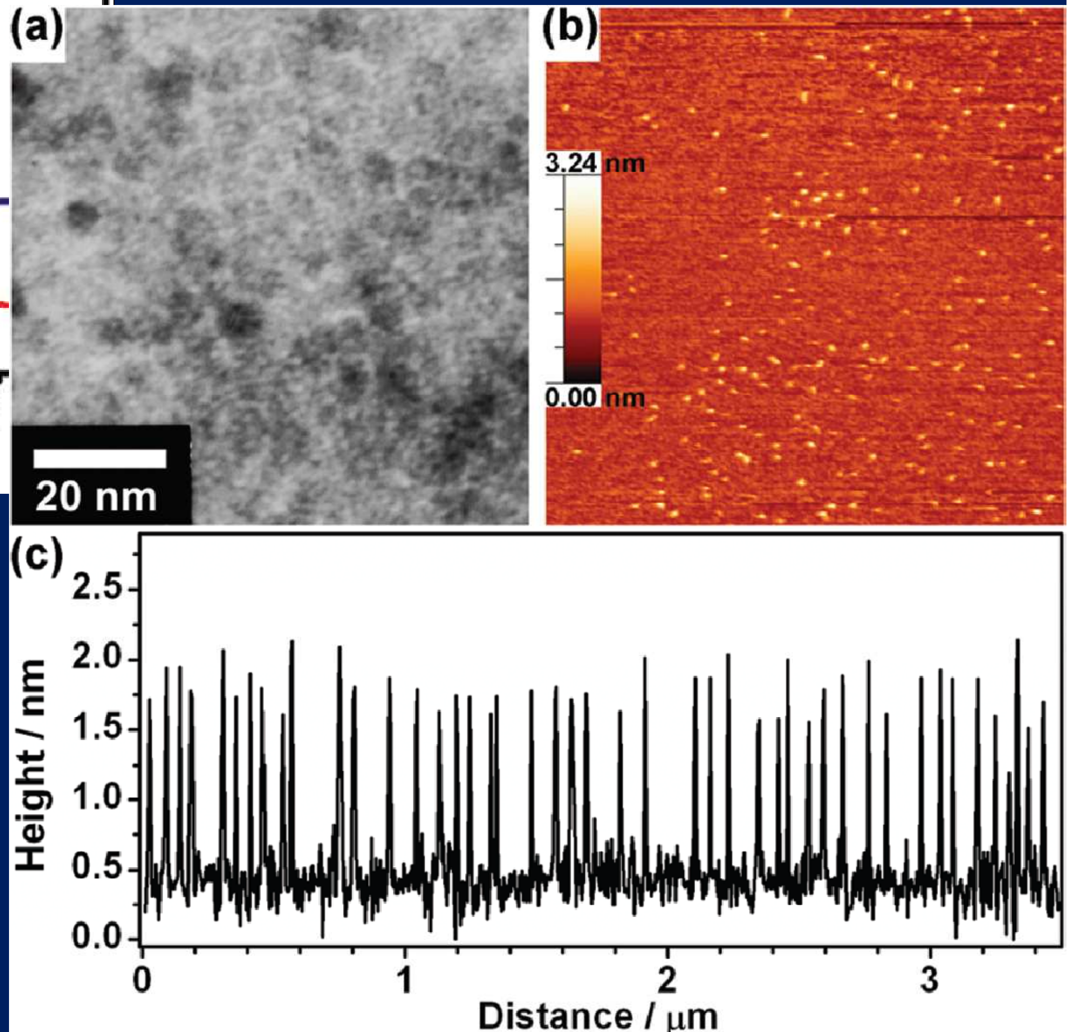
Optical properties of colloid solution of $(CdSe)_{33,34}$



