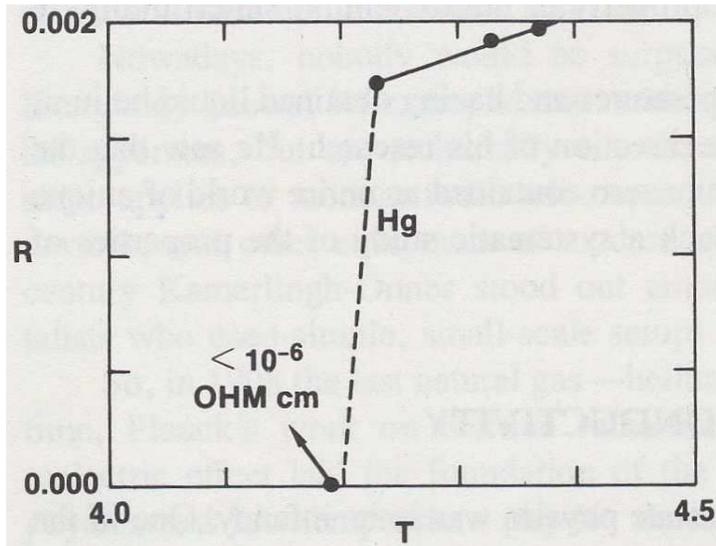


Superconducting State of Small Nanoclusters

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H. Kamerling - Onnes
(1911)

$R=0$

“The experiment left no doubt that the resistance disappeared. Thus the mercury at 4.2K has entered a new state which can be called the state of **superconductivity**”.

H.Kamerling-Onnes

At present:

-25 pure elements (highest transition temperature:

Nb ($T_c=9.2\text{K}$))

- \approx 6000 alloys and compounds

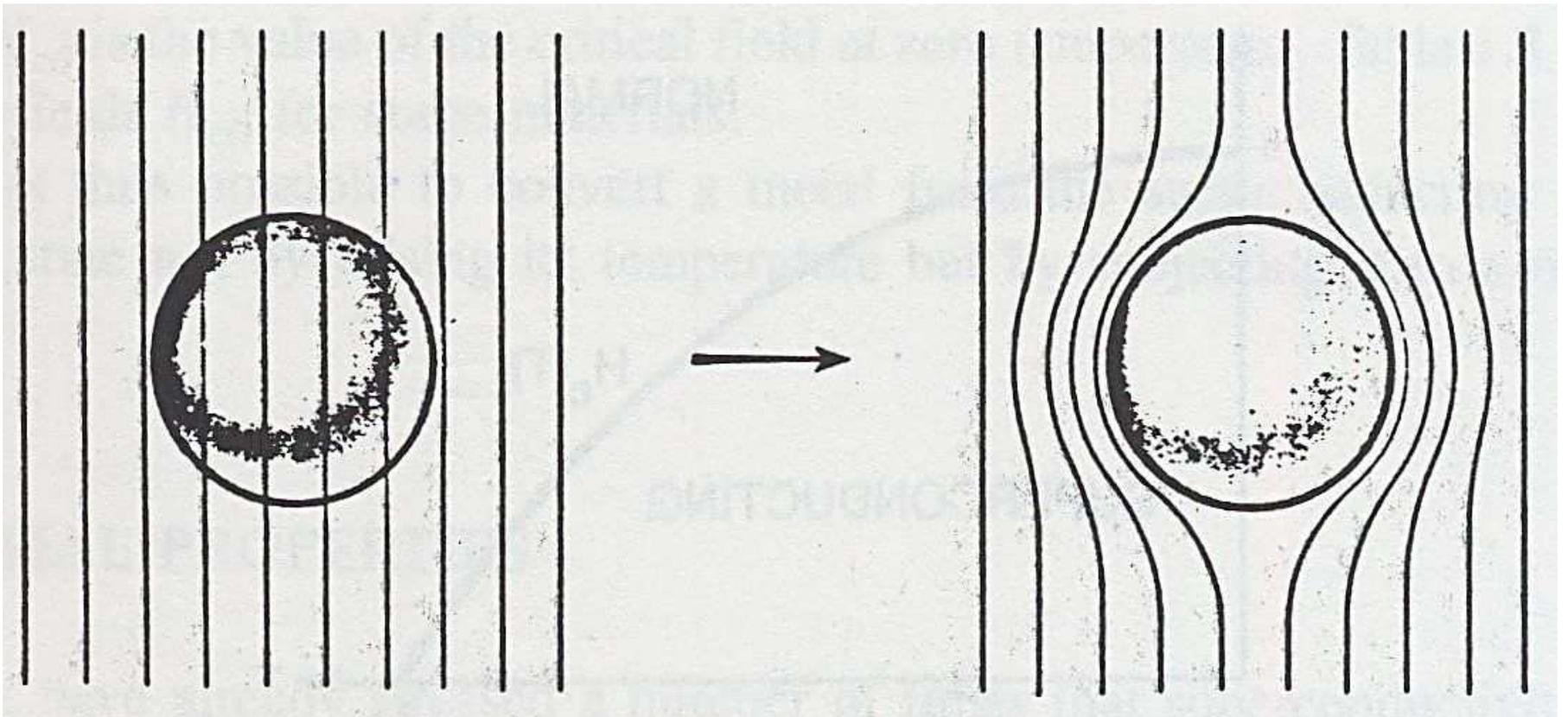
Superconducting state is a peculiar state of matter. Superconducting materials possess anomalous magnetic, thermal and other properties

