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Article

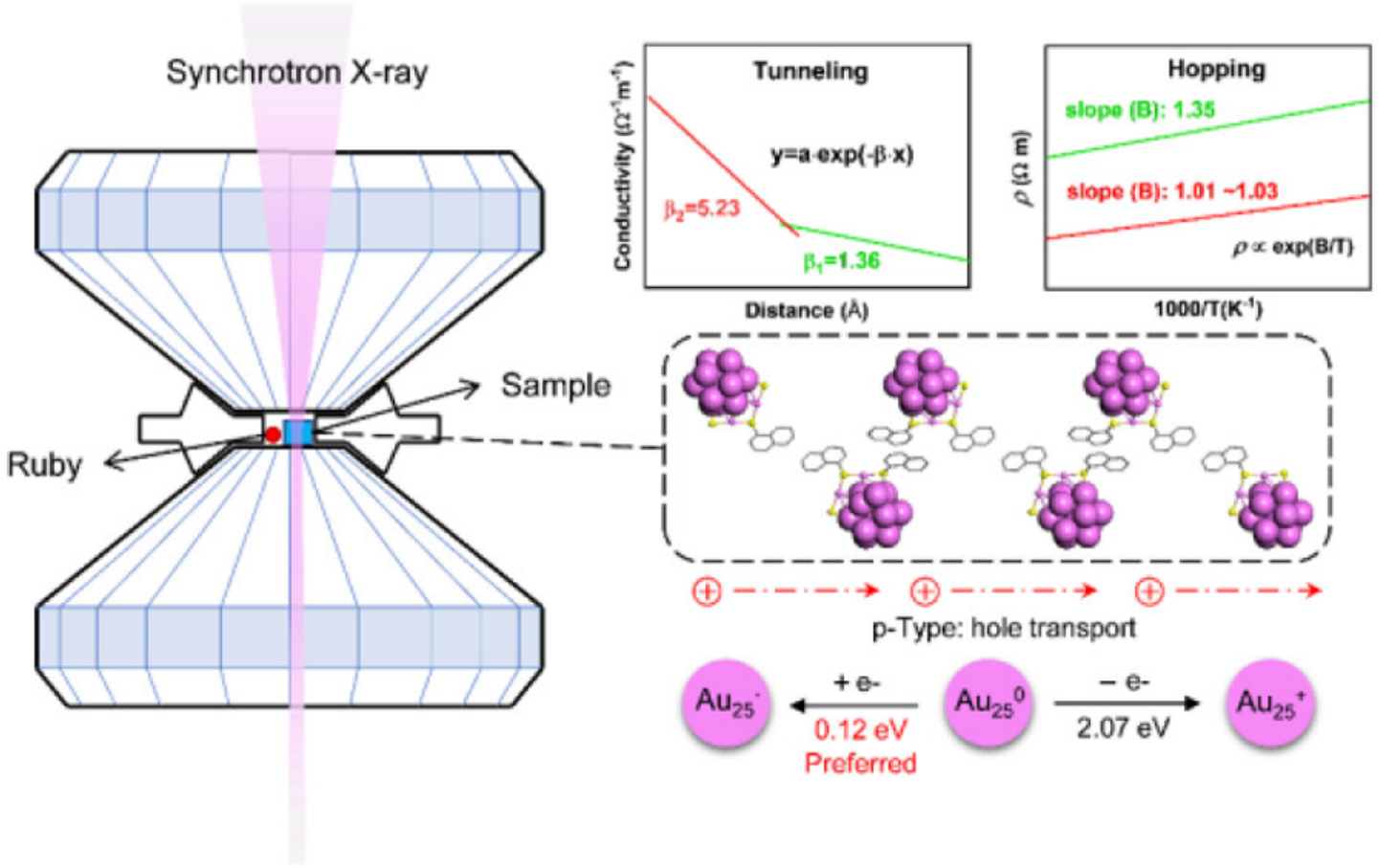
Coexistent, Competing Tunnelling, and Hopping Charge Transport in Compressed Metal Nanocluster Crystals

Shiyu Ji, Di Peng, Fang Sun, Qing You, Runguo Wang, Nan Yan, Yue Zhou, Weiyi Wang, Qing Tang,* Nan Xia,* Zhi Zeng,* and Zhikun Wu*

- Key Laboratory of Materials Physics, Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, HFIPS, Chinese Academy of Sciences, Hefei 230031, P. R. China.
- University of Science and Technology of China, Hefei 230601, P. R. China.
- School of Chemistry and Chemical Engineering, Chongqing Key Laboratory of Theoretical and Computational Chemistry, Chongqing University, Chongqing 401331, China.
- Institute of Physical Science and Information Technology, Anhui University, Hefei 230601, P. R. China.

October 30, 2023

Abstract


Synchrotron X-ray
Sample
Ruby
Tunneling
y=a·exp(-β·x)
β2=5.23
β1=1.36
Conductivity (Ω-1m-1)
Distance (Å)
Hopping
slope (B): 1.35
slope (B): 1.01 ~1.03
ρ ∝ exp(B/T)
ρ (Ω m)
1000/T(K-1)
p-Type: hole transport
Au25-
+ e-
0.12 eV
Preferred
Au25 0
– e-
2.07 eV
Au25+

Background

CHEMICAL REVIEWS

Review

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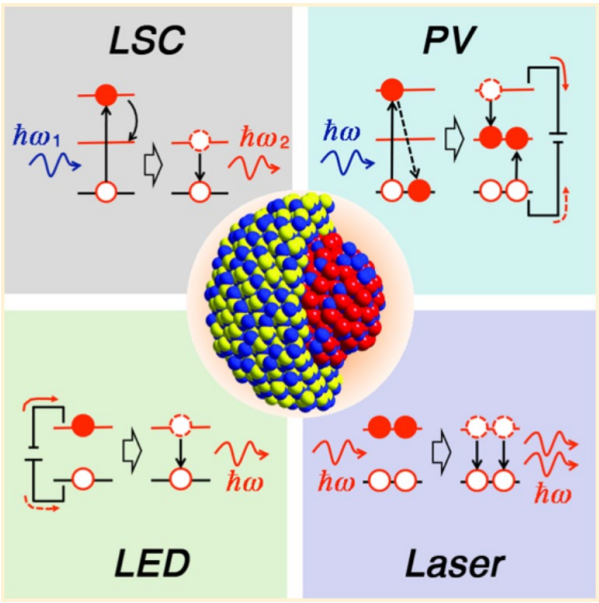
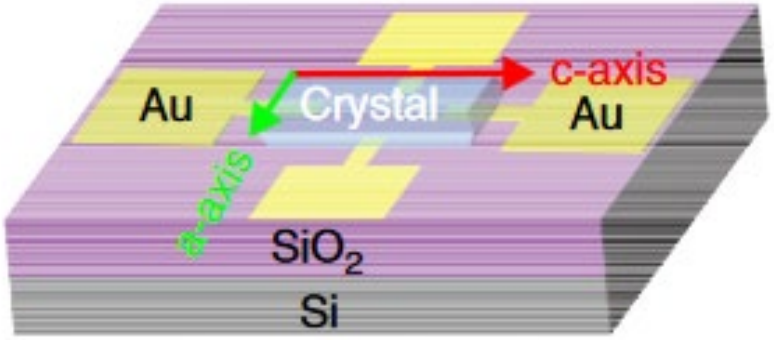
Spectroscopic and Device Aspects of Nanocrystal Quantum Dots

Jeffrey M. Pietryga,[†] Young-Shin Park,[†,‡] Jaehoon Lim,[†] Andrew F. Fidler,[†] Wan Ki Bae,[§] Sergio Brovelli,[∥] and Victor I. Klimov*[,†]



Solvent-mediated assembly of atom-precise gold–silver nanoclusters to semiconducting one-dimensional materials

Peng Yuan[1,3], Ruihua Zhang[1,3], Elli Selenius[2], Pengpeng Ruan[1], Yangrong Yao[1], Yang Zhou[1], Sami Malola[2], Hannu Häkkinen[2✉], Boon K. Teo[1], Yang Cao[1✉] & Nanfeng Zheng[1✉]



Motivation

- Requirement of semiconductor materials which are stable and efficient at nanoscale.
- In depth understanding of mechanism of conductivity in atomically precise metal nanoclusters.
- Knowledge on effect of ligands, cluster size, cluster shape and inter-cluster distance in the crystals to tune nanoclusters to suit our needs.
- The initiation of metal nanocluster semiconductor research.

Why this paper?

