Scale Up, Size Down (SU-SD)

Nanomaterials Lab, Swansea University, Wales not England

Swansea University
Prifysgol Abertawe

Richard Palmer

Nanomaterials Lab, College of Engineering

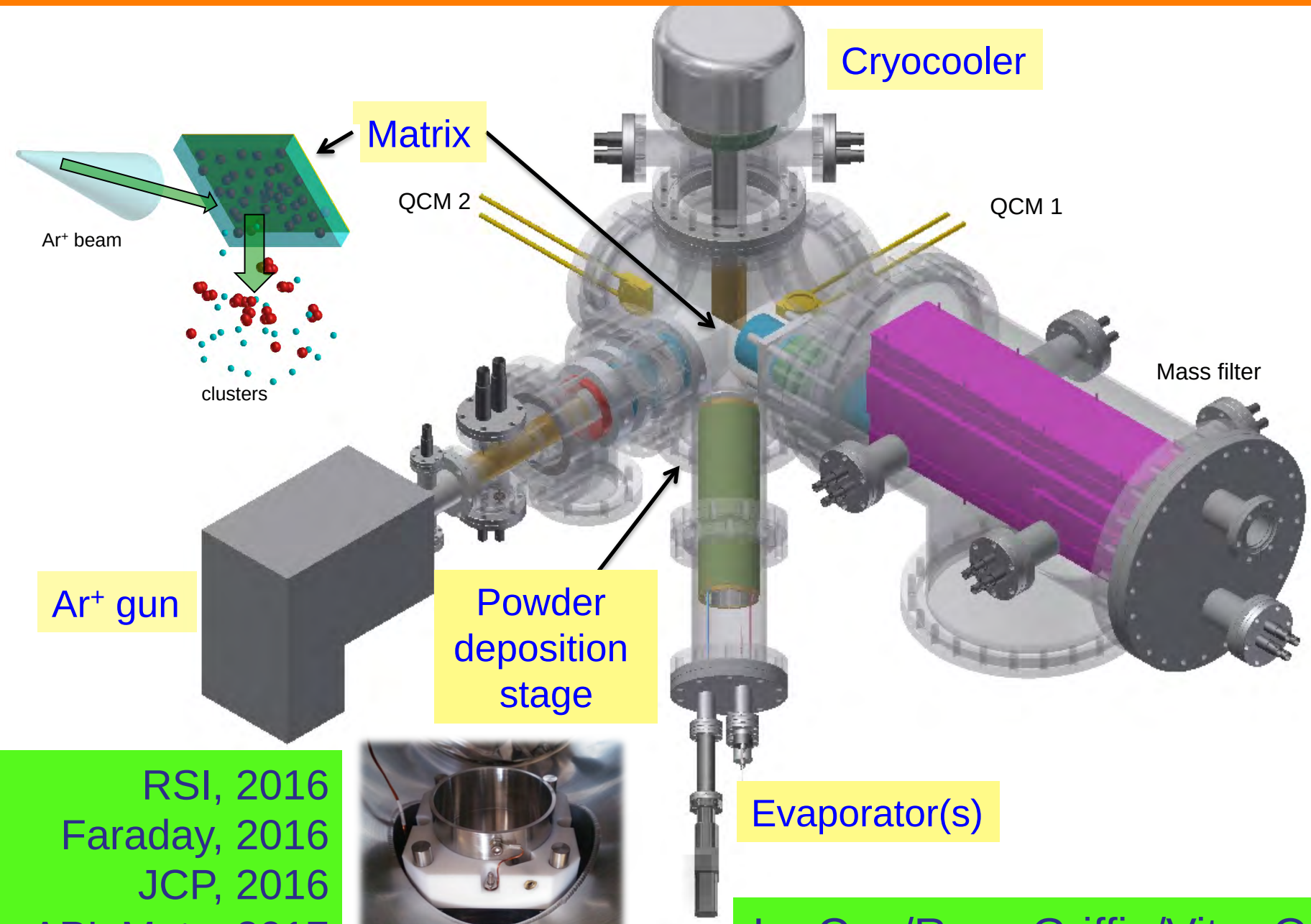
Can we arrange the atoms (in clusters) the way we want?