e.g., electronic heat capacity:

$$C_{el}^n = \gamma T; C_{el}^s = a e^{-\frac{b}{T}}$$

Meissner effect

(anomalous diamagnetism)



Nature of superconductivity

A.Einstein (1922)

F.Bloch and L.Landau (1932)

W.Heisenberg (1947)

M.Born (1948)

1957

J.Bardeen, L.Cooper, J.Schrieffer (BCS)

Theoretical remark on the superconductivity of metals*

A. Einstein

translated by Bjoern S. Schmekel (Cornell University)[†]

The theoretical oriented scientist cannot be envied, because nature, i.e. the experiment, is a relentless and not very friendly judge of his work. In the best case scenario it only says “maybe” to a theory, but never “yes” and in most cases “no”. If an experiment agrees with theory it means “perhaps” for the latter. If it does not agree it means “no”. Almost any theory will experience a “no” at one point in time - most theories very soon after they have been developed. In this paper we want to focus on the fate of theories concerning metallic conductivity and on the revolutionary influence which the discovery of superconductivity must have on our ideas of metallic conductivity.

After it had been recognized that negative electricity is caused by subatomic carriers of particular mass and charge (electrons), there were good reasons to believe that metallic conductivity rests on the motion of electrons. Furthermore, the fact that heat is conducted much better by metals than by non-metals as well as the Wiedemann-Franz law about the substance-independence of the ratio of electric and thermal conductivity of pure metals (at room temperature) led to attribute the thermal conductivity to electrons as well. Under these circumstances there were reasons for an electron-based theory of metals similar to the kinetic gas theory (Riecke, Drude, H. A. Lorentz). In this theory free electron motion is assumed which resembles gas molecules with thermal mean kinetic energy $3/2 kT$ neglecting collisions