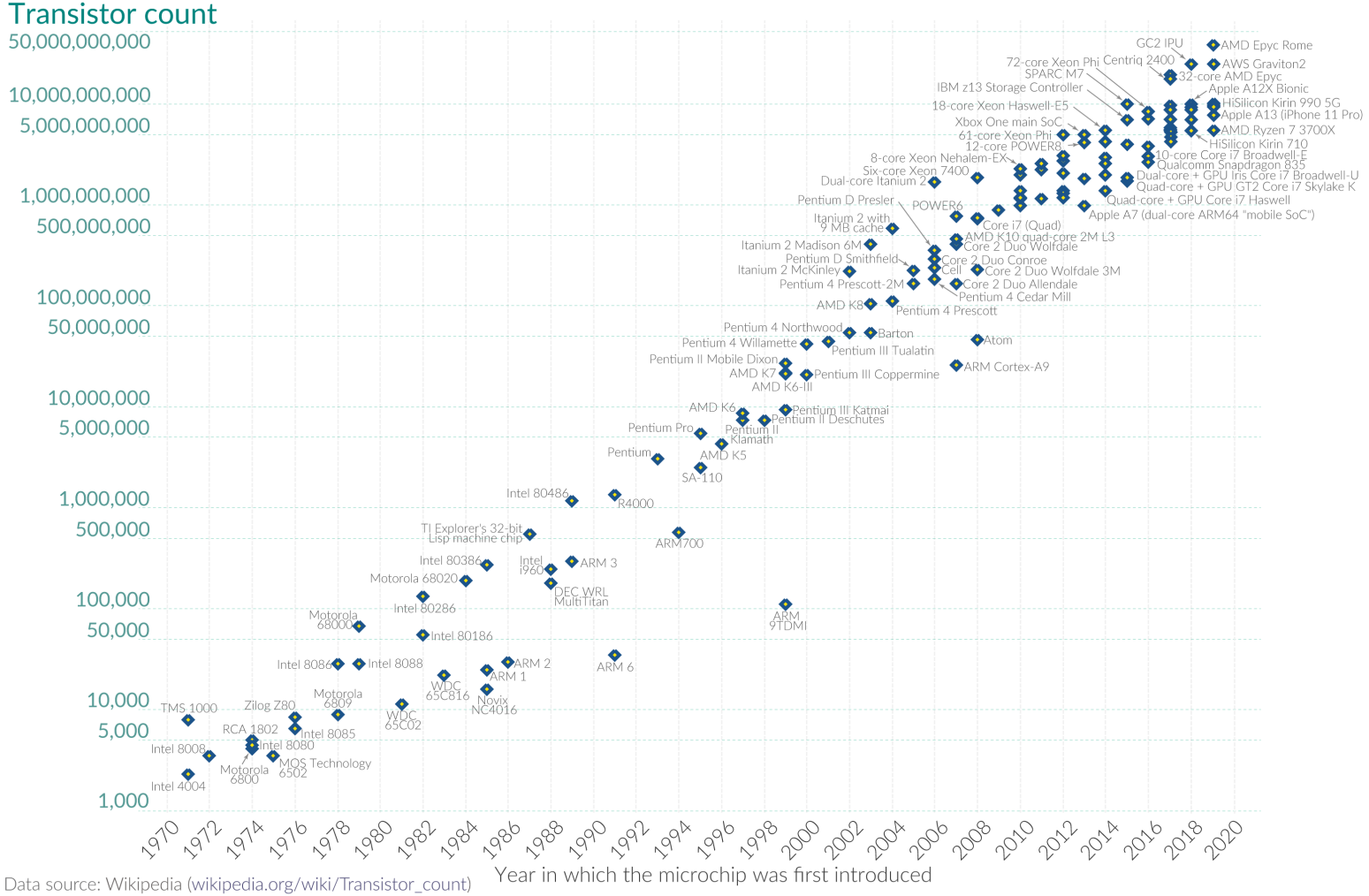
- Provides a comprehensive analysis of how ligands, cluster size, cluster shape, and inter-cluster distance affect the conductivity of nanocluster crystals.
- This study will assist in predicting which systems may exhibit favorable conductivity prior to performing conductivity measurements, aiding in the selection of systems for further study.

Introduction

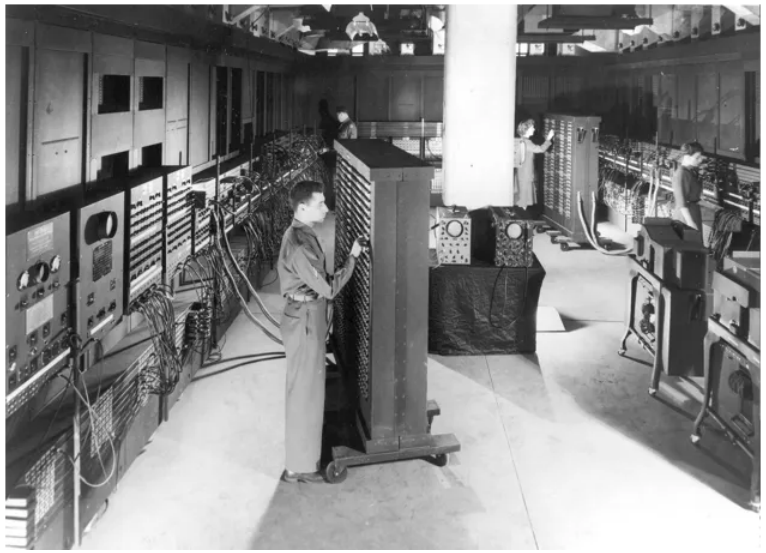
Moore's Law: The number of transistors on microchips doubles every two years

Our World in Data

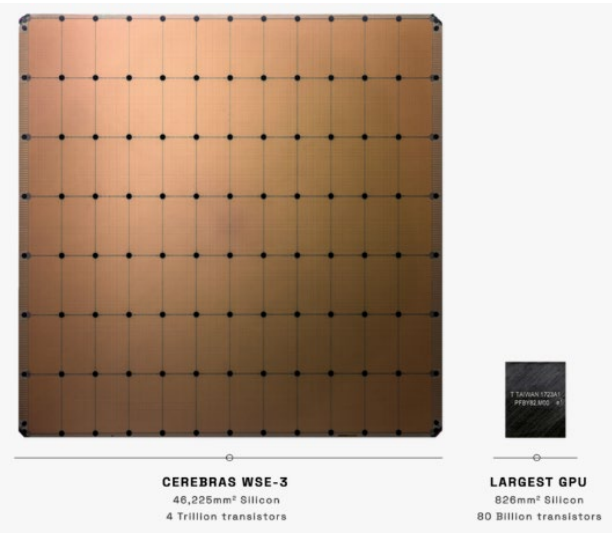
Moore's law describes the empirical regularity that the number of transistors on integrated circuits doubles approximately every two years.
This advancement is important for other aspects of technological progress in computing – such as processing speed or the price of computers.



Data source: Wikipedia (wikipedia.org/wiki/Transistor_count)
OurWorldinData.org – Research and data to make progress against the world's largest problems.



The year: 1945 — Transistor Size: few centimetres.



The year: 2024 — Transistor Size: ~5 nanometres. The highest transistor count in a single chip. 4 trillion MOSFETs.