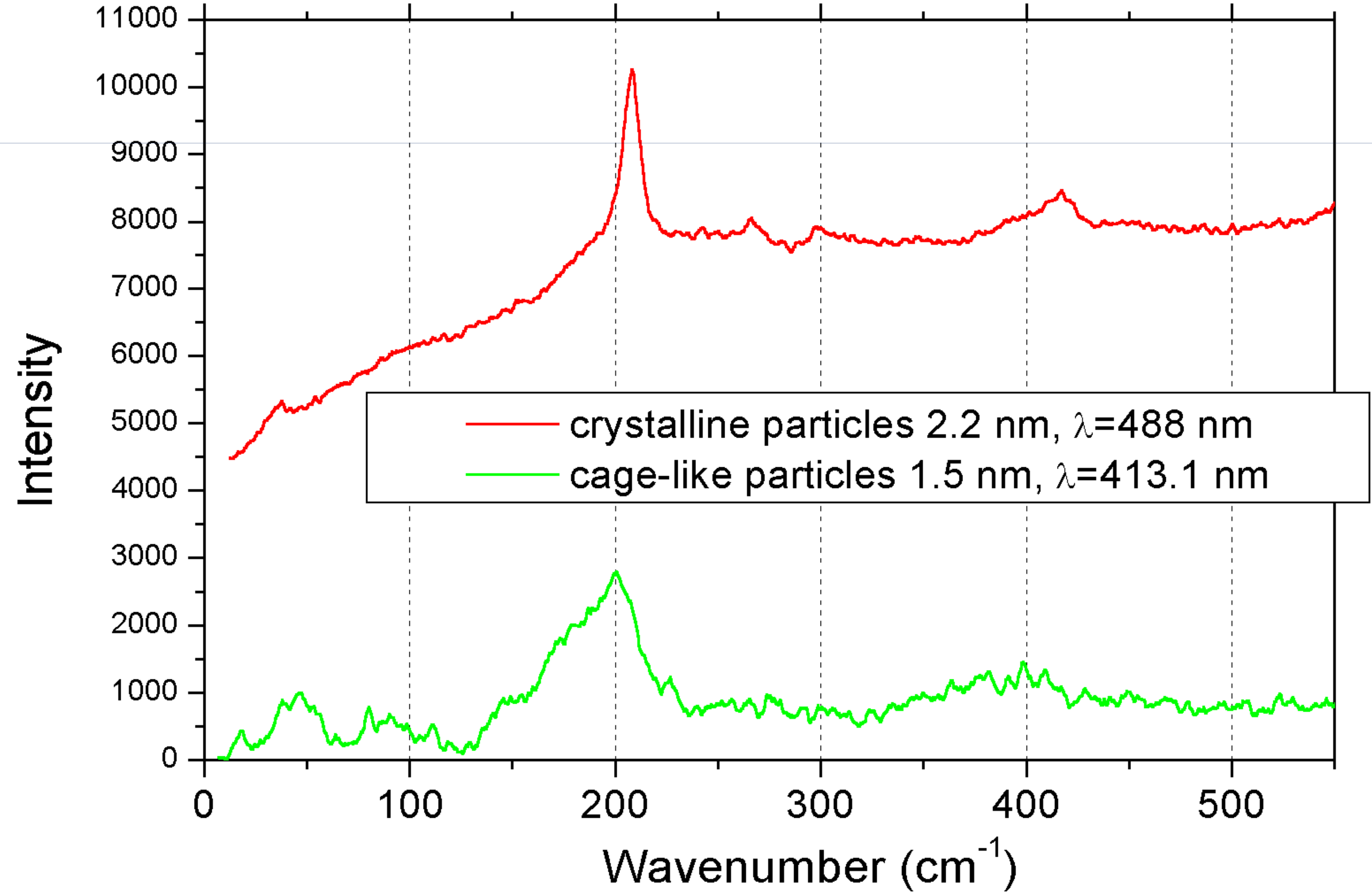


L-cysteine capped CdSe nanoclusters in water

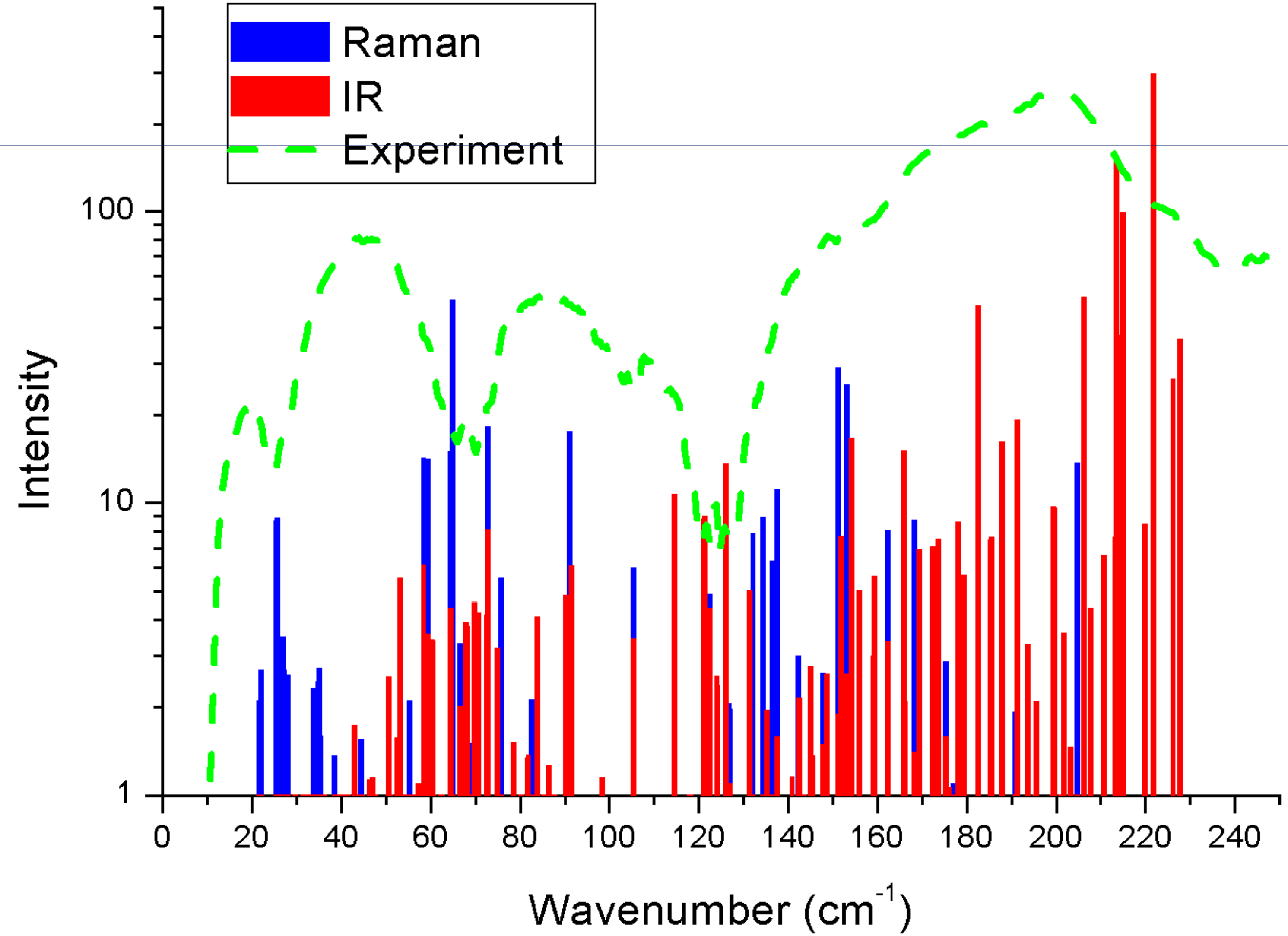




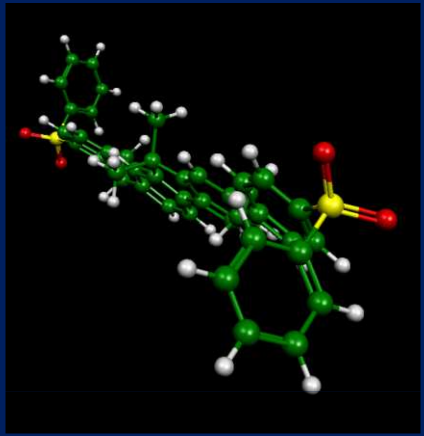
Raman scattering

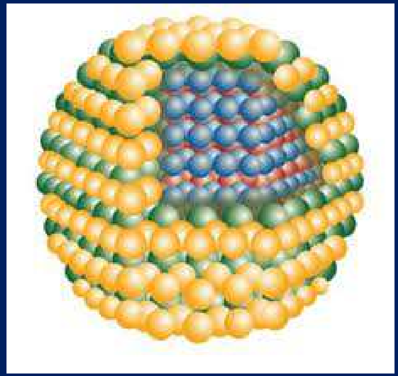


Raman scattering



Organic dyes vs semiconductor nanocrystals

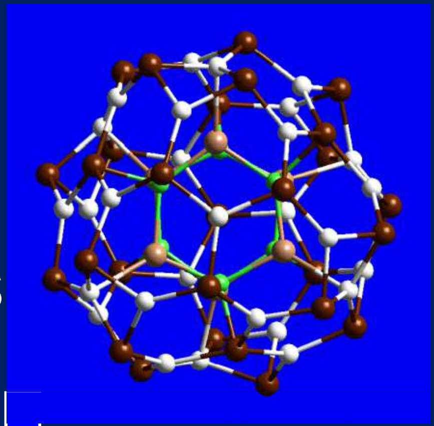




