Superconducting State of Small Nanoclusters

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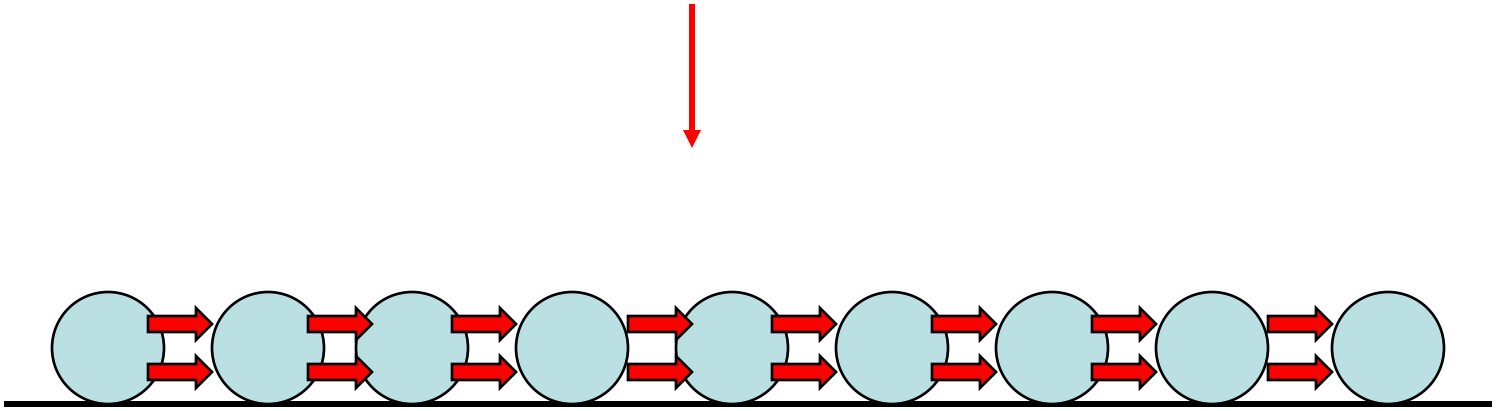
☐Superconducting state of small metallic nanoparticles

$N \approx 10^2 - 10^3$

(N is a number of delocalized electrons)

New family of high T_c superconductors

Macroscopic superconducting current at high temperatures



Superconducting state of metallic nanoparticles

M. Tinkham et al. (Harvard U.)
1995-

$N \approx 10^4 - 10^5$

Small metallic nanoparticles (clusters)

$N \approx 10^2 - 10^3$

Temperature dependence of even-odd electron-number effects in the single-electron transistor with a superconducting island

M. Tinkham, J. M. Hergenrother, and J. G. Lu
Physics Department and Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138
(Received 27 December 1994)

A simple quasiequilibrium model is presented that accounts in some detail for the observed temperature dependence of the crossover from $2e$ to e periodicity (vs gate charge) in the current through a single-electron tunneling transistor with a mesoscopic superconducting island.

The single-electron tunneling transistor consists of a small metallic island weakly coupled to two bias leads by high-resistance, low-capacitance tunnel junctions, and capacitively coupled to a gate electrode by a capacitance C_g. The current I through the device for a given bias voltage V is a periodic function of the voltage V_g on the gate electrode. If the island is of normal metal, the period corresponds to a change in the gate charge $Q_0=C_gV_g$ by a single electronic charge e, whereas if the island is superconducting, the period can be $2e$ or e, depending on the temperature and the bias voltage across the two tunnel junctions. Qualitatively, the period is $2e$ if as many electrons as possible on the superconducting island are paired; the period becomes e when at least one excess quasiparticle is present, whether by injection at high bias voltages or by thermal excitation as the temperature is raised. In this paper we present a simple model calculation which gives insight into how this crossover in period takes place as a function of temperature in the limit of low bias voltage, together with some illustrative experimental data.

To calculate the actual device current $I(V,V_g)$ theoretically, it is necessary to make a kinetic calculation,[1,2] solving a master equation to find the self-consistent steady-state nonequilibrium populations of all relevant states, and the resulting current. However, in the limit of low bias voltage, state populations will be near to the $V=0$ *equilibrium* values for the same gate voltage V_g. At sufficiently low bias voltages, we expect the current through the device to be proportional to V with a coefficient[3] which is a function of V_g and T, dependent on the equilibrium populations. Thus, we expect that the *period* (e or $2e$) of the current will be determined by the *period* with which the populations vary with V_g, allowing us to use the periodicity of the equilibrium populations as a proxy for the periodicity of the current at low bias voltages. The enormous simplification which this entails is the motivation for pursuing this approach, even if it is limited to finding the period of $I(V_g)$, without being able to find its magnitude and wave form. It seems likely that an analytic prescription could be developed for calculating the linear response $dI/dV|_{V=0}$ as a function of V_g based on the knowledge of the equilibrium populations, but that remains for future work.

We start by recalling that if the island is in the *normal* state, with $V\approx 0$, the part of the electrostatic energy which depends on n, the number of excess electrons on the island, is given by

$$E=\frac{(Q_0-ne)^2}{2C_\Sigma}\equiv E_c\left[\frac{Q_0}{e}-n\right]^2. \tag{1}$$

Here $Q_0=-C_gV_g+Q_{00}$ is the charge induced by the gate plus any intrinsic offset charge Q_{00} from charged impurities, e is the charge of the electron including its sign, C_Σ is the total capacitance of the island to the bias leads and the gate electrode, and $E_c\equiv e^2/2C_\Sigma$ characterizes the Coulomb charging energy. As is evident from the plot in Fig. 1(a), this expression is minimized if ne always takes on the value nearest to Q_0. Thus, as V_g is swept, n changes by unity every time Q_0 passes through a half-integral value. This leads to a variation of the populations, and hence of the current $I(V_g)$ at fixed bias V, which is e periodic.