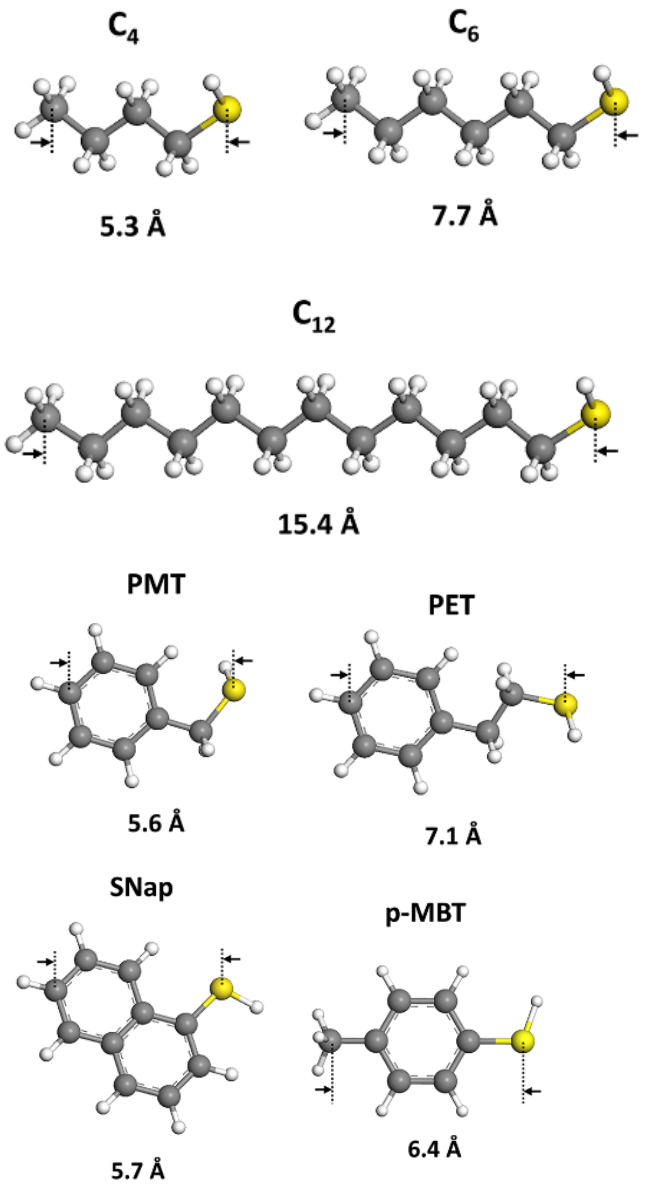
Introduction

- When traditional semiconductor materials such as silicon and germanium are reduced to thicknesses below ~10 nm, they lose their conductivity and become unstable, limiting their use in ultrasmall devices.
- Gold is very stable metal with excellent conductivity, and even at sizes below 2nm, it shows certain semiconducting properties and relative stability.
- However, despite growing interest, the study of gold nanoclusters in electronics is still in its early stages, and several fundamental issues need to be addressed. One of these issues is understanding the mechanisms of charge transfer (CT) in gold nanocluster solids, including crystals, powders, and films.

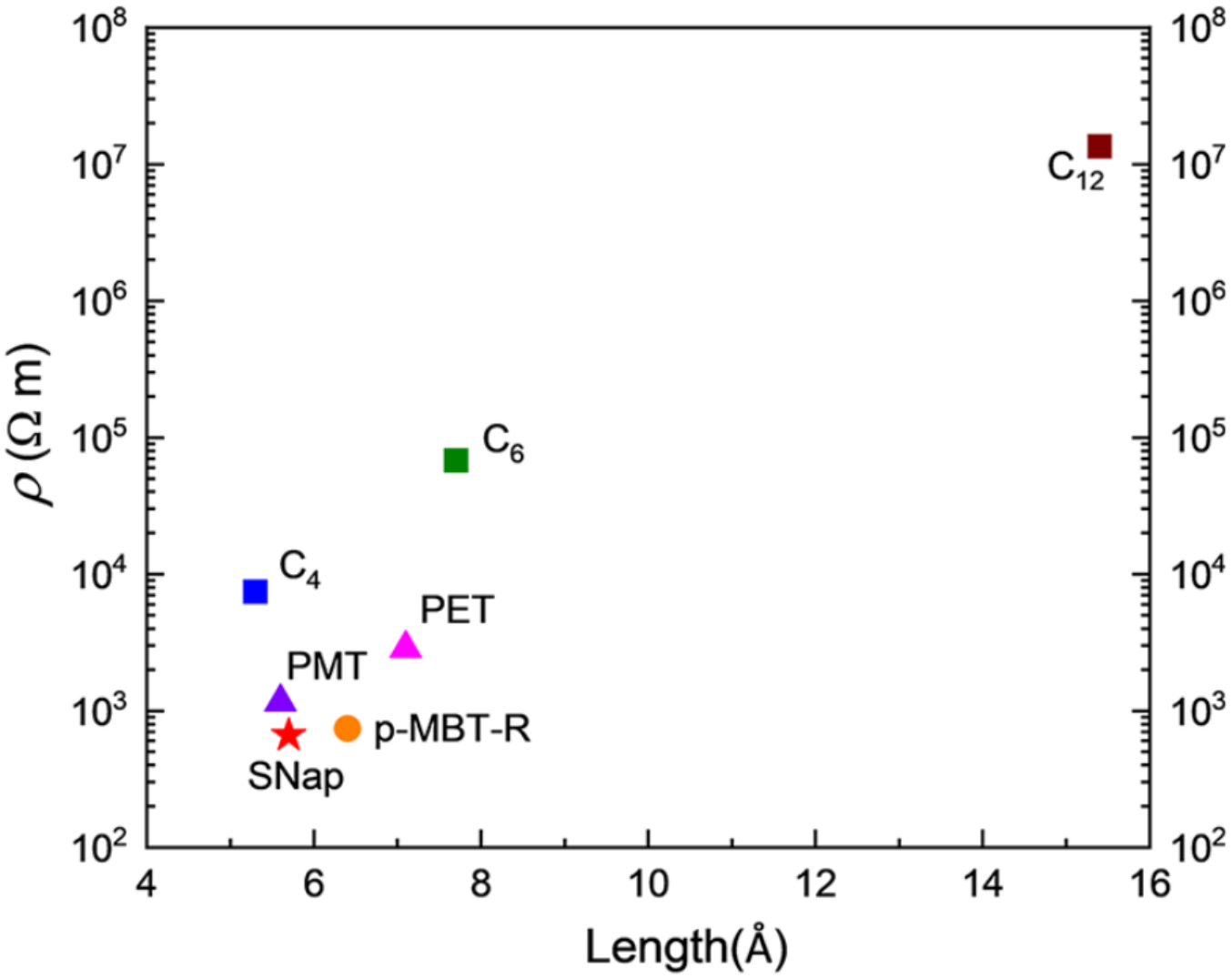
Results and Discussion

- Size effect – Au_{25}, Au_{44}, Au_{99} and Au_{144}.
- Ligand effect – series of Au_{25} nanoclusters with ligands 1-butanethiolate (C_4), 1-hexanethiolate (C_6), 1-dodecanethiolate (C_{12}), 2-phenylethanethiolate (PET), phenylmethanethiolate (PMT), and 1-naphthalenethiolate (S-nap).
- Shape effect – Au_{25}, Au_{38} and Au_{34}.
- Inter-cluster distance effect – high pressure resistivity measurements.
- Hall measurements – type of charge carriers in the nanocluster crystals.