	dyes	nanocrystals
Size	0.5 nm	6-60 nm
Molar absorption coefficient	10^4-10^5 M^{-1} cm^{-1}	10^5-10^6 M^{-1} cm^{-1}
Quantum yield	0.5-1.0	0.1-0.8
Stokes shift	50-150 nm	<50 nm
Photostability	moderate	high
Blinking	no	yes
Sensitivity to environment	yes	low

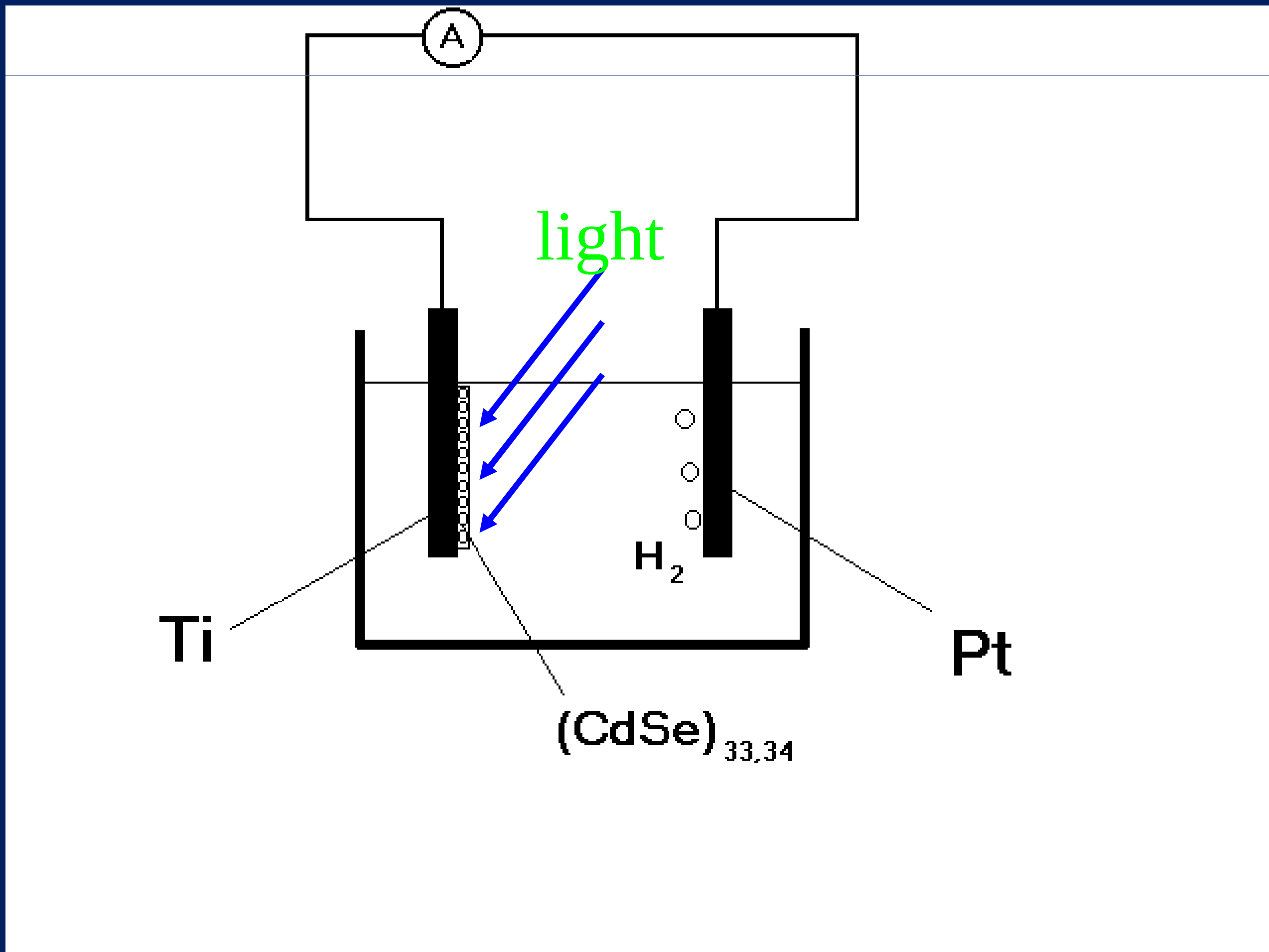
Organic dyes vs semiconductor nanocrystals