Can we transform cluster science into a manufacturing technology?

Yubiao Niu, **Maria Chiara Spadaro**, Jerome Vernieres, Rongsheng Cai, Yingdi Yan, Theo Pavloudis, James McCormack, Chris Evans + *6 collaborating Faculty*

Four different types of cluster deposition source + ac-STEM + XPS + AFM + UHV-STM + DFT ➔ apply/collaborate/visit

Matrix Assembly Cluster Source (MACS 1)



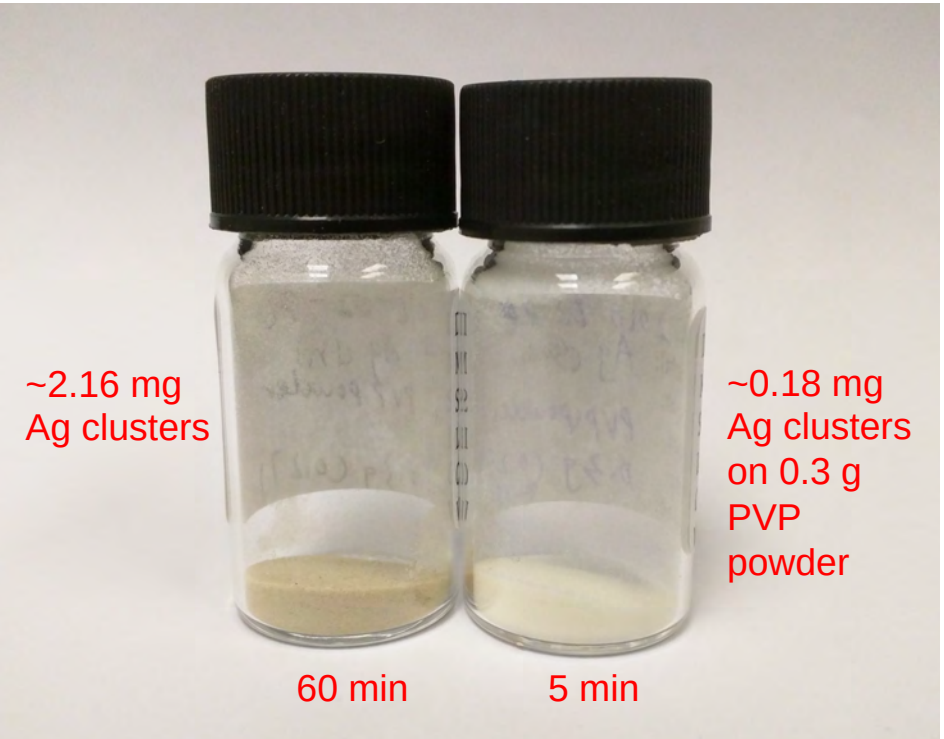
RSI, 2016
Faraday, 2016
JCP, 2016
APL Mats, 2017

Lu Cao/Ross Griffin/Vitor Oiko

The product: Ag clusters on TiO_2 powders

1 gram TiO_2 powder, 1% loading Ag clusters (10 mg), mean size 1.5nm.