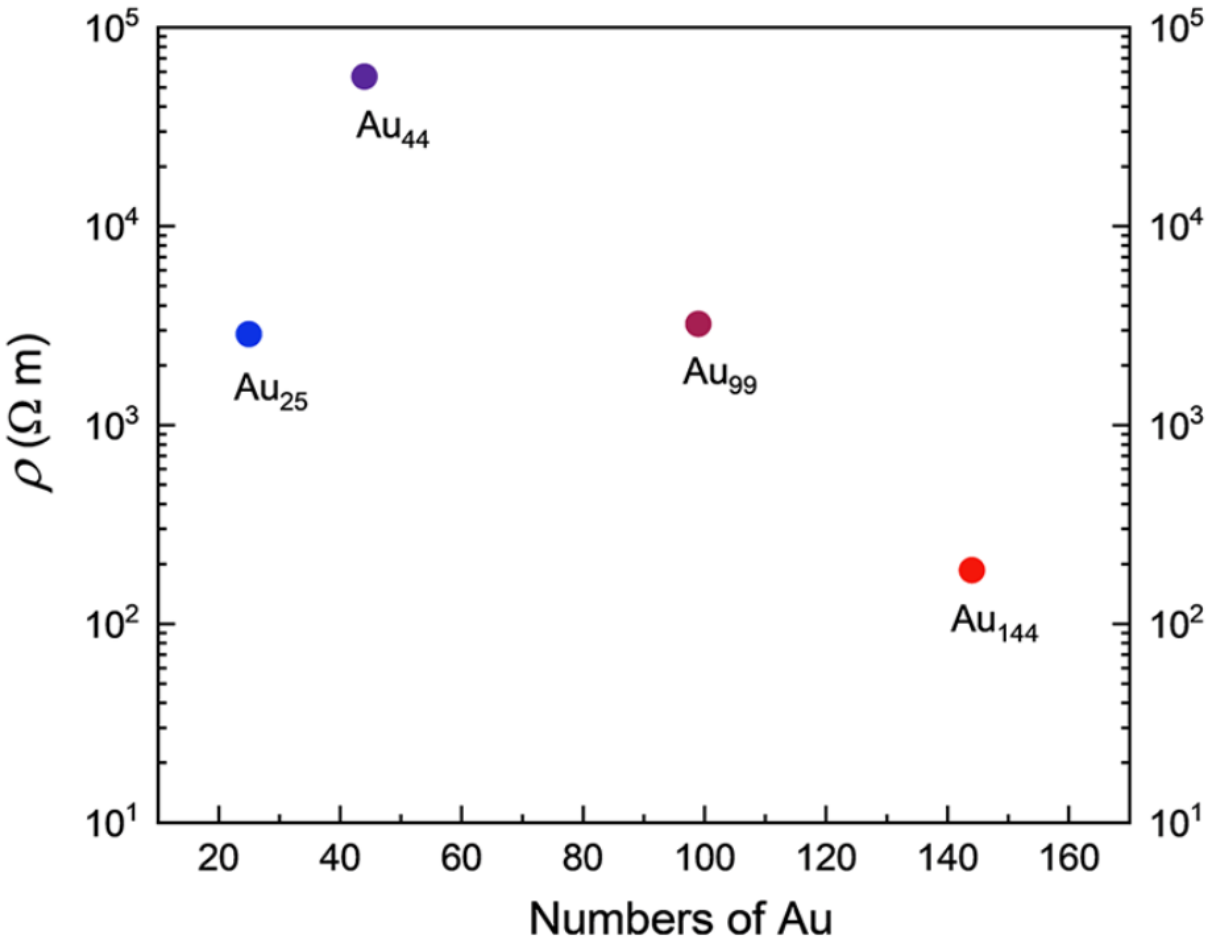
Effect of Ligand



$Au_{25}(SR)_{18}$



Effect of Cluster size

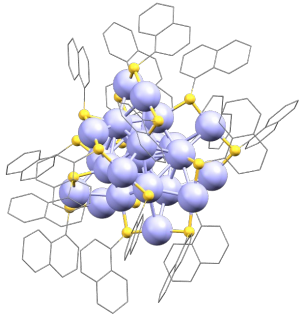


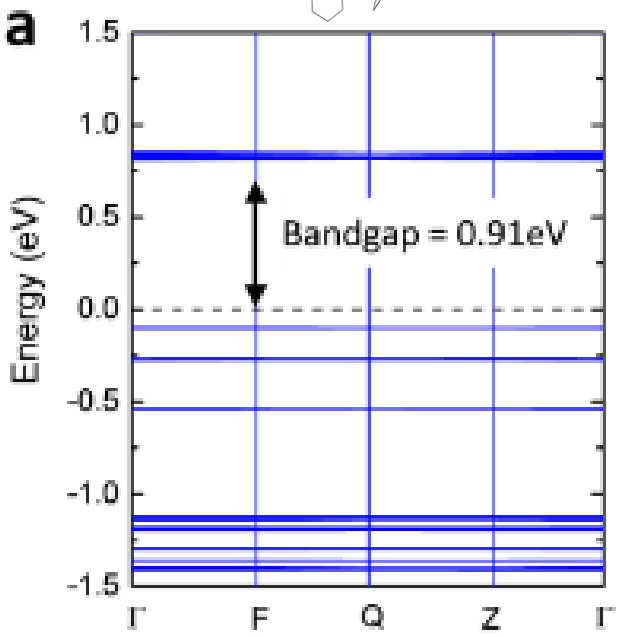
All are PET protected nanoclusters.

- As the cluster size increases, the resistivity of the nanocluster solid decreases.
- But Au_{25} shows sudden decrease in resistivity which is not following the trend.
- This may be attributed to the effect of shape of the nanoclusters on their conductivity.