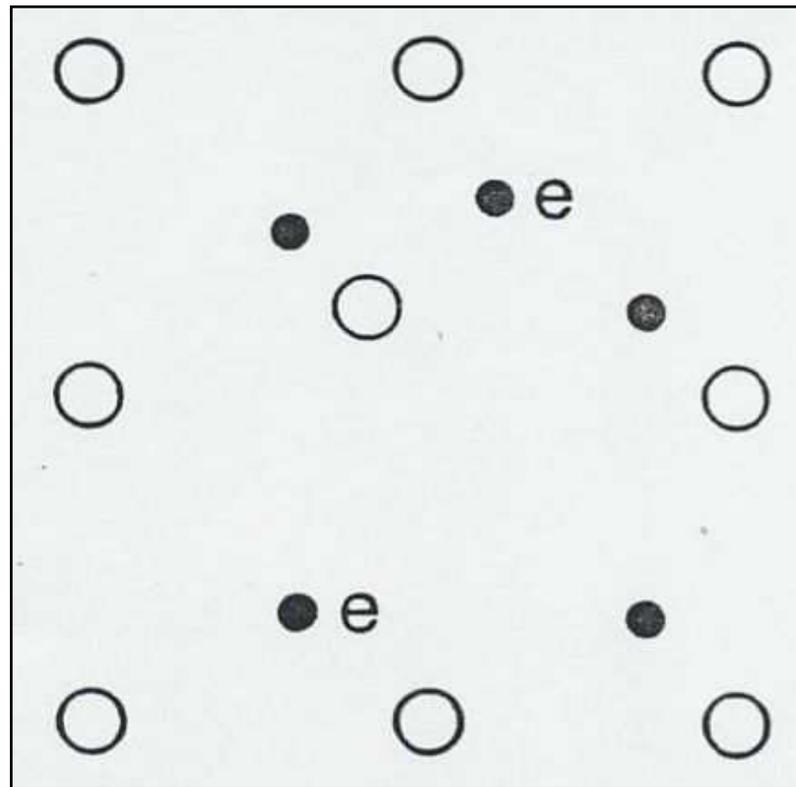
*from “Gedenkenboek aangeb. aan H. Kamerlingh Onnes, eaz. Leiden, E. IJdo, 1922, pp. 435” / translated with courtesy of the Kamerlingh Onnes Laboratory, Leiden - Institute of Physics, Leiden University

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BCS

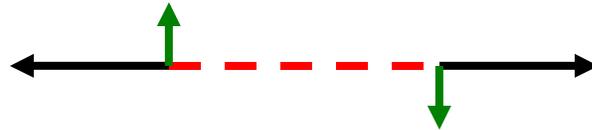
Electron-electron attraction

$$F = \frac{e_1 e_2}{\epsilon^2}; \epsilon < 0;$$

BCS

Electron-electron attraction



Pairing (the attraction between the pair
($p, s=1/2; -p, s=-1/2$) is the strongest

Electronic system:

↓
set of bound pairs (bound energy: 2Δ (energy gap))

excitation of the electronic system → breakup of such a pair



Applied superconductivity

(electronics, large scale magnets, etc.)

Restriction:



superconductivity -low temperature phenomenon

Direction:



search for a new class of materials with high value of the transition temperature (T_c).