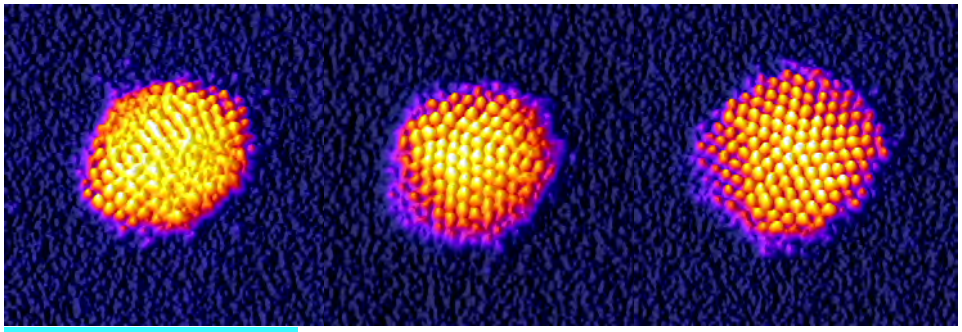
Production in MACS 1+, deposition time 2 hours.



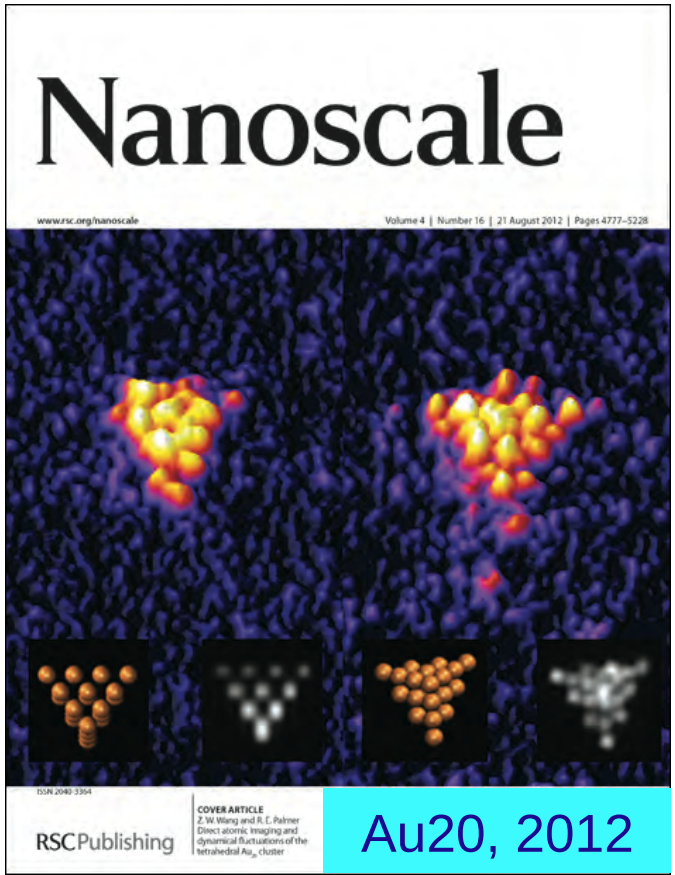
Ross Griffin, Lu Cao

Imaging size-selected Au clusters

11 Feb 1921 – 27 Aug 2014



Au923
PRL, 2012

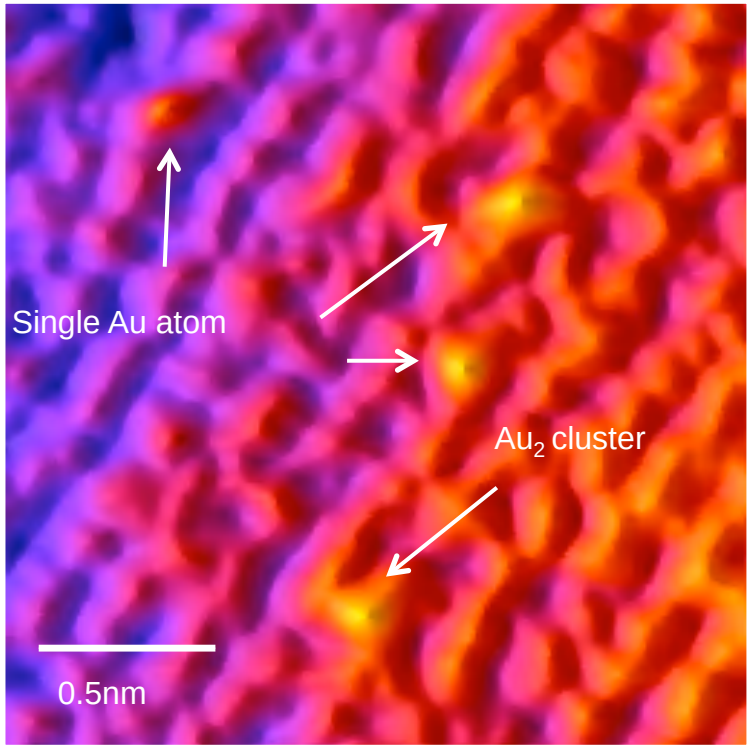


Au20, 2012

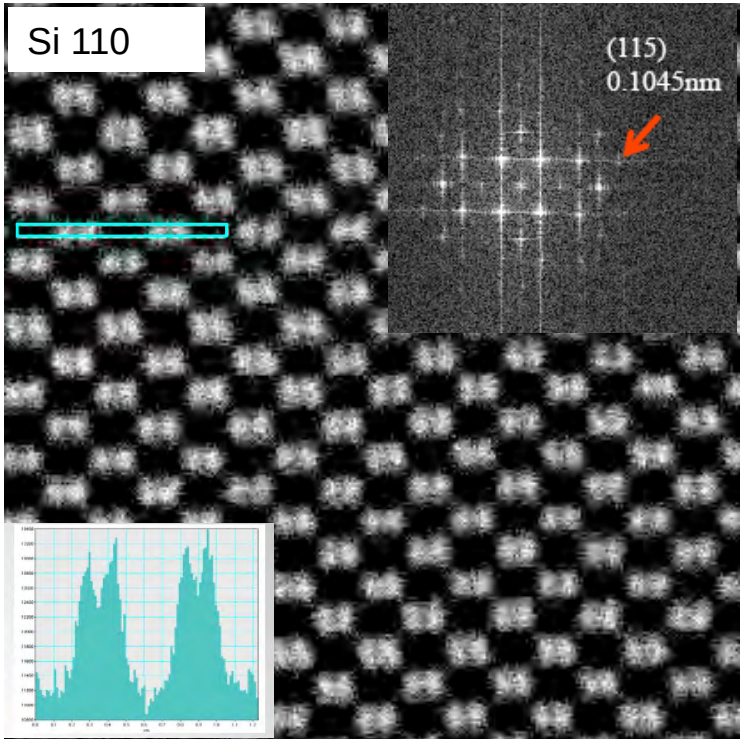
*"one can also think of looking at the **actual form of aggregates** of a few heavy atoms on light substrates"*
Jacques Friedel, Summary, ISSPIC-2 (1980)

Aberration-corrected STEM instrument

Imaging single atoms



Angstrom or even sub-Å resolution obtainable



Nan Jian in Rogers et al, ACS Catalysis 5 4377 (2015)