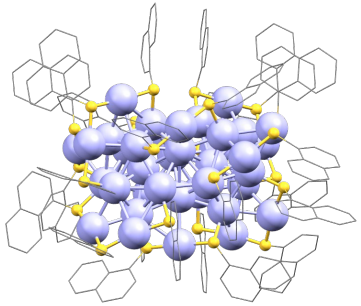
Effect of shape

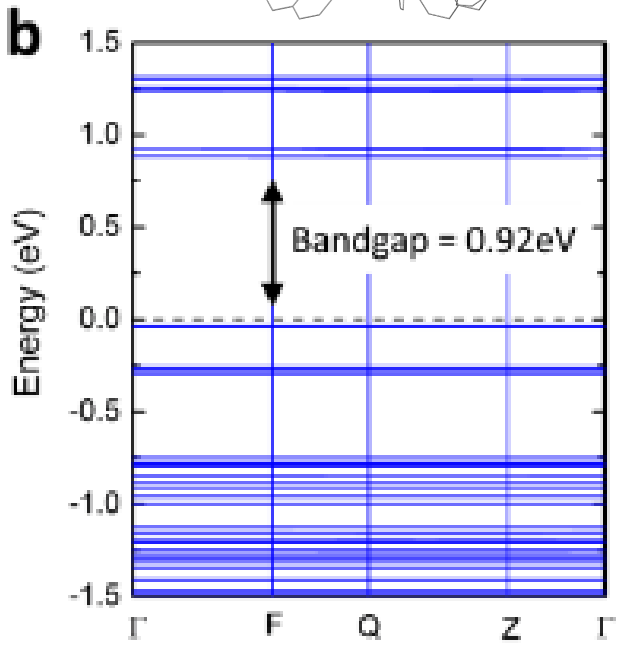
$Au_{25}(SNap)_{18}$



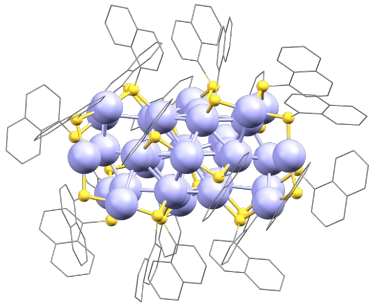


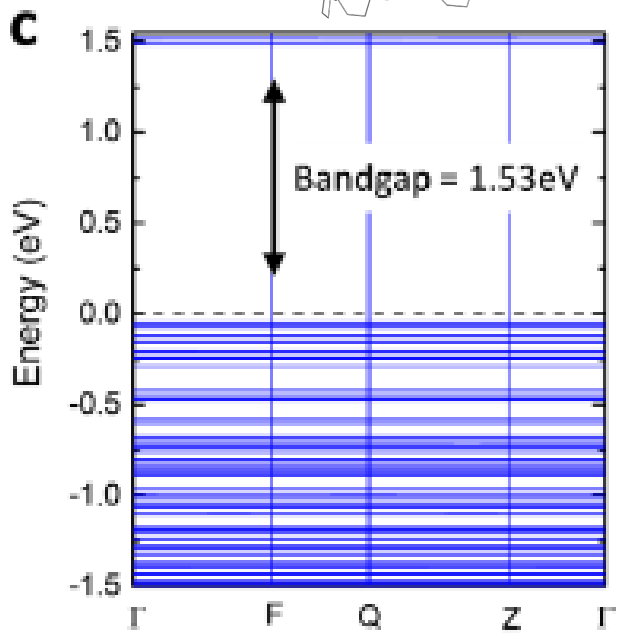
$Au_{38}(SNap)_{24}$





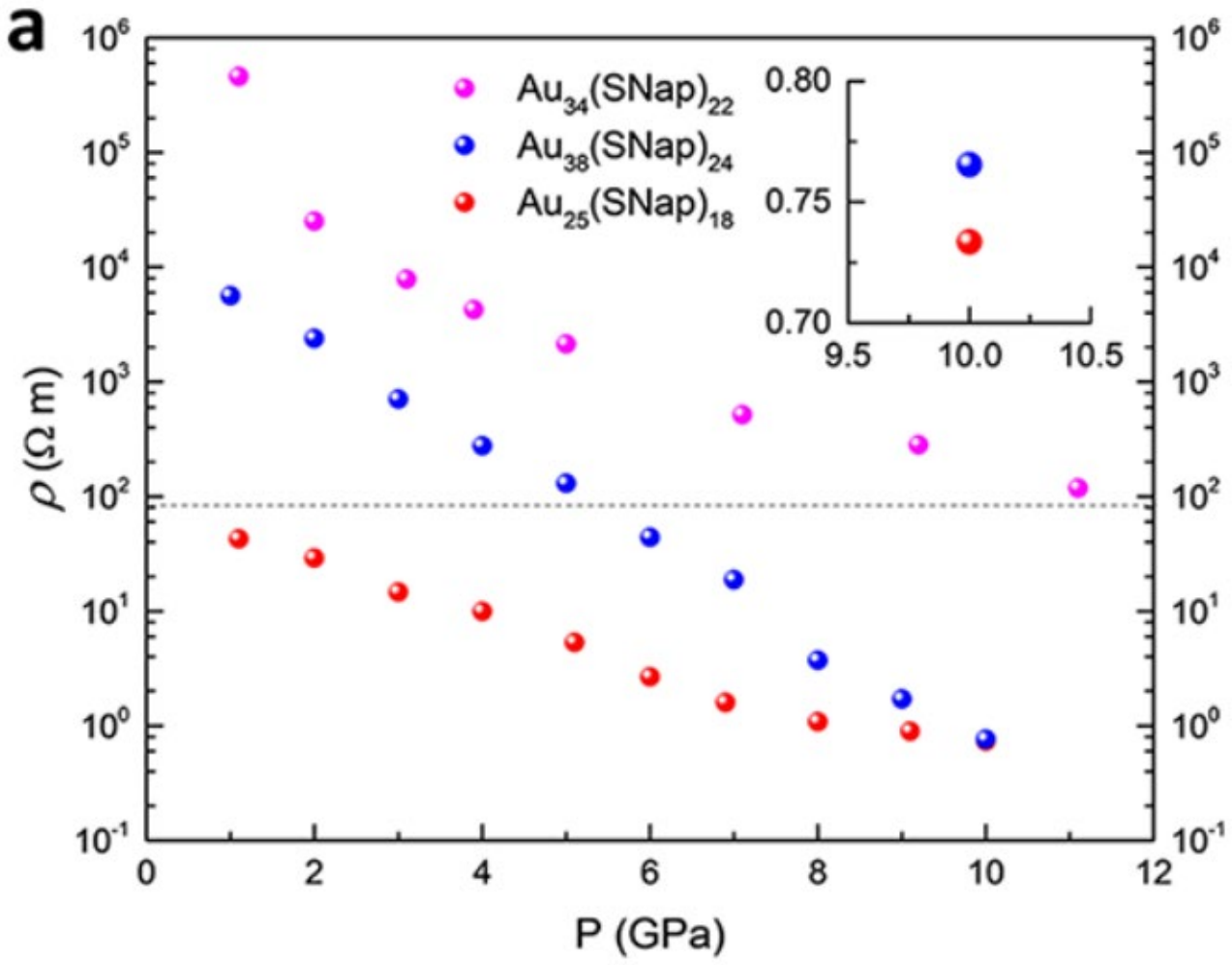
$Au_{34}(SNap)_{22}$





Order of resistivity: $Au_{25}(SNap)_{18} < Au_{38}(SNap)_{24} < Au_{34}(SNap)_{22}$

Effect of interparticle distance



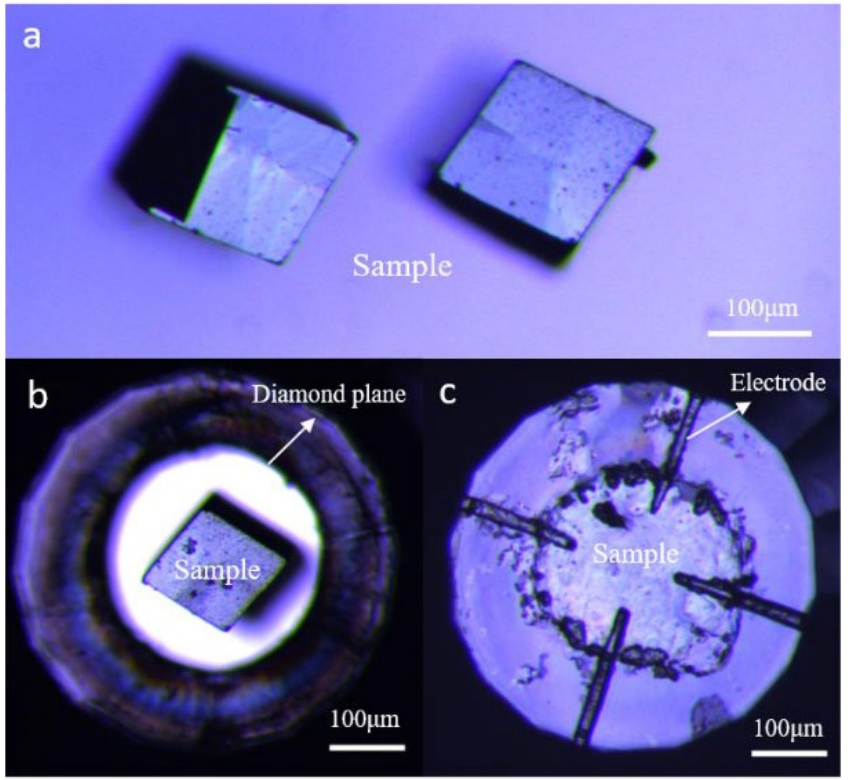
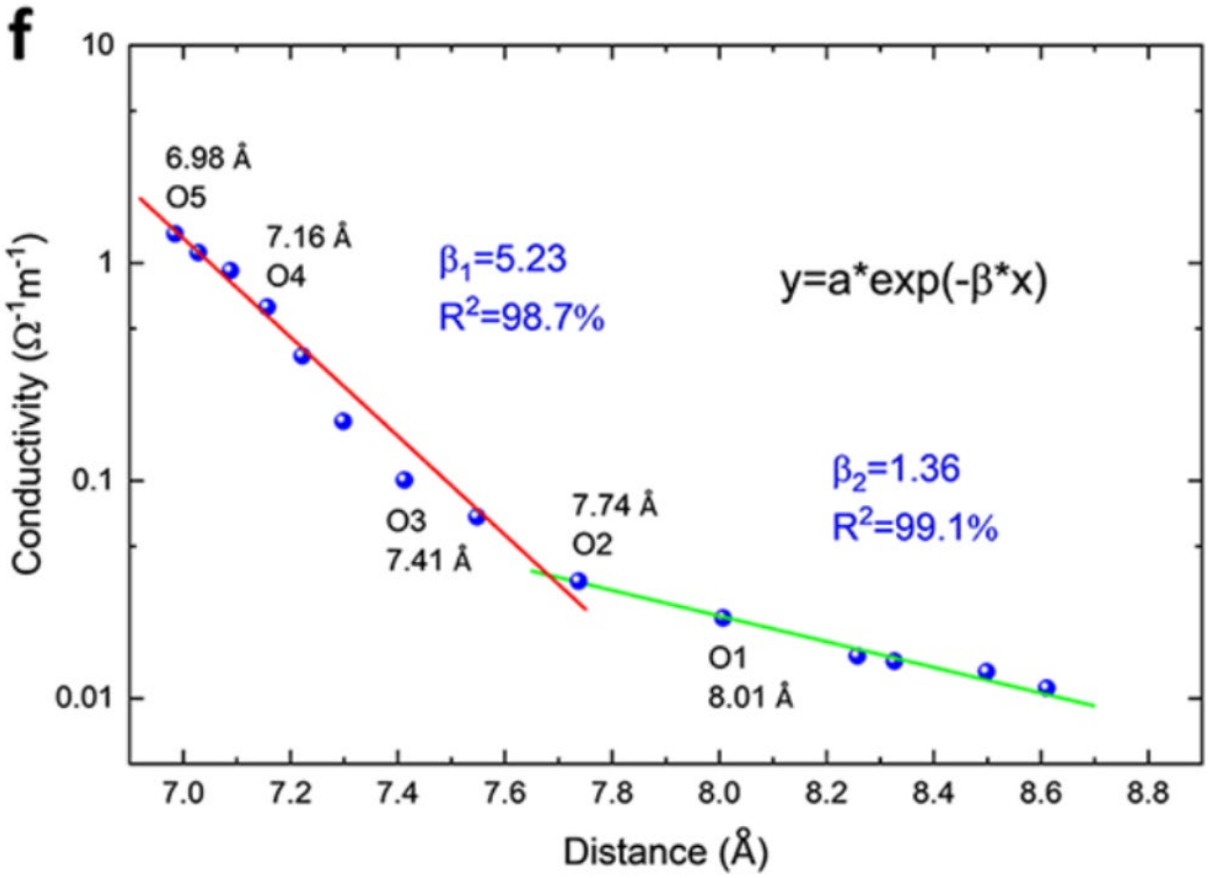