If the island is a *superconductor,* the above results are modified by the electron pairing. If the total number N of conduction electrons on the island is even, the BCS ground state is fully paired; if N is odd, the ground state must include one quasiparticle above the energy gap Δ. To describe this distinction, Averin and Nazarov[4] introduced an explicit additive energy term, which has the value Δ in odd-N states, and zero in even-N states. As can be seen from Figs. 1(b) and 1(c), this has the effect of introducing a $2e$ periodicity in the energy level diagram, and hence in the populations of the various possible states. This in turn should be reflected in a $2e$ periodicity in the low-voltage current through the device at low temperatures, but at sufficiently high temperatures we expect to recover the e periodicity of the normal state. The objective of this paper is to clarify the nature of this transition from $2e$ to e periodicity with increasing temperature.

Although $2e$-periodic currents in an *SSS* transistor (i.e., one in which leads and island are both superconducting) had been reported earlier by Geerligs *et al.*,[5] this even-odd electron number effect on the tunnel current was first clearly demonstrated and interpreted by Tuominen *et al.*,[6,7] also using an *SSS* device. Their work showed that the $2e$ periodicity changed to an e periodicity upon warming through a temperature T^*, far below T_c, where $\Delta(T^*)\approx\Delta(0)\gg k_BT$ and the material is still

Nanoclusters

Clusters – small aggregates of atoms or molecules

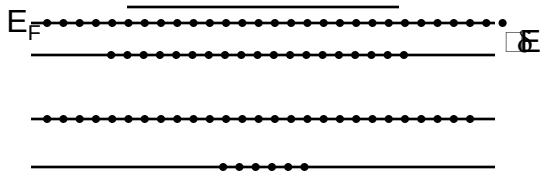
A_n (e.g., Na_n , Zn_n, Al_n)

e.g., Al_{56} : N = 56 x 3 = 168 (each Al atom has 3 valence electrons)

Zn_{66} : N = 66 x 2 = 132

Metallic nanoclusters

Discrete energy spectrum



Energy spacing depends on the particle size

Pairing is not essential if $\delta E >> \Delta$

Superconducting pairing is essential if $\delta E \lesssim \Delta$

Shell structure

Discovery (1984)

Clusters
preparation, spectroscopy,
catalytic activity, absorption (surface),
cluster crystals

France

(Orsay, Grenoble, Lyon)

Germany

(Karlsruhe, Stuttgart, Berlin, Freiburg)

Switzerland

(Lausanne)

Belgium

(Leuven)

Phys. Rev. Lett. 52, 2141 - 2143 (1984)

Electronic Shell Structure and Abundances of Sodium Clusters

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Department of Physics, University of California, Berkeley, California 94720, and Clarendon Laboratory, Oxford OX1 3PU, United Kingdom

Keith Clemenger, ***Walt A. de Heer***, and ***Winston A. Saunders***

Department of Physics, University of California, Berkeley, California 94720

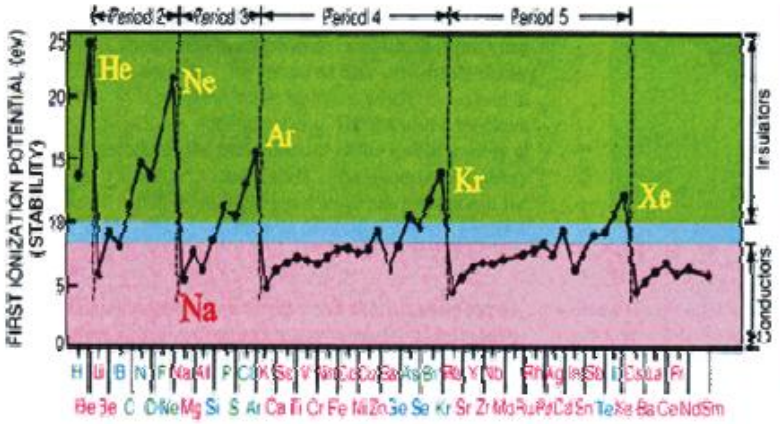
M. Y. Chou and ***Marvin L. Cohen***

Department of Physics, University of California, Berkeley, California 94720,

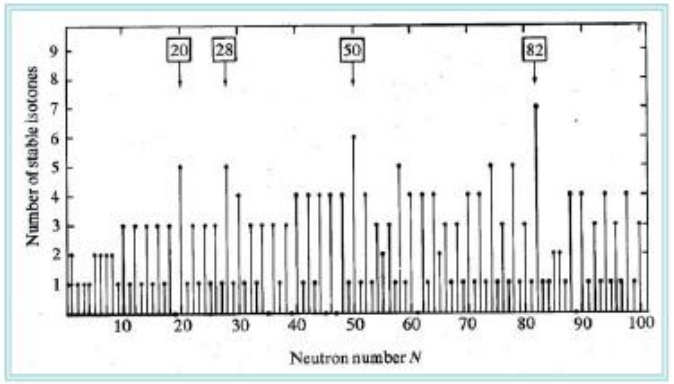
•Mass spectra are presented for sodium clusters of *N* atoms per cluster (*N*=4-100) produced in a supersonic
•Expansion with argon carrier gas. The spectra show large peaks or steps at *N*=8, 20, 40, 58, and 92. These can
• be understood in terms of a one-electron shell model in which independent delocalized atomic 3*s* electrons are
•Bound in a spherically symmetric potential well.