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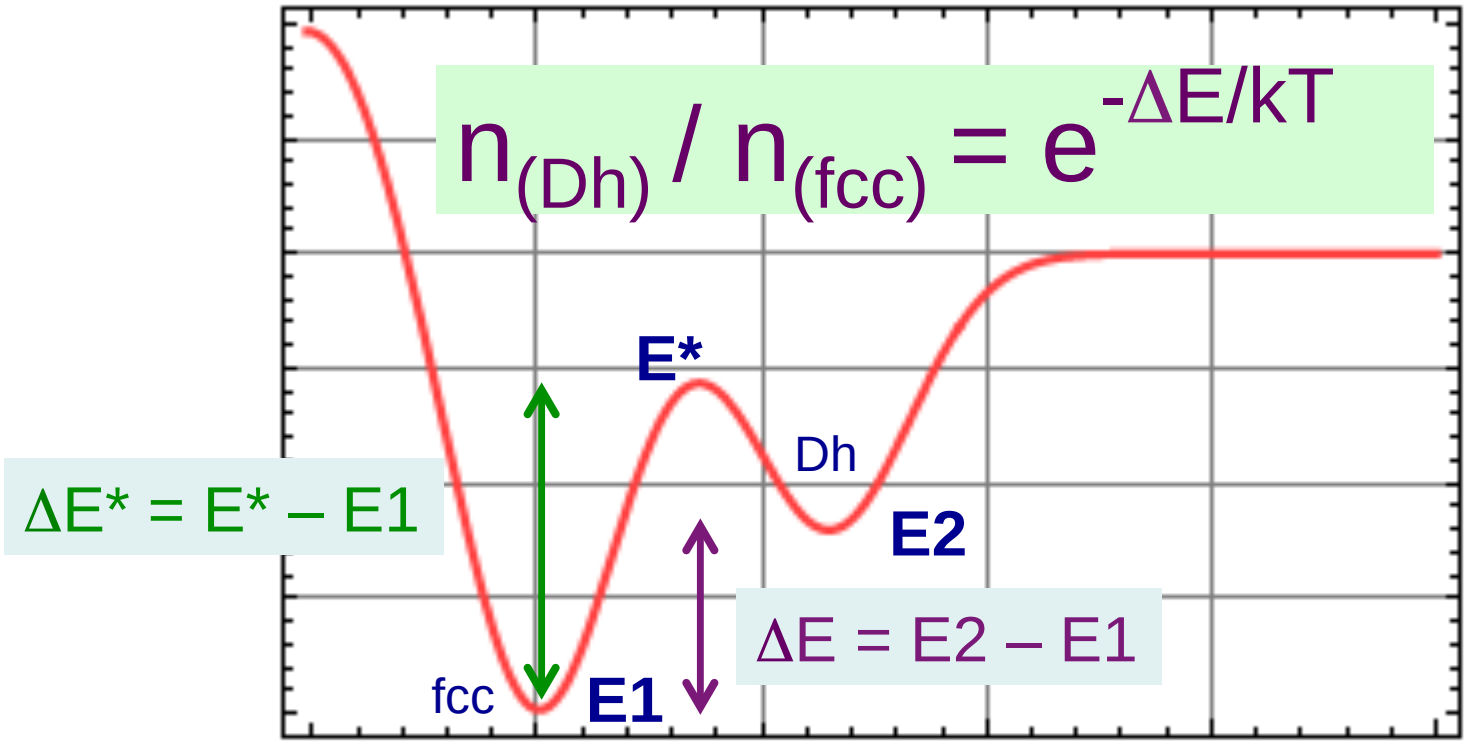
Equilibrium: relative populations of (two) isomers



- The **populations** of structural isomers observed as a function of temperature give the **energy difference** between them.
- (Do the **residence times** in each state versus T lead to the **activation energy** barriers between the states?)