Magic nanoclusters



	dyes		nanocrystals
Size	0.5 nm	1-2 nm	6-60 nm
Molar absorption coefficient	10^4-10^5 M^{-1} cm^{-1}	10^5-10^6 M^{-1} cm^{-1}	10^5-10^6 M^{-1} cm^{-1}
Quantum yield	0.5-1.0	0.01	0.1-0.8
Stokes shift	50-150 nm	~20 nm	<50 nm
Photostability	moderate	high	high
Blinking	no	?	yes
Sensitivity to environment	yes	high	low

Application



Papers

1. **Ultra-stable nanoparticles of CdSe revealed from mass spectrometry**. A.Kasuya, R.Sivamohan, Yu.A.Barnakov, I.M.Dmitruk, et al. Nature Materials, 2004, V.3, 99-102.

2. **ZnO clusters: laser ablation production and time-of-flight mass spectroscopic study**. A.Dmytruk, I.Dmitruk, I.Blonskyy, R.Belosludov, Y.Kawazoe, A.Kasuya. Microelectron. J (2009), 40 (2), 218-220.

3. **Ultra-Stable Nanoparticles in $A_{II}B_{VI}$ (A_{II} = Cd, Zn; B_{VI} = S, Se, Te) Compounds**. V.R.Romanyuk, I.M.Dmitruk, Yu.A.Barnakov, R.V.Belosludov, A.Kasuya, J. of Nanoscience and Nanotechnology, V. 9, 2009 , 2111-2118(8).