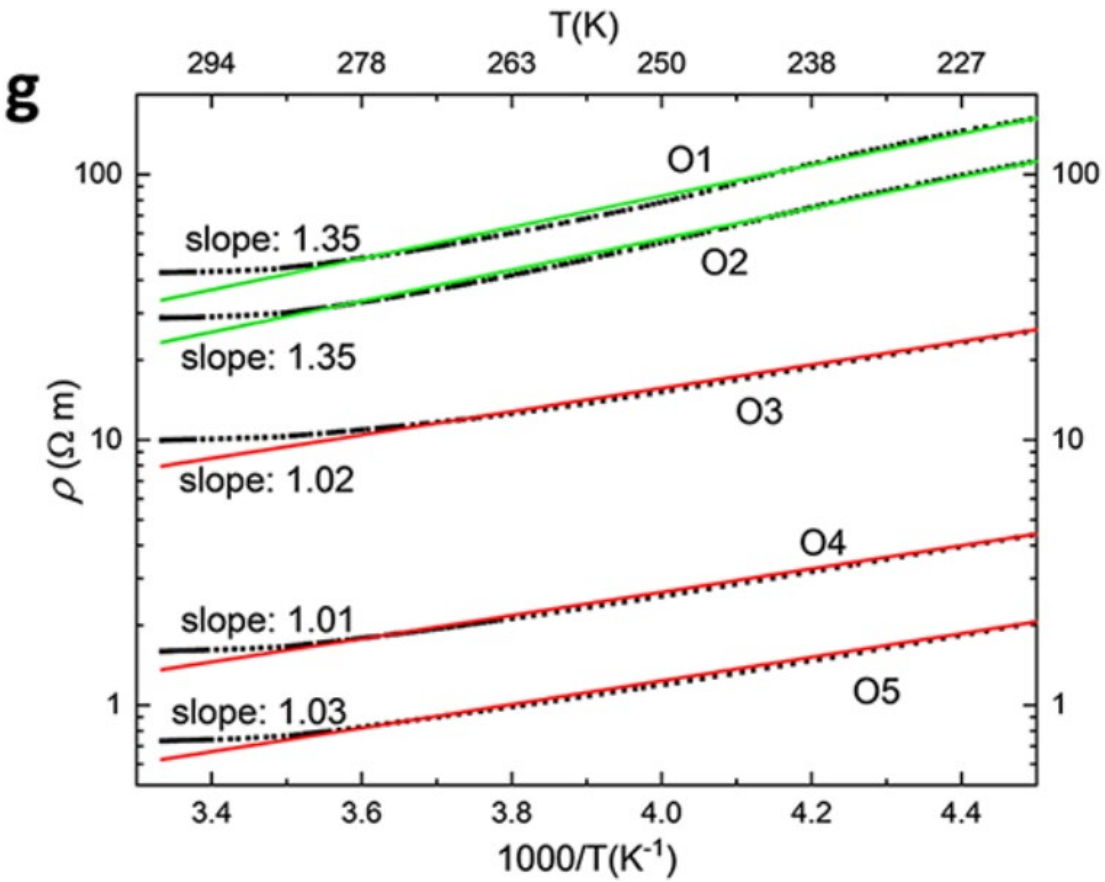
Fig. S29 The crystal samples of SNap protected nanoclusters: (**a**) outside the DAC, (**b**) just putting in the DAC, and (**c**) after pre-pressing to connect with the four electrodes.

Mechanism of charge transport

$$\sigma = Aexp(-\beta d),$$

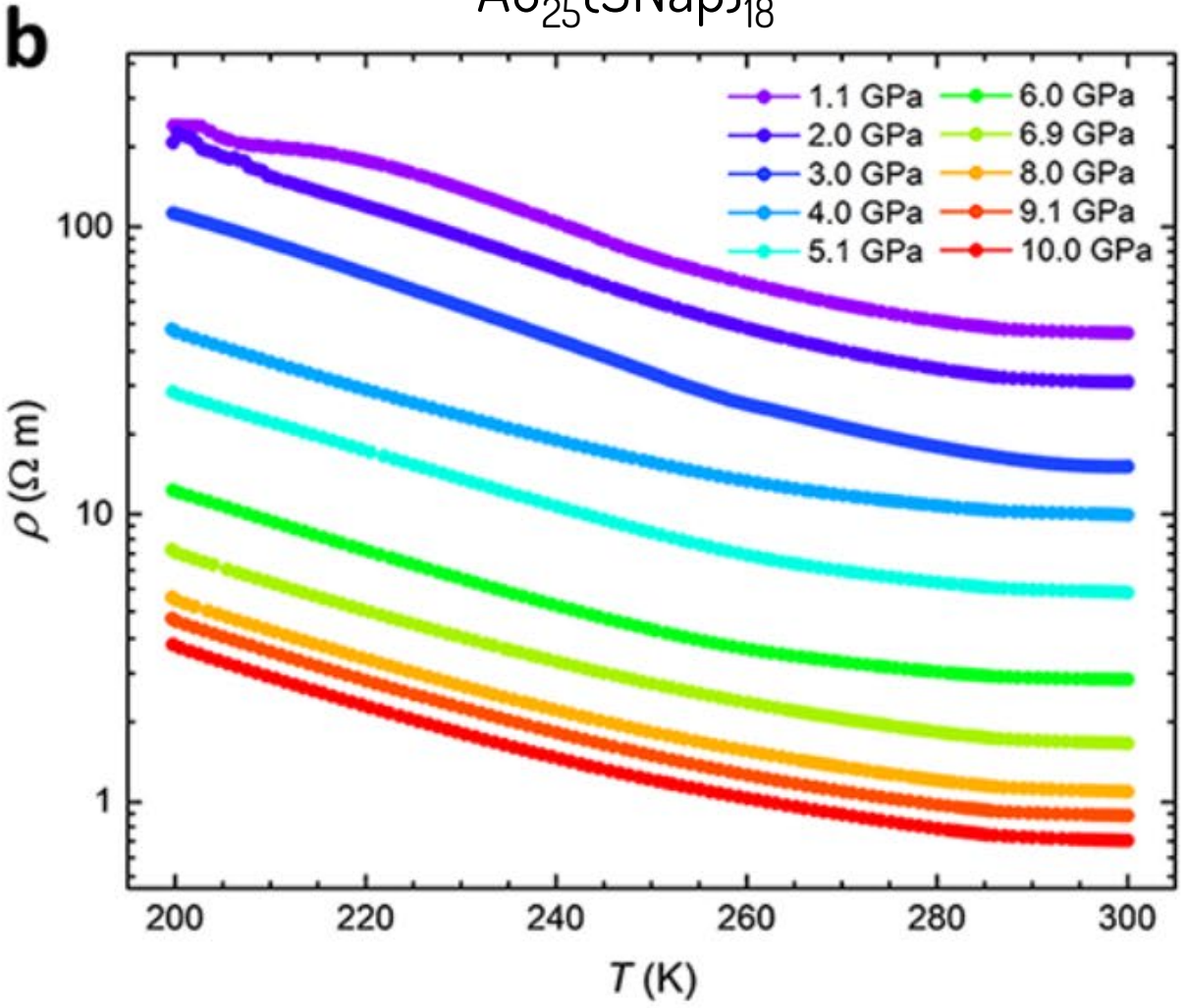
$$\rho \propto \exp\left(\frac{B}{T}\right),$$