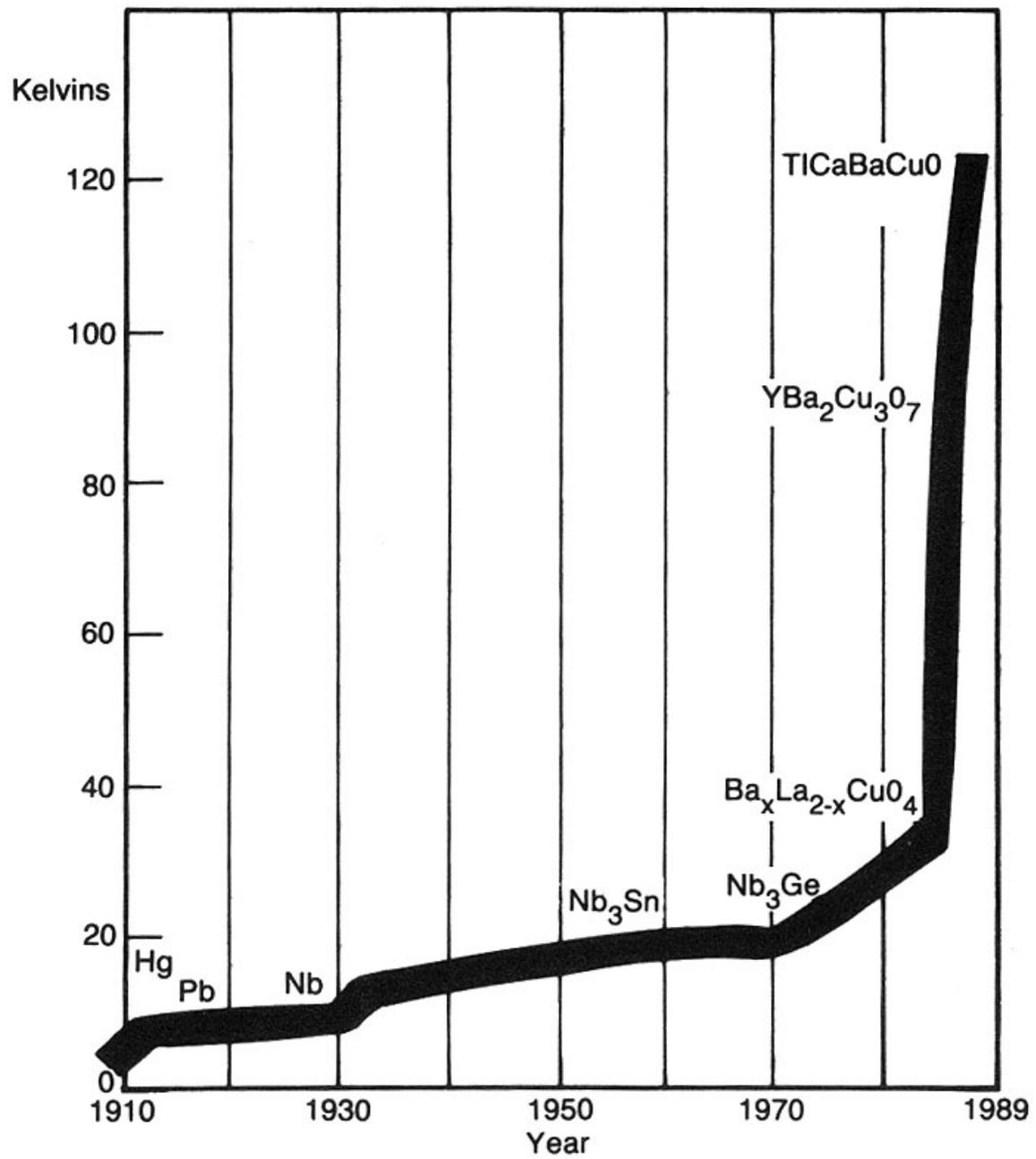
Goal:



Room temperature superconductor

“The magnet floats freely above the sheet supported entirely by its magnetic field. The field provides a cushion on which the magnet rests. It is easy to imagine hovecraft of the future utilizing this principle to carry passengers and cargo above roadways of superconducting sheet, moving like flying carpet without friction and without material wear or tear . We can even imagine riding on magnetic skis down superconducting slopes and ski jumps- many fantastic things would become possible”

W.Little, Scientific American (1965)



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

Superconducting state of metallic nanoparticles

Granular films
Tunneling (Harvard U.)

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

Small metallic nanoparticles (clusters)

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

Nanoclusters

Clusters – small aggregates of atoms or molecules

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

e.g., Al_{56} : $N = 56 \times 3 = 168$

(each Al atom has 3 valence electrons)

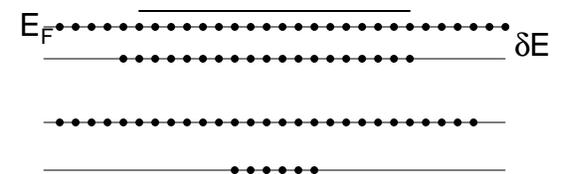
Zn_{66} : $N = 66 \times 2 = 132$

Metallic nanoclusters



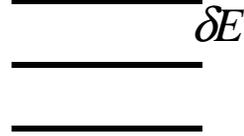
Discrete energy spectrum

Energy spacing depends on the particle size



Nanoparticles

Discrete energy spectrum



The pairing is not essential if $\delta E > \Delta$
(Anderson, 1959)