Shell Structure

Metallic clusters contain delocalized electrons whose states form **shells** similar to those in atoms or nuclei

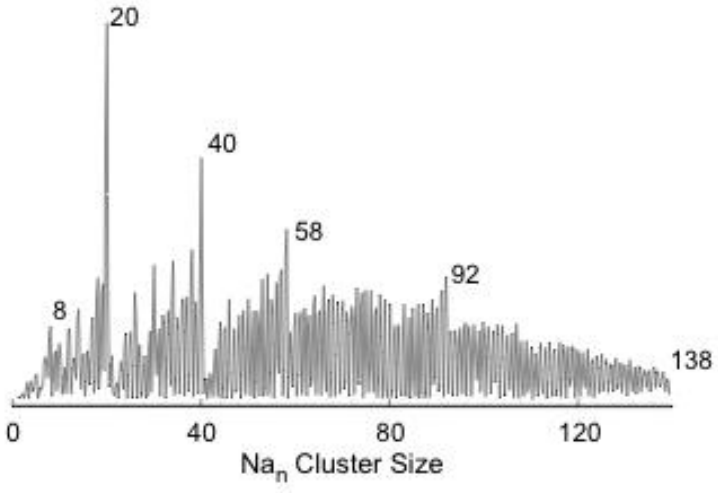


Periodic table

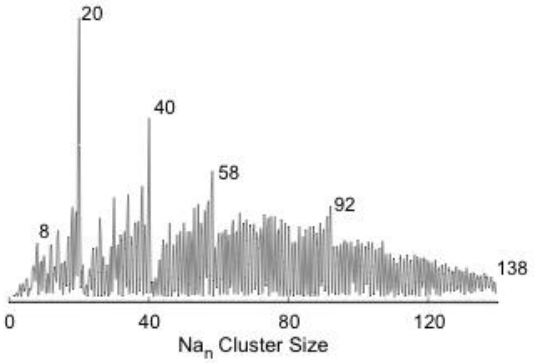


Nuclear stabilities

Clusters



Metallic clusters

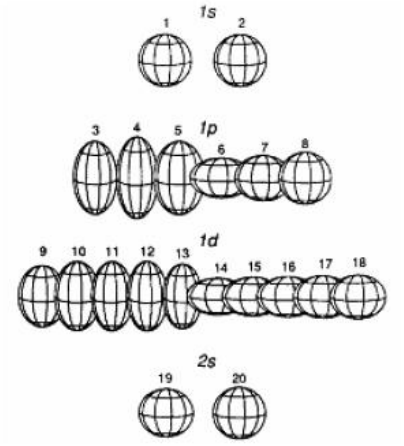


Mass spectra of metallic clusters display
magic numbers

Magic numbers (N_m=8,20,40,…,168,…,192,…)
correspond to filled electronic shells (similar to inert atoms)

Cluster shapes

Clusters with closed electronic shells are spherical



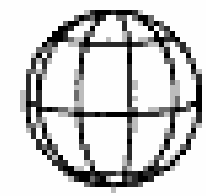
There is a strong correlation:

Number of electrons → shape → energy spectrum

“Magic” clusters

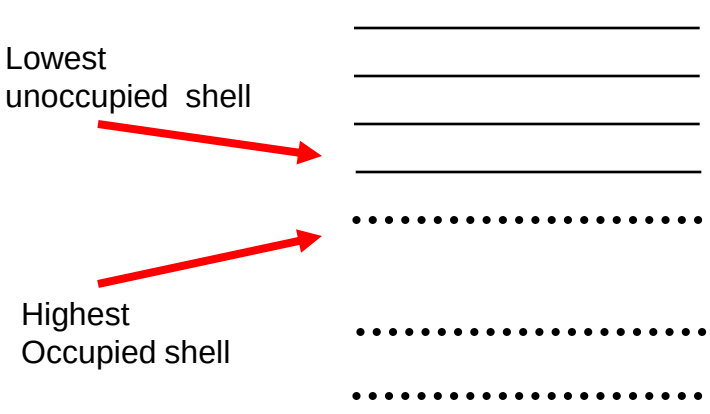
spherical shape (quantum numbers: n,L)

degeneracy : $g = 2(2L+1)$



e.g. $N_m = 168$; $L = 7$

$g = 30$ (!)



Incomplete shell

e.g., $N_m = 168$

↓

N =166 (removal of two electrons)

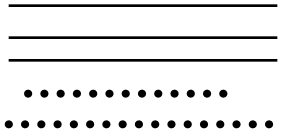
↓

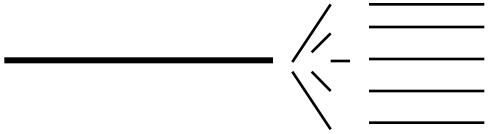
Jahn-Teller shape deformation

sphere → ellipsoid

↓

splitting

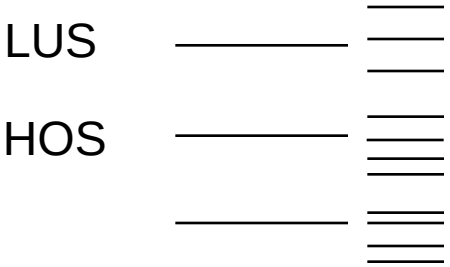


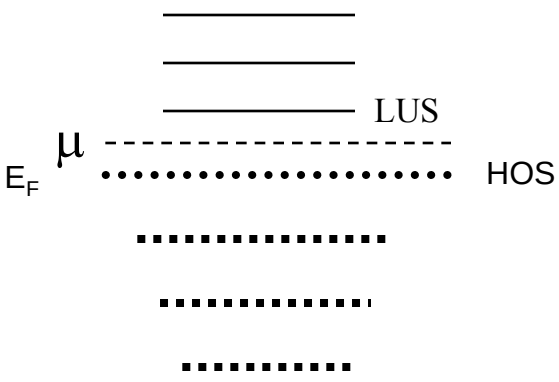


Factors:

- splitting

– μ(T)





high degeneracy

↓

peak in density of states
(similar to van Hove)

↓

increase in T_C

$\lambda = V\nu$

e.g., L = 7 (N=168; e.g., Al_{56}

degeneracy G = 2(2L +1) = 30

(30 electrons at E_F)

↓

favorable for pairing

Pairing is similar to that in nuclei

A.Bohr , B.Mottelson, D.Pines (1958)
S.Beljaev (1959)
A.Migdal (1959)

The pair is formed by two electrons
$\{m_j, 1/2; -m_j, -1/2\}$

Metallic clusters

- Coulomb forces
- electrons and ions
- electronic and vibrational energy levels

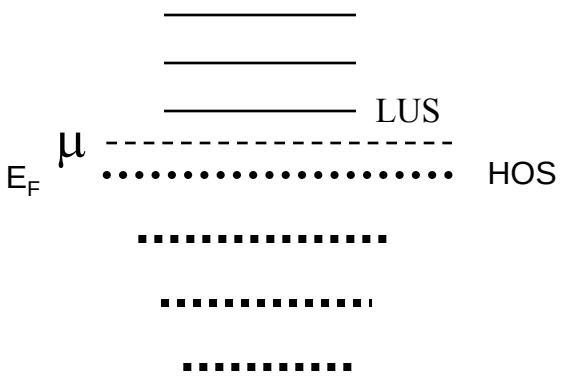
↓

electron- vibrational interaction

-increase in size → bulk metal

Critical temperature

$T = T_C$



$$\Delta(\omega_n) Z = \lambda \frac{E_F}{N} T \sum_j g_i \sum_{\omega_{n'}} \frac{\tilde{\Omega}^2}{(\omega_n - \omega_{n'})^2 + \tilde{\Omega}^2} \bullet \frac{\Delta(\omega_{n'})}{\omega_{n'}^2 + (\varepsilon_j - \mu)^2} \Big| T_C$$

$$N = \sum_j \frac{g_i}{1 + \exp\left[(\varepsilon_j - \mu)/T\right]}$$

$$\omega_n = (2n+1)\pi T_C$$

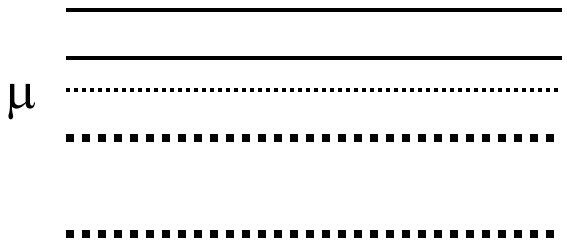
Matrix method:

$$\Delta_n = \sum_m K_{nm'} \Delta_{m'}$$

$$\left| 1 - K_{nn'} \right| = 0$$

$$K_{nn'} \propto (G_L + G_H)$$

C.Owen and D.Scalapino (1971)
V.Kresin, H.Gutfreund, W.Little (1987)



Parameters: N, $\Delta\varepsilon_{LH}$, g_L, g_H; E_F, $\lambda_{b,}$ $\tilde{\Omega}$

Examples:

N = 168; $\Delta\varepsilon_{LH}$ = 70meV,

g_L = 30; g_H = 18; $\tilde{\Omega}$= 25meV; λ_b = 0.5; E_F=10^5K

(L = 7) (L = 4)

T_C=150K

Ga_{56} (N = 168) T_C=160K (T_c^b =1.1K)

Zn_{190}(N=380) T_C=105K (T_c^b =0.9K)

Fluctuations

$T \sim T_c$

↓

Ginzburg - Landau functional

↓

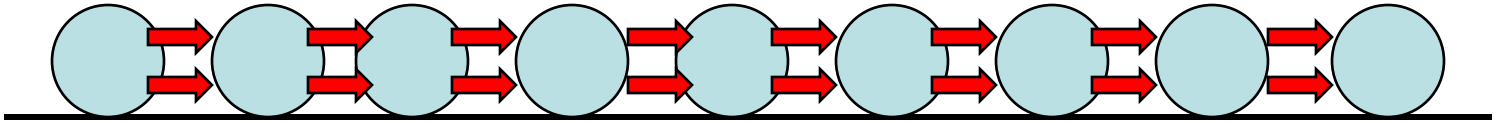
δT_c(broadening of the transition)

$$\frac{\delta T_c}{T_c} \approx 5 - 10\%$$

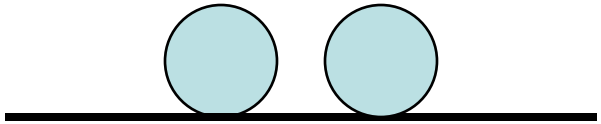
Clusters with pair correlation are promising

building blocks for tunneling networks.