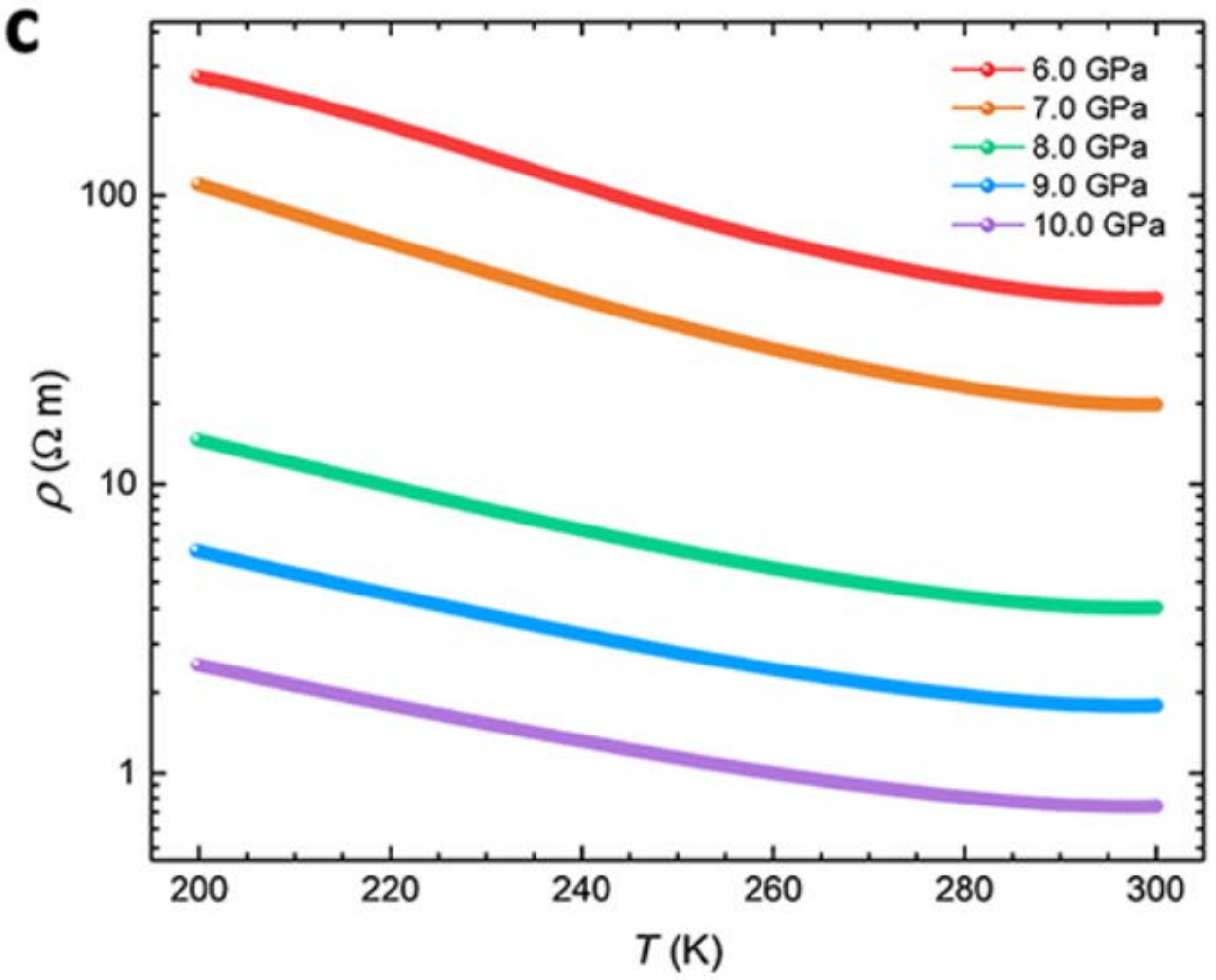


Effect of temperature

$Au_{25}(SNap)_{18}$

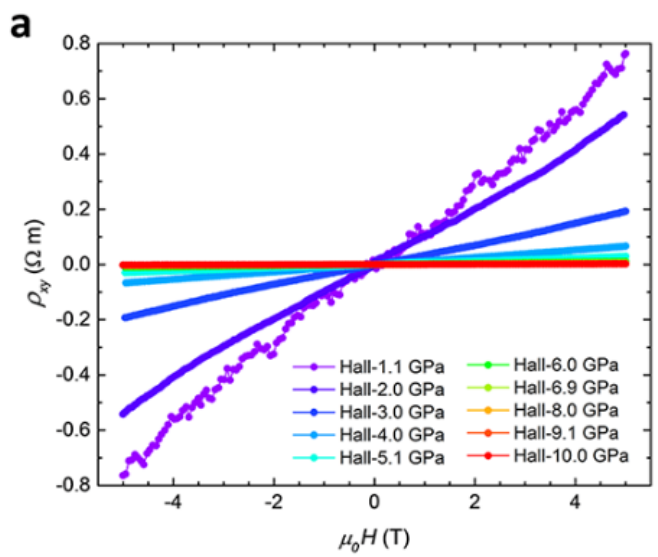


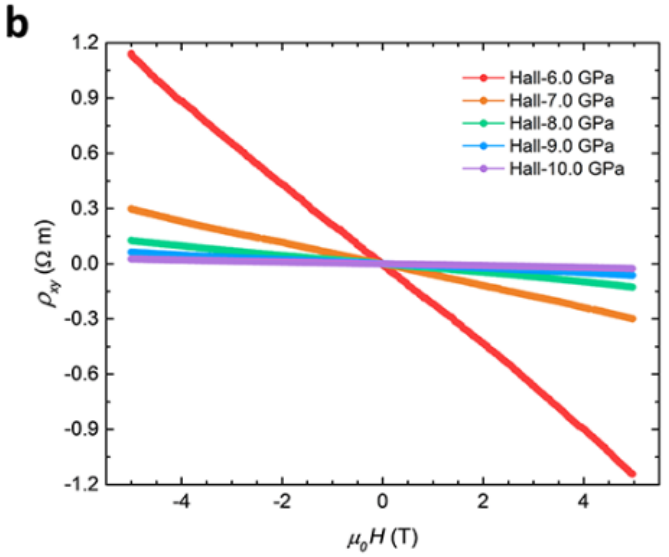
$Au_{38}(SNap)_{24}$

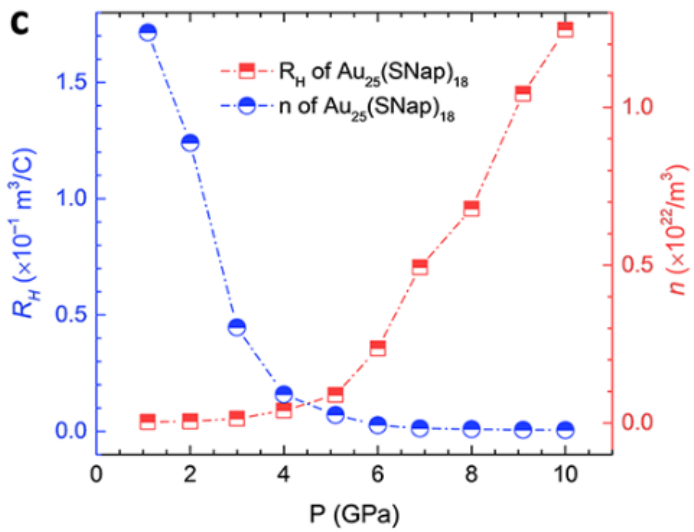


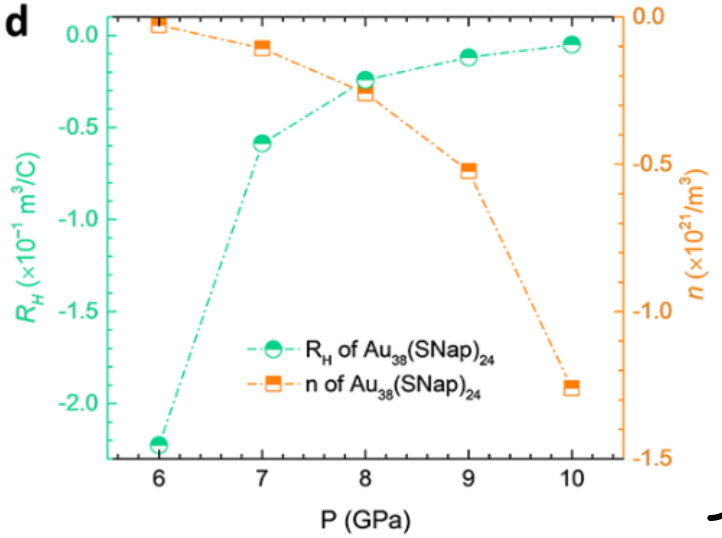
Hall measurements

$Au_{25}(SNap)_{18}$





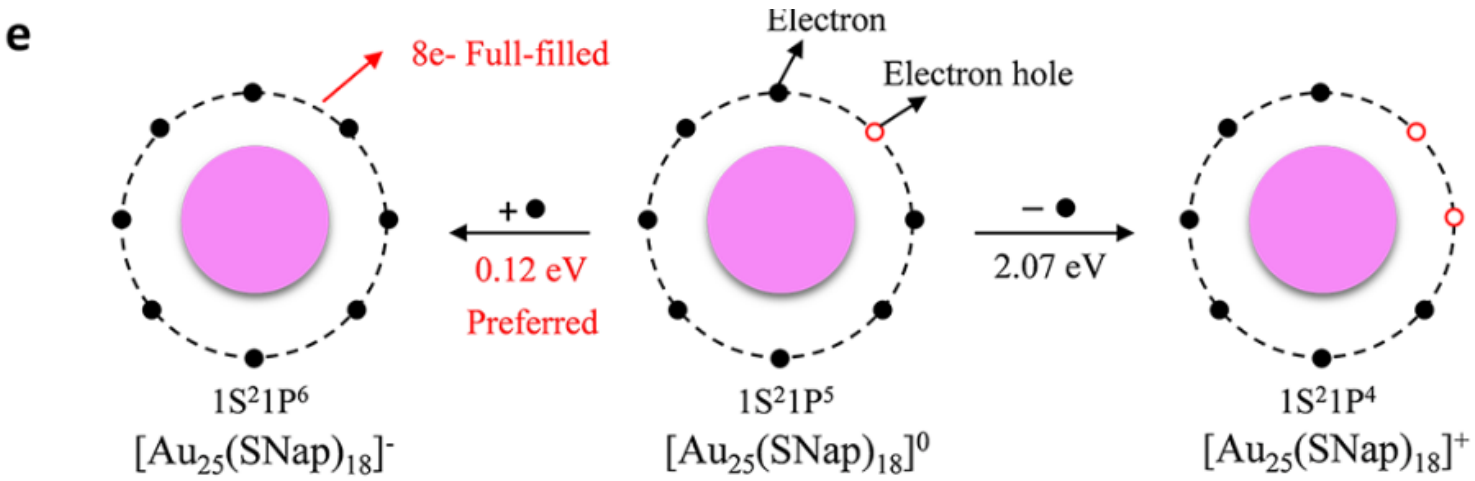




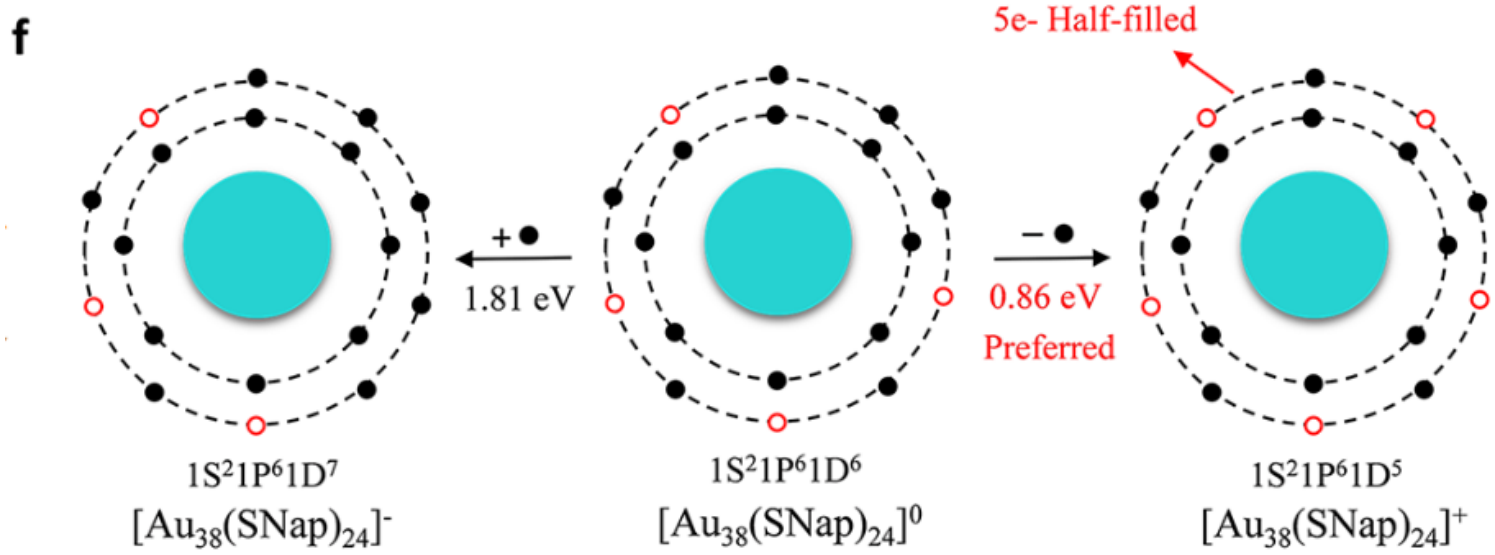
$Au_{38}(SNap)_{24}$

Charge carrier type

p-type carrier



n-type carrier



Conclusion

- This study provides valuable insight into the charge transport of metal nanocluster solids through a combination of precise structure analyses, high-pressure techniques, and theoretical calculations.