The pairing is important if $\delta E < \Delta$

Usual superconductors : $\Delta \approx 10K$

Estimation:

$$\delta E \sim \frac{E_F}{N} \quad ; E_F \approx 10^5 K$$

$$\text{if } N \approx 10^3 \quad ; \quad \delta E \approx 10^2 K \gg \Delta$$

Condition: $N \gtrsim 10^4$ ($\delta E \approx 10K$)

Assumption : the energy levels are equidistant (?)

shell structure



Metallic nanoclusters

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

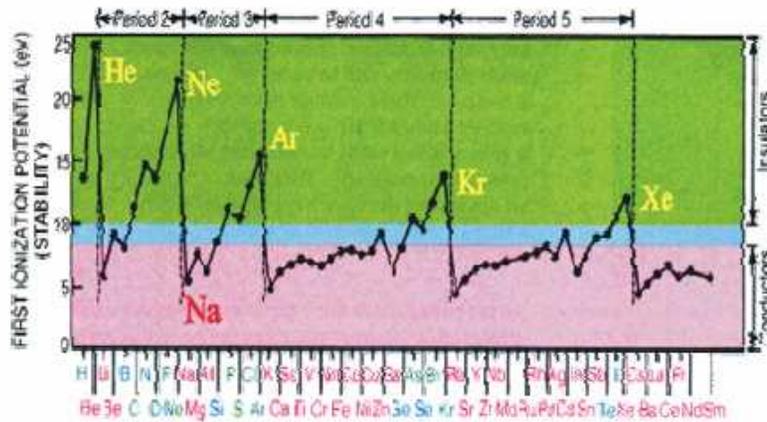
Shell structure



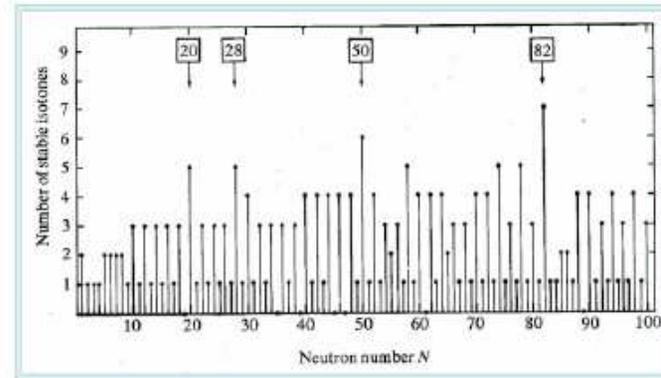
W. Knight et al. (Berkeley, 1984)