Macroscopic superconducting current at high temperatures



Depositing clusters on a surface without strong disturbance of the shell structure



Two clusters are embedded in dielectric matrix

Josephson effect for bulk superconductors

$$J_c = J_c^0 Sin(\varphi_1 - \varphi_2)$$
$$E_j = E_j^0[1 - Cos(\varphi_1 - \varphi_2)]$$

$$J_c^0 = t^2 T \sum_n \int \int d\xi d\xi' \frac{\Delta_\alpha \Delta_\beta}{\left(\omega_n^2 + \xi^2 + \Delta_\alpha^2\right)\left(\omega_n^2 + \xi'^2 + \Delta_\beta^2\right)}$$

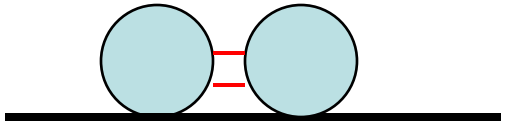
Assume $S_\alpha = S_\beta$

$$J_c = (\pi/2eR)\Delta th(\Delta/2T)$$
$$T = 0K; J_c = (\pi/2eR)\Delta$$
$$T \approx T_c; J_c = (\pi/4eR)\Delta^2/T_c$$

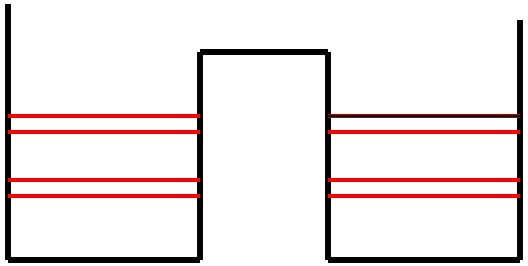
Clusters →

$$\int d\xi \to \sum_k \xi_k$$
$$\xi_k = E_k - \mu; \mu \approx (E_{LUS} - E_{HOS})/2$$

discrete energy spectrum

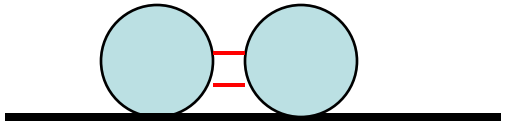


Tunneling



Splitting δE

$$j = \left\{ \frac{ie}{m}\left(\frac{\partial}{\partial r'} - \frac{\partial}{\partial r} \right) - \frac{2e^2 A(r)}{m} \right\} G(r, r') \Big|_{r' \to r}$$



$$j = \left\{ \frac{ie}{m}\left(\frac{\partial}{\partial r} - \frac{\partial}{\partial r'} \right) - \frac{2e^2 A(r)}{m} \right\} G(r, r') \Big|_{r' \to r}$$

$$G = T \sum_{\omega_n} \sum_{E} \frac{e^{-\omega_n(\tau - \tau')}}{-i\omega_n + E} \hat{f}_E(r, \tau) \hat{f}_E^{+}(r', \tau')$$

$$\begin{pmatrix} \hat{K} & \Delta \\ \Delta & -\hat{K} \end{pmatrix} \hat{f} = E \hat{f}$$

$$\hat{K} = -\frac{1}{2m} \frac{\partial^2}{\partial r^2} + \mu + V(r)$$

$T \ll T_c$

$$J_0 = e\,|t|^2 \sum_{s_\alpha, s_\beta} \frac{\Delta_\alpha \Delta_\beta}{(\varepsilon_a + \varepsilon_\beta)\varepsilon_a \varepsilon_\beta}$$

$$\varepsilon_a = [(E_a - \mu)^2 + \Delta_\alpha^2]^{1/2}$$

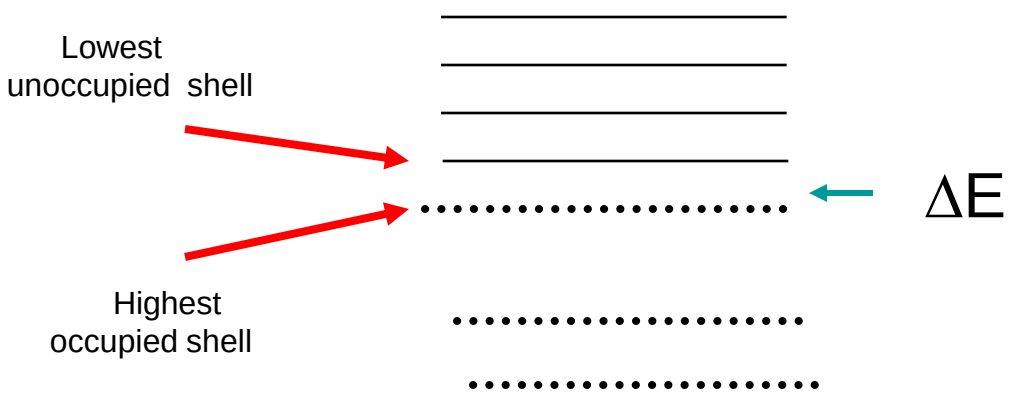
Assume → $\Delta_\alpha \equiv \Delta_\beta$