Measured populations vs T for Au_{561} on a:Si_3N_4

nature COMMUNICATIONS

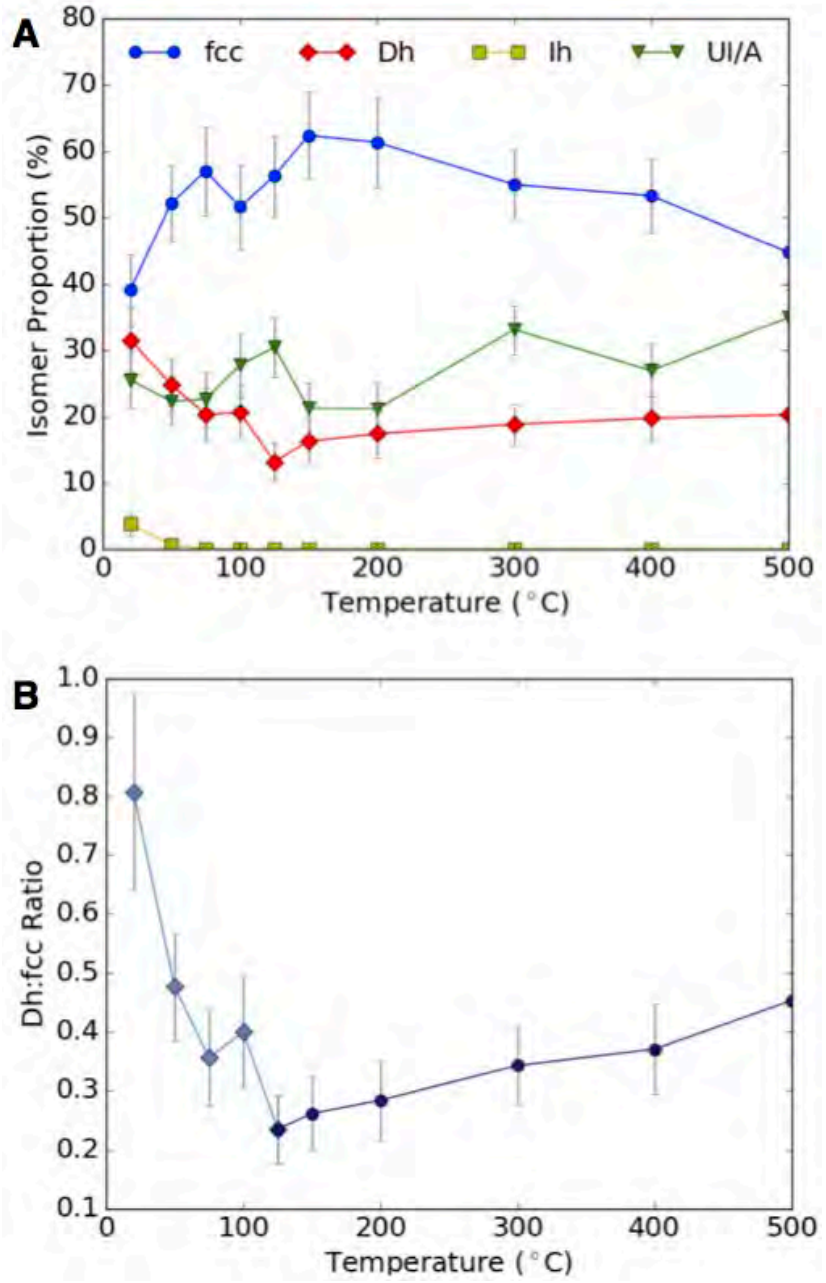
ARTICLE

DOI: 10.1038/s41467-018-03794-9 OPEN

Experimental determination of the energy difference between competing isomers of deposited, size-selected gold nanoclusters

D.M. Foster[1], R. Ferrando[2] & R.E. Palmer[3]

The equilibrium structures and dynamics of a nanoscale system are regulated by a complex potential energy surface (PES). This is a key target of theoretical calculations but experimentally elusive. We report the measurement of a key PES parameter for a model nanosystem: size-selected Au nanoclusters, soft-landed on amorphous silicon nitride supports. We obtain the energy difference between the most abundant structural isomers of magic number Au_{561} clusters, the decahedron and face-centred-cubic (fcc) structures, from the equilibrium proportions of the isomers. These are measured by atomic-resolution scanning transmission electron microscopy, with an ultra-stable heating stage, as a function of temperature (125–500 °C). At lower temperatures (20–125 °C) the behaviour is kinetic, exhibiting down conversion of metastable decahedra into fcc structures; the higher state is repopulated at higher temperatures in equilibrium. We find the decahedron is 0.040 ± 0.020 eV higher in energy than the fcc isomer, providing a benchmark for the theoretical treatment of nanoparticles.