Shell Structure

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

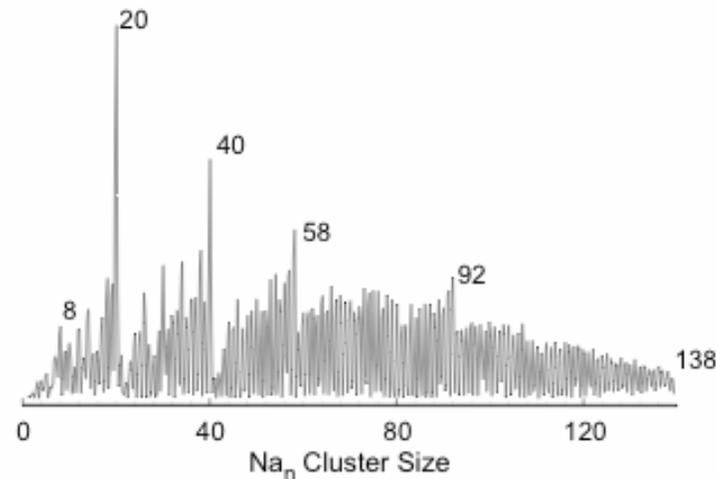


Periodic table



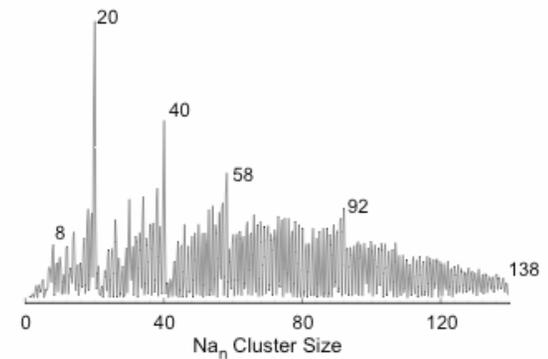
Nuclear stabilities

Clusters



Metallic clusters

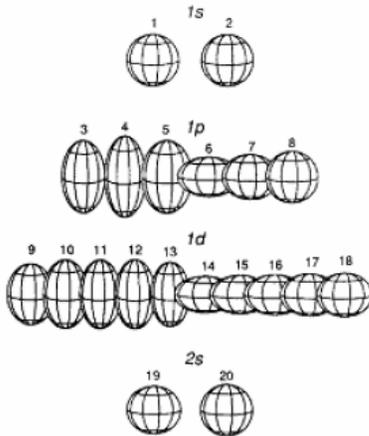
Mass spectra of metallic clusters display **magic numbers**



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

Cluster shapes

Clusters with closed electronic shells are spherical



There is a strong correlation:

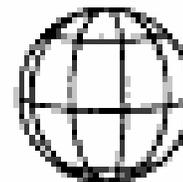
Number of electrons \rightarrow shape \rightarrow energy spectrum

“Magic” clusters

spherical shape

(quantum numbers: n, L)

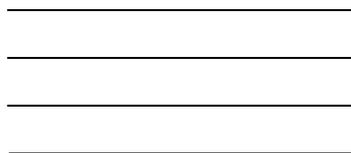
degeneracy : $g = 2(2L+1)$



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

$g = 30$ (!)

Lowest unoccupied shell



Highest Occupied shell

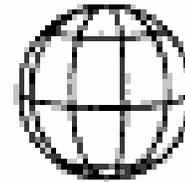


“Magic” clusters

spherical shape

(quantum numbers: n, L)

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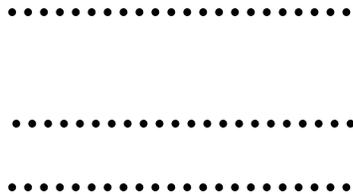


e.g. $N_m = 168$; $L = 7$

Lowest unoccupied shell



Highest Occupied shell



$g = 30$ (!)

Electrons at HOS (E_F) can form the pairs



Superconducting state

Pairing is similar to that in nuclei

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

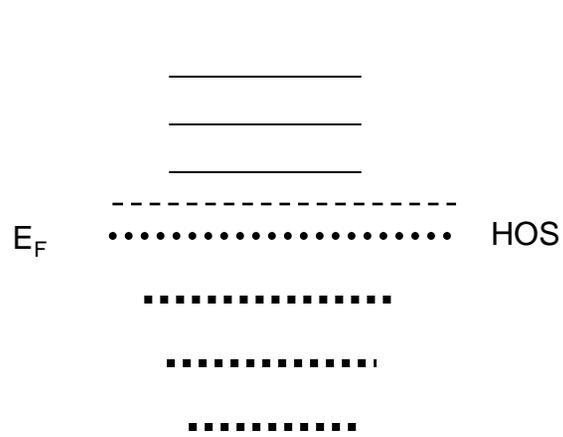
The pair is formed by two nucleons
 $\{m_j, 1/2; -m_j, -1/2\}$

Metallic clusters

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

Mechanism: electron- vibrational interaction

-increase in size \rightarrow bulk metal



high degeneracy



peak in density of states
(similar to van Hove)



increase in T_C

$$\lambda = Vv_F$$

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

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

(30 electrons at E_F)

Arbitrary strength of the electron – vibrational coupling

$$\Delta(\omega_n)Z = \lambda \frac{E_F}{N} T \sum_i g_i \sum_{\omega_n} \frac{\tilde{\Omega}^2}{(\omega_n - \omega_n')^2 + \tilde{\Omega}^2} \cdot \frac{\Delta(\omega_n')}{\omega_n'^2 + (\epsilon_j - \mu)^2 + \Delta^2(\omega_n')}$$