↓

$$j_0^{cl.} \approx e\,|t|^2 \frac{\Delta^2}{(\Delta\varepsilon)^3}$$

$$j_0^{bulk} \approx e\,|t|^2 \frac{\Delta^2}{T_c E_F^2}$$

$$E_F >> \Delta\varepsilon \rightarrow j_0^{cl.} >> j_0^{bulk};$$



$$j_0^{cl.} / j_0^{bulk} \approx 10^3$$

$T \approx T_c$

$$J_0 = e\,|t|^2 \sum_{s_\alpha, s_\beta} \frac{\Delta_\alpha \Delta_\beta}{(\xi_a + \xi_\beta)\xi_a \xi_\beta}$$

$$\xi_a = E_a - \mu$$

$$\Delta_\alpha \equiv \Delta_\beta$$

$$\downarrow$$

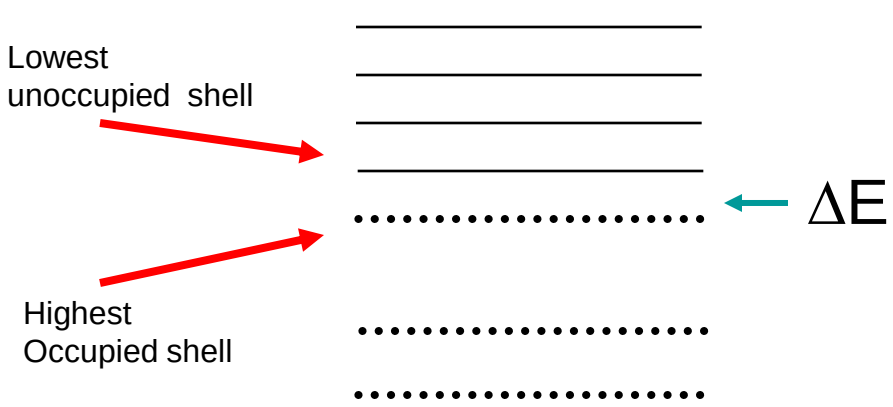
$$j_0^{cl.} \approx e\,|t|^2 \frac{\Delta^2}{(\Delta E)^3}$$

$$j_0^{bulk} \approx e\,|t|^2 \frac{\Delta^2}{T_c E_F^2}$$

$\Delta E \approx 10^3 K$; $E_F \approx 10^5$

$$E_F >> \Delta E \rightarrow j_0^{cl.} >> j_0^{bulk}; j_0^{cl.} \approx 10^8\, A/sm^2 \text{ vs } j_0^{bulk} \approx 10^5\, A/sm^2$$

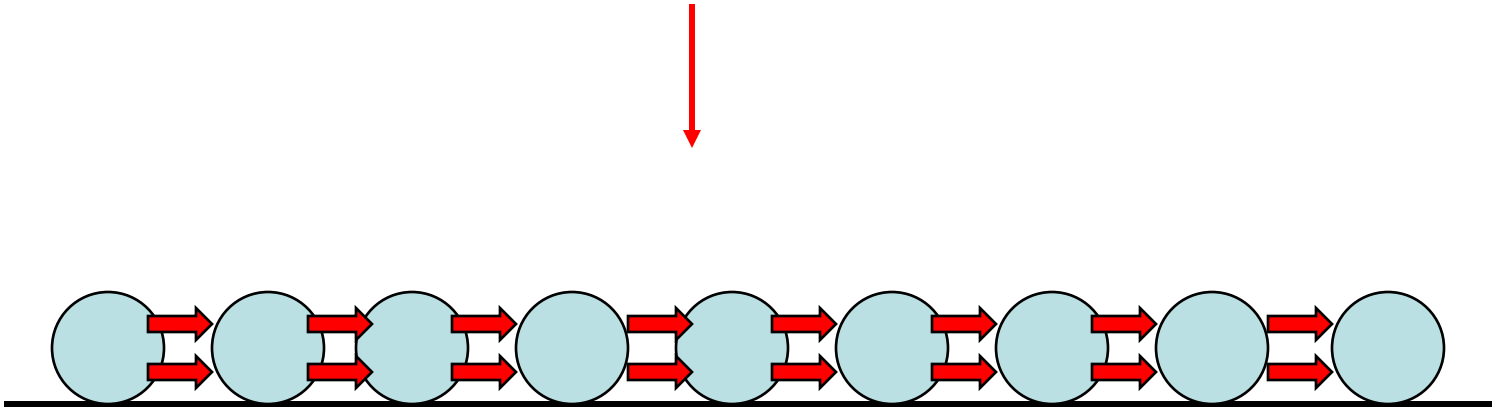
$$j_{0;max} \approx e k_B T_c / \square$$



$$j_0^{cl.} >> j_0^{bulk}$$

Tunneling Network

Macroscopic superconducting current at high temperatures



Josephson Coupled Quantum Dot Artificial Solids

I.Weitz, Jennifer L. Sample, Ryan Ries, Eileen M. Spain, and James R. Heath*

UCLA Department of Chemistry and Biochemistry, 405 Hilgard Avenue, Los Angeles, California 90095-2000 ; **J.Phys.Chem.B 2000,104,4288**

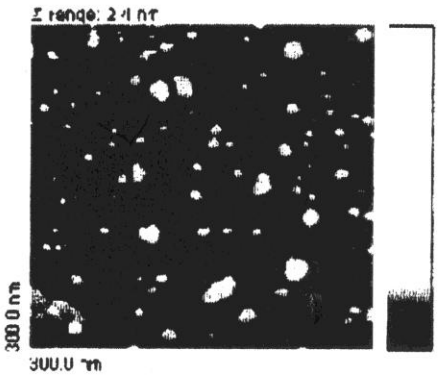
Josephson coupled quantum dot artificial solids were prepared from 20 ± 4 nm diameter organically functionalized Pb particles. Interparticle separation distances were varied from approximately 26 to 11 A by varying the passivating organic ligand. Isolated particles were too small to exhibit a Meisner effect by themselves, and so it was possible to employ SQUID magnetometry as a zero-background probe for Cooper pair delocalization in these solids. As the interparticle separation distance was decreased, the quantum dot solids progressed from a Mott insulator to a strongly localized superfluid, and finally to a superfluid.