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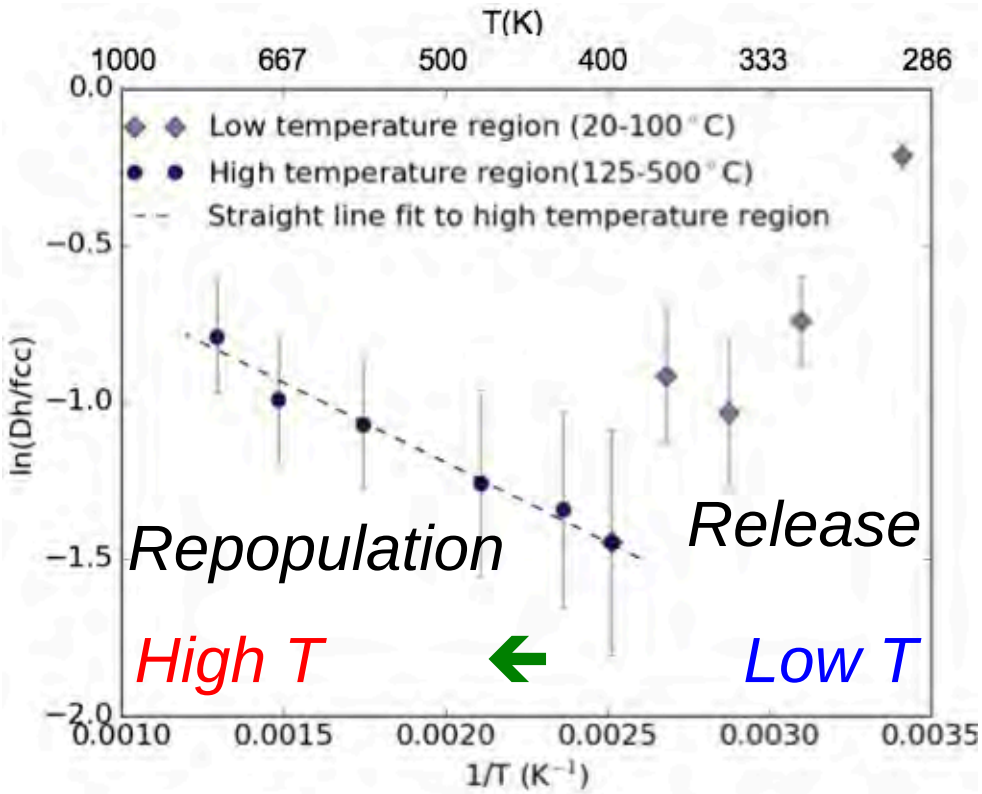
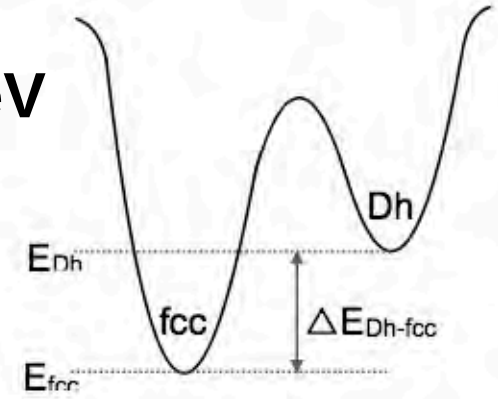
Measured populations vs T for Au_{561} on a:Si_3N_4



ΔE=0.04eV



- **Van 't Hoff plot** of the ratio of Dh/fcc isomers for Au_{561}
- **Lower temperature range:** metastable Dh transform to fcc due to the elevated temperatures
- **Higher temperature range:** clusters are now in equilibrium (obvious from dynamic behaviour at these temperatures); as the temperature is increased the proportion of Dh increases slightly ➔ Dh higher in energy.
- **Dh only marginally higher (0.04eV) in energy than fcc**, the two structures are almost degenerate.

Dawn Wells, Riccardo Ferrando

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Can we transform cluster science into a manufacturing technology?

Do these things for nano-alloys...!
(Chiara, Yubiao)