- This is the first study to reveal that the ligand conjugation structure benefits charge transport and that the nanocluster structure influences the conductivity at least partially by tuning the interparticle distance.
- This comprehensive investigation not only enhances the understanding of charge transport in nanocluster solids but also highlights the potential of metal nanoclusters as (semi)conductor materials for both fundamental research and practical applications.

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Instead of

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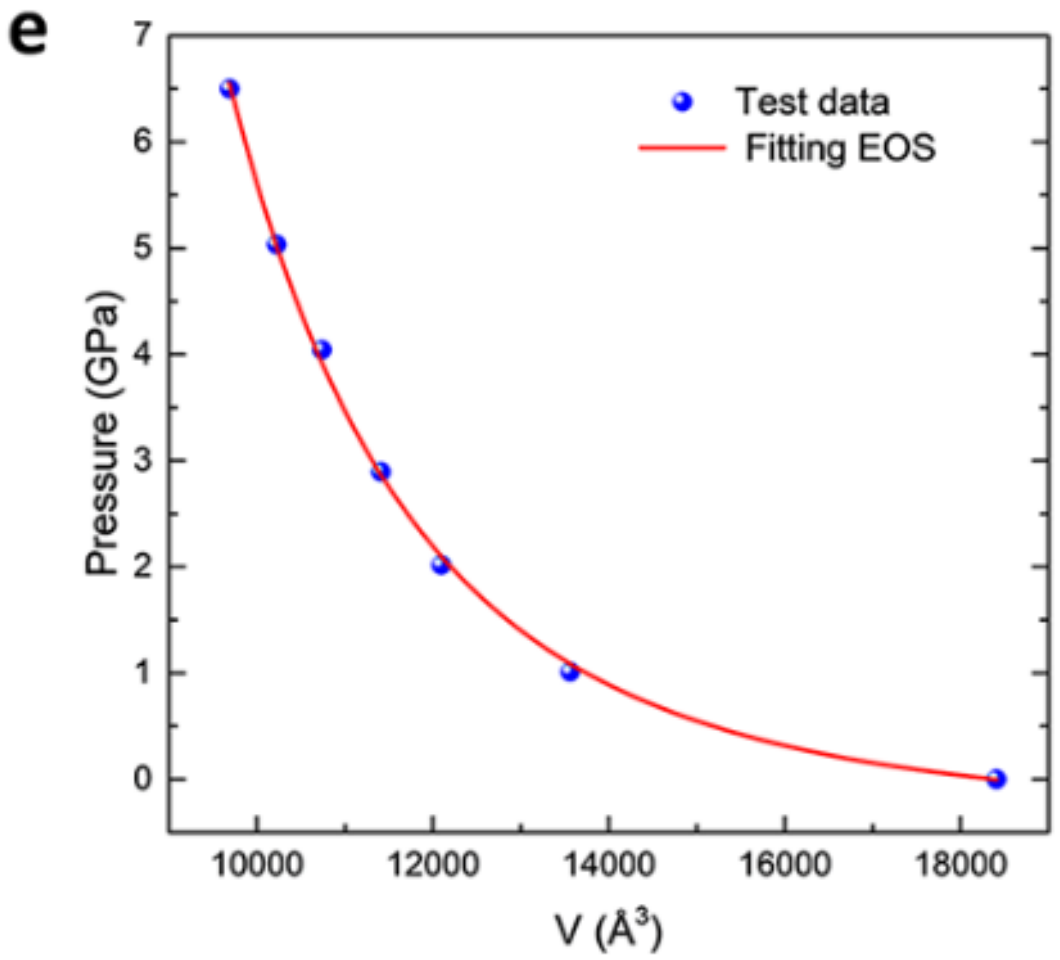
Shiyu Ji, Di Peng, Fang Sun, Qing You, Runguo Wang, Nan Yan, Yue Zhou, Weiyi Wang, Qing Tang,* Nan Xia,* Zhi Zeng,* and Zhikun Wu*

Thank You!

Effect of pressure



Murnaghan equation of state

$$P(V) = 0.27\left(\left(\frac{18411}{V}\right)^{4.92} - 1\right)$$