Individual (bi-)metallic clusters deposited on flat surfaces

Research is conducted on individual (bi-)metallic clusters, deposited on very flat surfaces. We examine the influence of the surface on shape, structure and mobility of the deposited clusters and we also probe the electronic structure of the clusters.

The deposited clusters can be examined by many different techniques. To get information about shape, structure and mobility, experiments with Scanning Tunneling Microscopy (STM), High Resolution Electron Spectroscopy (HREM), Auger Spectroscopy and Reflection High Energy Electron Diffraction (RHEED) among others, are conducted. To get insight in the electronic properties of the clusters, we use low temperature Scanning Tunneling Spectroscopy (STS).

The current research is focussed on Au_n clusters deposited on a Au surface. To produce these gold samples, a 200 nm gold layer is deposited on MICA. On top of the gold layer we can also deposit a self-assembled monolayer of hexanethiol to form an insulating layer between the surface and the deposited clusters. This insulating layer is needed when couble tunnelling barrier STS is performed.



The image shown in figure 1 is an STM image of Au_n clusters deposited on a Au surface. Interpretation of this image enables us to get information about cluster heights, sizes and mobility. We can find on the surface clusters of which sizes vary between 15 over 100 Å. The fact that the number of large clusters found on the surface is larger then the number originally produced gives evidence for the fact that diffusion takes place on the surface, so that several clusters can agglomerate to form larger entities.

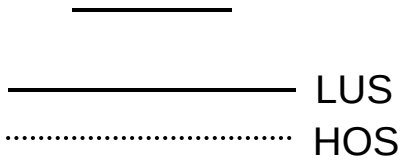
Superconducting state of nanoclusters :

Proposed Experiments

Energy spectrum

experimentally measured excitation spectrum

(e.g. HOS – LUS internal (ΔE)) is temperature dependent $\left(\Delta E_{IT\approx OK} >> \Delta E_{IT>T_C}\right)$



- clusters at various temperatures
  1)$T<<T_c$; 2)$T>T_c$

e.g., Cd_{83} (N=166) : $\hbar\omega_{min.} \approx 34$ meV($T>T_c$); $\hbar\omega_{min.} \approx 6$ meV ($T<<T_c$)

photoemission spectroscopy

Odd-even effect

the spectrum strongly depends on the number of electrons being odd or even

Magnetic moment

Recent progress

-Spectroscopy

B.von Issendorff and O.Cheshovsky
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-Preparation

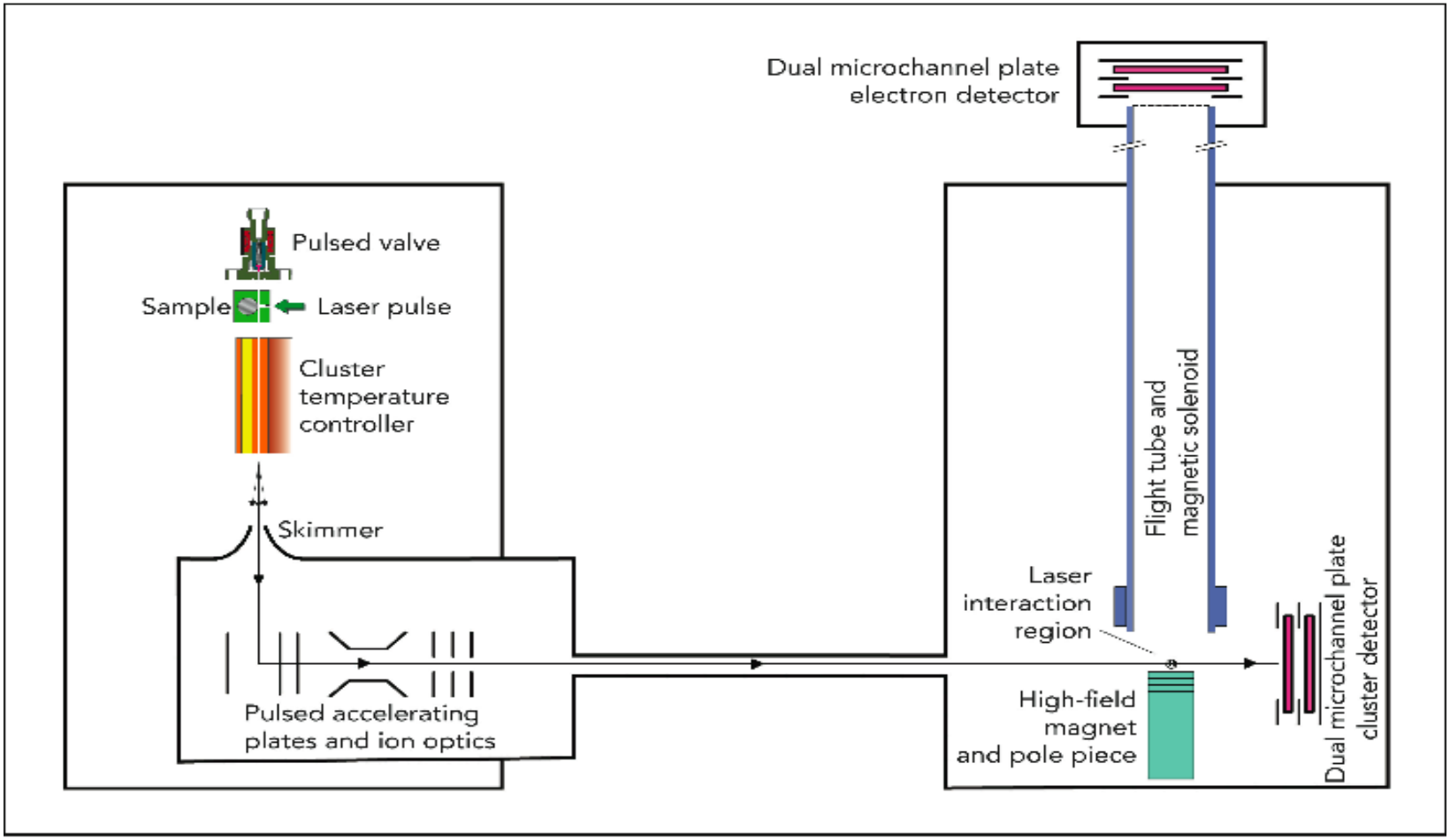
Experiments:

Selection (mass spectroscopy;e.g., Ga_{56})

- Cluster beams at different temperatures ($T>T_c$ and $T<T_c$)
- Spectroscopy (photoemission)

- Magnetic properties

L.Bloomfield, A.Post (U.of Virginia)



- In the first chamber, the clusters pass through a narrow copper channel which is connected to a liquid N_2 bath
- The cluster anions travel through the pipe to the detector, which registers a spike for each mass as a function of time. This allows us to just focus on the magic cluster of interest
- To measure the energies, a UV laser is sent into the "interaction region", just before the cluster detector. The photons remove the extra electron from the Al^-_n clusters
- The photodetached electrons are directed up another long pipe to a detector. Their kinetic energy is deduced from their flight time, and from that we get the binding energy
- At T_C, Cooper pairing will lower the electron energy, increasing the minimum energy needed to photodetach them

Simple metallic clusters (Al, Ga, Zn, Cd)

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$T_c \approx 150K$

Change in the parameters ($\tilde{\Omega}$, ΔE, etc)

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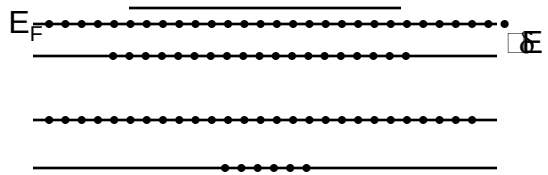
Room temperature



Conditions:

- small HOS-LUS energy spacing
- large degeneracy of H and L shells
- small splitting for slightly unoccupied shells
  e.g., N=168, 340; N=166

Conditions:

-Large value of L → number of electrons

g=2(2L+1) is large

(e.g.,for Al_{56} L=7

$g_{HOS} = 30(!)$)

-The spacing HOS-LUS should be small;

e.g.,

$\tilde{\Omega} = 50 meV$

$\Delta E = 0.2 eV$

$k_F = 1.7 \times 10^8 sm^{-1}$ → T_c=240K

$m^* = 0.5 m_e$

$R = 5.5 Å$

Summary

The presence of shell structure and the accompanying high level of degeneracy in small metallic nanoclusters leads to large increase in the value of the critical temperature

e.g., Ga_{56} : $T_c \approx 150K$

- It is possible to raise T_c up to room temperatures

- Experiments:

  Temperature dependence of the spectrum

  $\Delta E_{IT<Tc} \neq \Delta E_{IT>Tc}$

  Odd-even effect

- Clusters with superconducting pair correlation are promising building blocks for tunneling network

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Transition into superconducting state

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jump in heat capacity

- Selected nanoclusters display jump in heat capacity at high T; e.g., Al_{45}^- (N=136) has a jump at $T_c \approx 200K$(!). ← M.Jarrold B.Cao C.Neal A.Starace (Indiana U., Bloomington)

$$\beta = (4\pi^2/3)\frac{a}{T_c}\left(\frac{T_c}{\tilde{\Omega}}\right)^2 N^{-1}$$

$$\Theta_s = \Theta_n - a\tau_c^2(1-t)^2$$

$$\tau_c = 2\pi T_c/\tilde{\Omega}, t = T/T_c$$

Value of the jump is in a good agreement with the data

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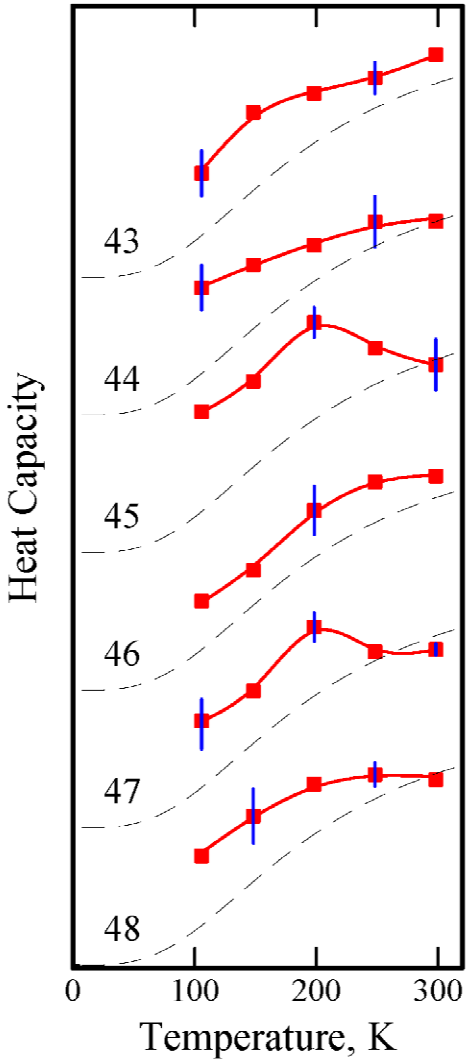
QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.


Heat Capacity
43
44
45
46
47
48
0
100
200
300
Temperature, K