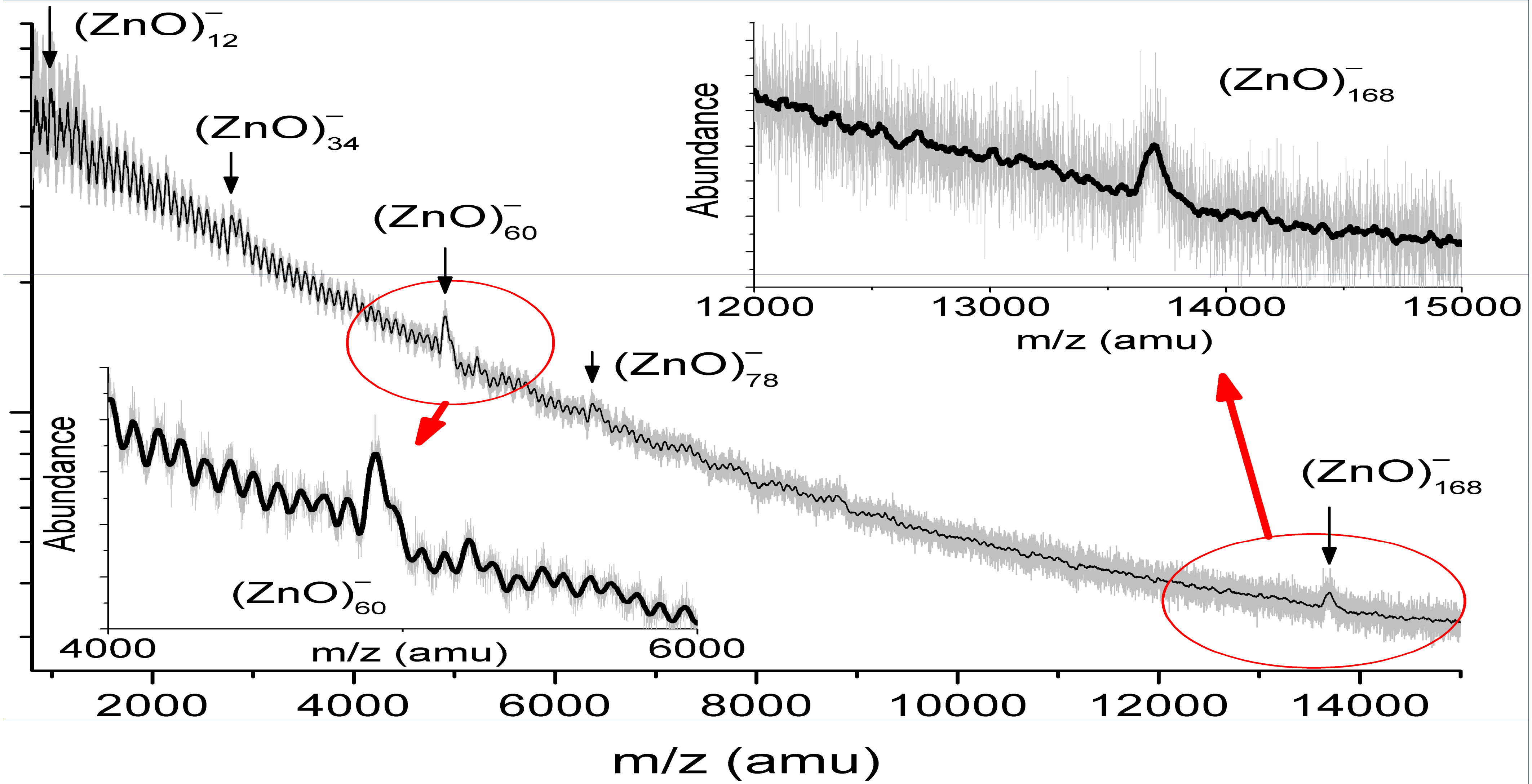
4. **Zinc peroxide precursor for ZnO clusters**. A.Dmytruk, I.Dmitruk, A.Kasuya. Mat.-wiss. u. Werkstofftech. 40, 2009, No. 4, 265.

5. **Laser ablation of CdSe and ZnO: alkylamine assisted formation of magic clusters**. A.Dmytruk, I.Dmitruk, R.Belosludov, Y.Kawazoe, A.Kasuya. NATO Science Series B. Nanostructured Materials for Advanced Technological Applications. 2009, V, 5, 201-206.

6. **Size-selective Growth and Stabilization of Small CdSe Nanoparticles in Aqueous Solution**. Y.-S.Park, A.Dmytruk, I.Dmitruk, A.Kasuya, et al. ACS Nano 2010 4 (1) 121-128.

7. **Aqueous Phase Synthesized CdSe Nanoparticles with Well-Defined Numbers of Constituent Atoms**. Y.-S. Park, A. Dmytruk, I. Dmitruk, A. Kasuya, et al, J. Phys. Chem. C 2010, 114, 18834–18840.

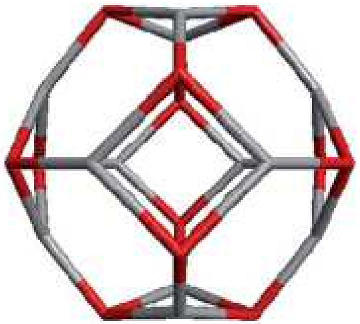
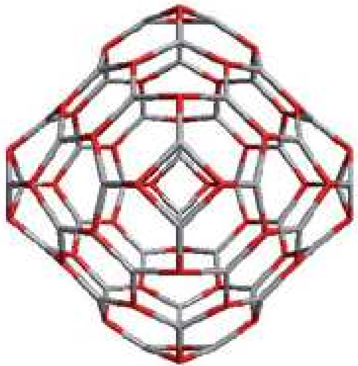
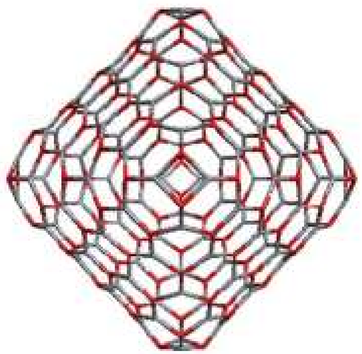
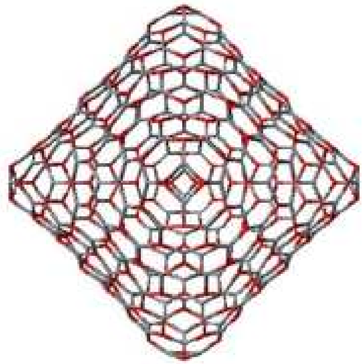
Mass spectroscopy of ZnO clusters



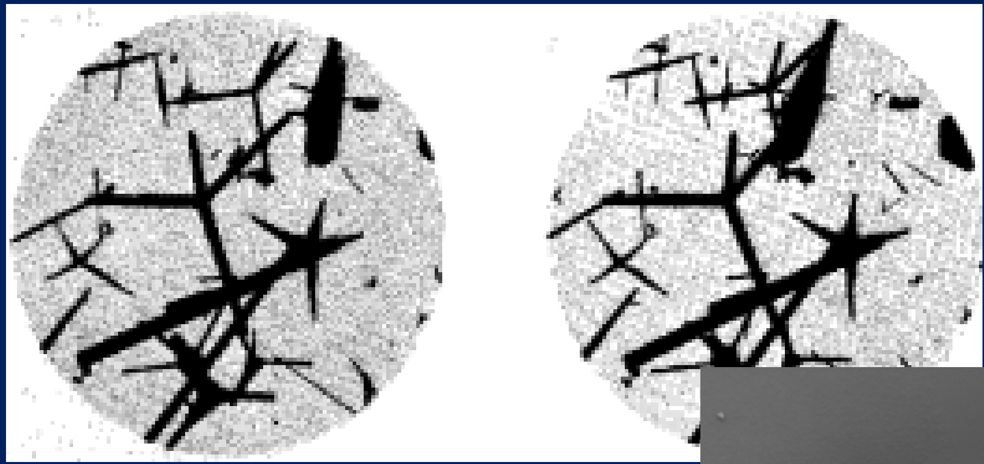
Why clusters $(ZnO)_n$ with n = 12, 34, 60, 168 are "magic"?

Netsed-shell structure of magic clusters

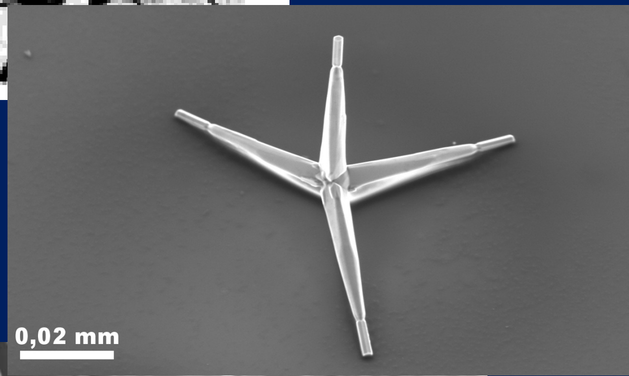
- **m=1:** $(ZnO)_{12}$
- **m=2:** $(ZnO)_{60}$ = $(ZnO)_{12}$ @ $(ZnO)_{48}$
- **m=3:** $(ZnO)_{168}$ = $(ZnO)_{12}$ @ $(ZnO)_{48}$ @ $(ZnO)_{108}$
- **m=4:** $(ZnO)_{360}$ = $(ZnO)_{12}$ @ $(ZnO)_{48}$ @ $(ZnO)_{108}$ @ $(ZnO)_{192}$
- **M. Goldberg.** Tohoku Math. J. **1937**, 43, 104.
- **J. H. Conway** et al. The Symmetries of Things. CRC Press, Taylor and Francis: New York, **2008**, p.448.
- **polyHédronisme** v0.2. http://levskaya.github.io/polyhedronisme/

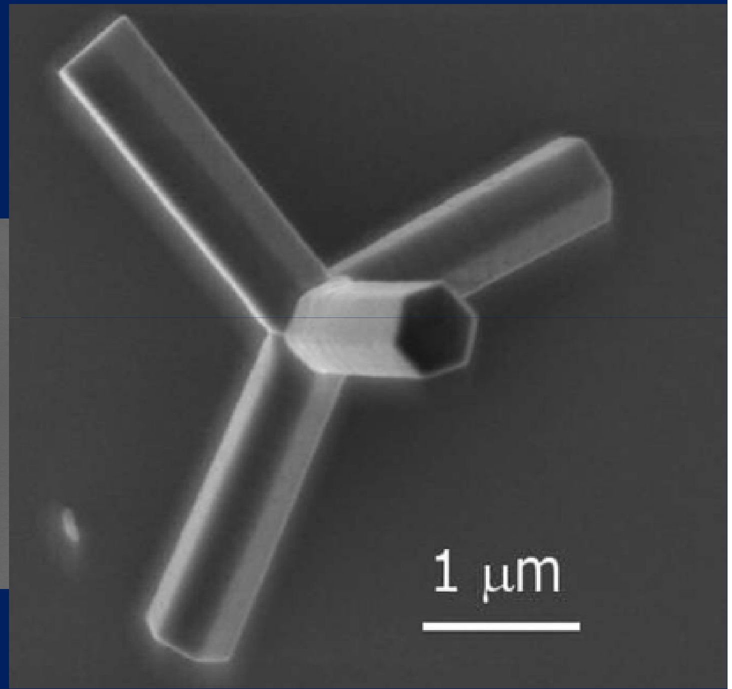
Shell number, m	1	2	3	4
Number of ZnO pairs, $n = 12m^2$	12	48	108	192
Goldberg polyhedron	$G_{IV}(1,1)$	$G_{IV}(2,2)$	$G_{IV}(3,3)$	$G_{IV}(4,4)$
Conway notation	tO	ctO	tktO	cctO
Rendered Conway polyhedron[a]				
AM1 optimized T_h symmetric $(ZnO)_n$ shell				

ZnO tetrapods



M. L. Fuller. J. Appl. Phys. **1944**, 15, 164





Newton et al.
Mater. Today **2007**, 10, 50

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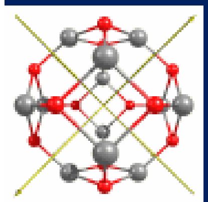
Why tetrapod structure?

Model of tetrapod nucleation

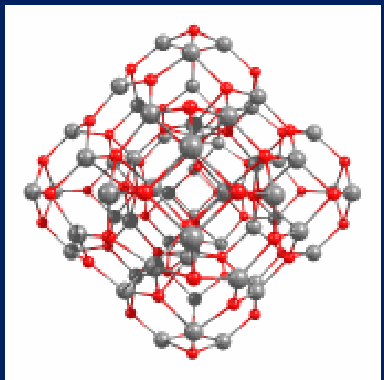
$(ZnO)_{12}$

T_h



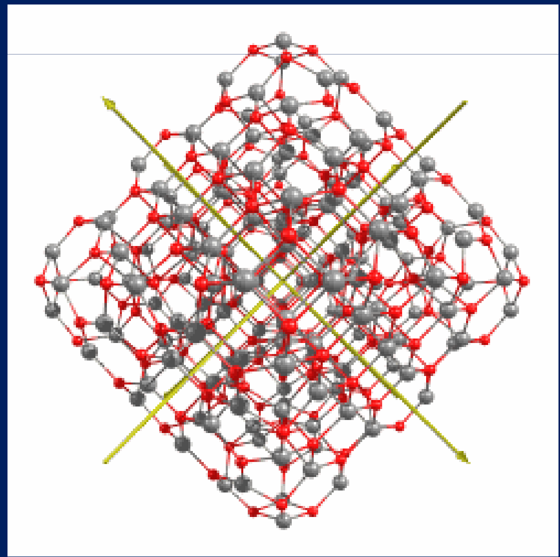
$(ZnO)_{60}$

C_1

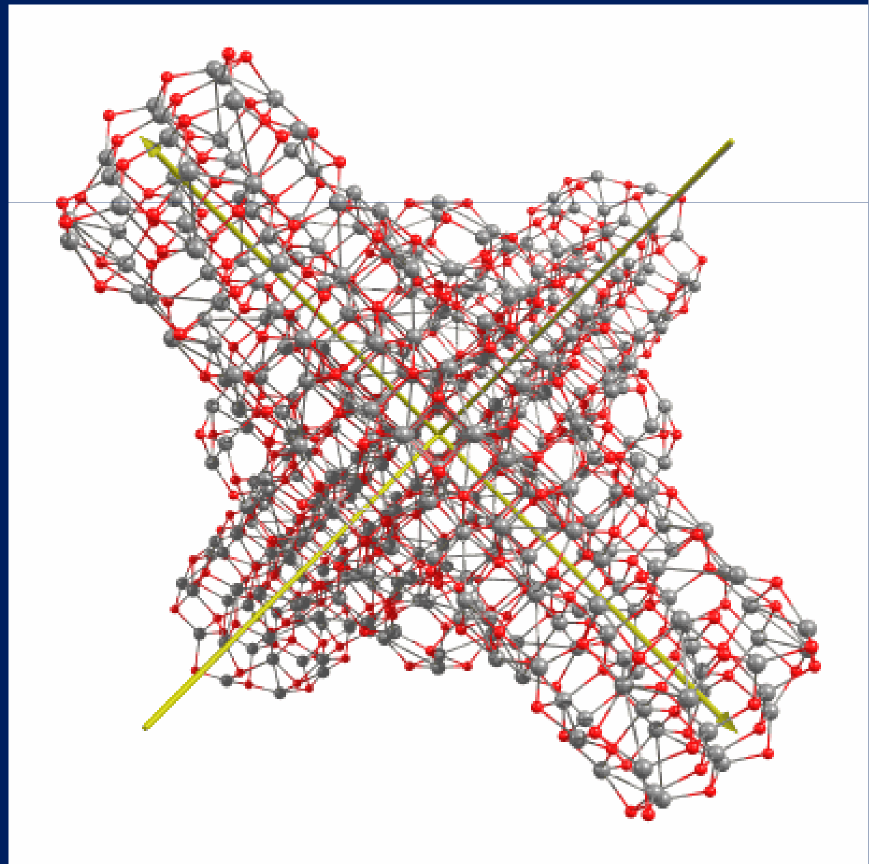


$(ZnO)_{168}$

T

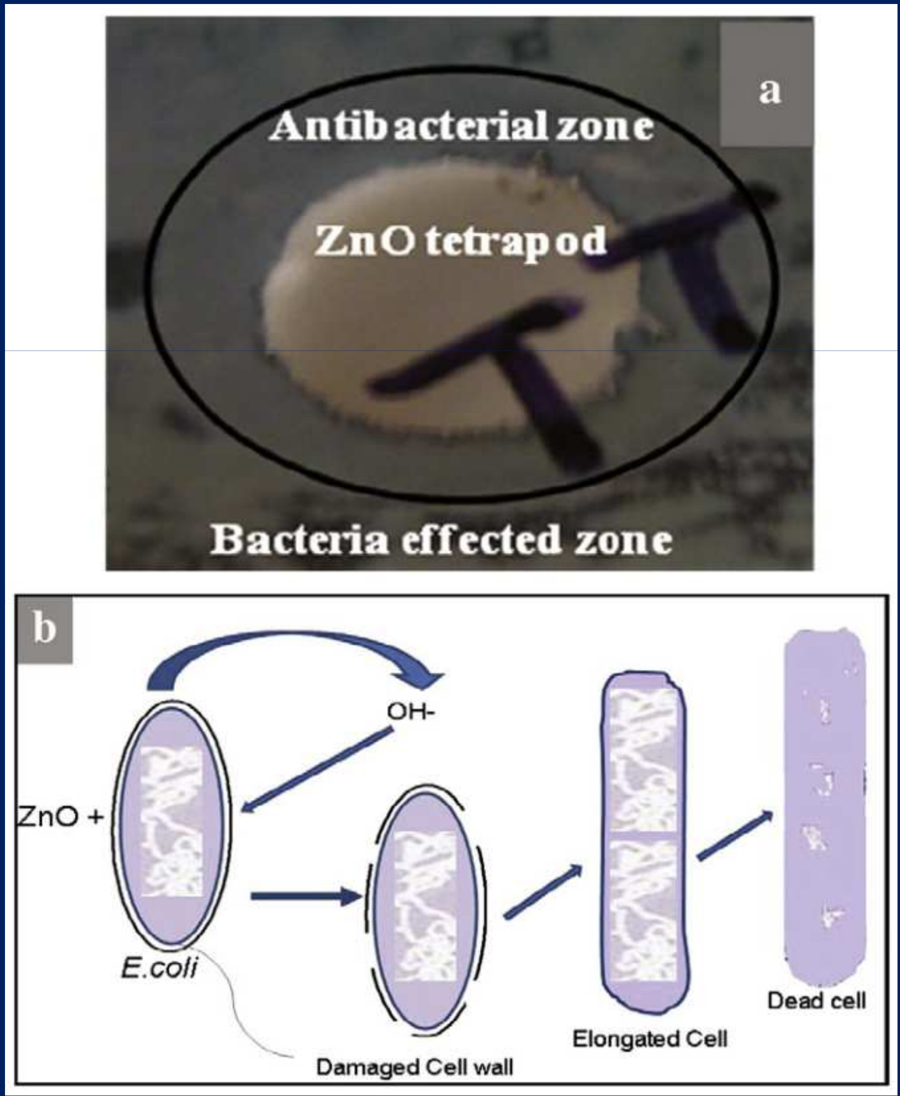


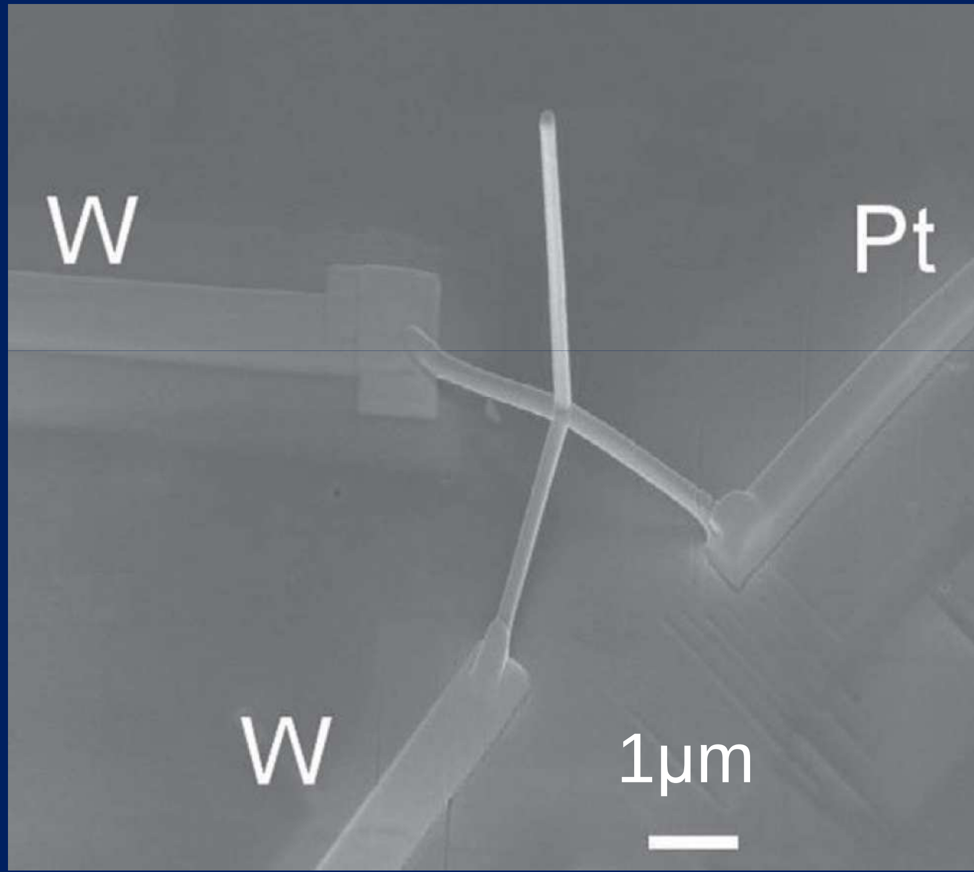
Tetrapod



A. Dmytruk, I. Dmitruk, Y. Shynkarenko, R. Belosludov, A. Kasuya.
“Zinc oxide nested shell magic clusters as tetrapod nuclei”.
RSC Advances 2017, 7, 21933-21942 (open access, IF=3.108)

Possible applications of ZnO tetrapods





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Thank you for attention!