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

$$\lambda = \frac{\langle I \rangle^2 v_F}{M \tilde{\Omega}^2} \quad (\text{W. McMillan (1968)})$$

Bulk

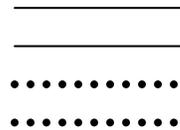
$$v_F \int d\epsilon$$

$$\mu = \epsilon_F$$

Clusters

$$\sum_j g_j$$

$$\mu \equiv \mu(T)$$



Critical temperature

$$T = T_C$$

$$\Delta(\omega_n)Z = \lambda \frac{E_F}{N} T \sum_j g_j \sum_{\omega_n'} \frac{\tilde{\Omega}^2}{(\omega_n - \omega_n')^2 + \tilde{\Omega}^2} \cdot \frac{\Delta(\omega_n')}{\omega_n'^2 + (\epsilon_j - \mu)^2} \quad |T_C$$

$$N = \sum_j \frac{g_j}{1 + \exp[(\epsilon_j - \mu)/T]}$$

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

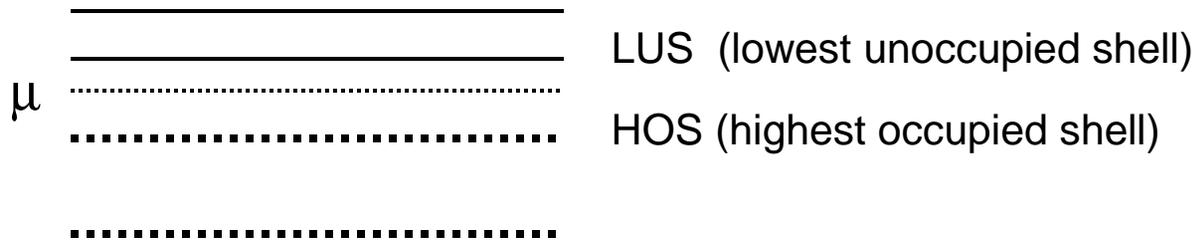
Matrix method:

$$\Delta_n = \sum_m K_{nm} \Delta_m$$

$$|1 - K_{nn}| = 0$$

C. Owen and D. Scalapino (1971)

V. Kresin (1987)



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

Examples:

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

$$g_{\text{HOS}} = 30; g_{\text{LUS}} = 18; \tilde{\Omega} = 25\text{meV}; \lambda_b = 0.5; E_F = 10^5\text{K}$$

(L = 7) (L = 4)

$$T_C = 150\text{K}$$

Ga₅₆ (N = 168)

$$T_C = 160\text{K}$$

$$(T_c^b = 1.1\text{K})$$

Zn₁₉₀ (N=380)

$$T_C = 105\text{K}$$

$$(T_c^b = 0.9\text{K})$$

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



$$T_c \approx 150\text{K}$$

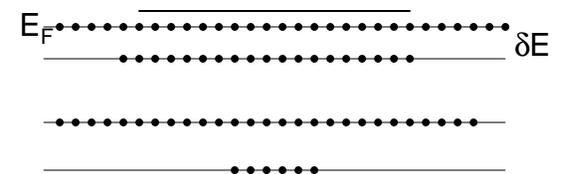
Change in the parameters ($\tilde{\Omega}$, ΔE , etc)



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



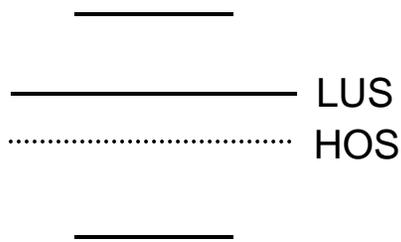
Superconducting state of nanoclusters :

_____ (manifestation, observables)

Energy spectrum

experimentally measured excitation spectrum

(e.g. HOS – LUS internal (ΔE)) is temperature dependent
 $(\Delta E_{IT \approx 0K} \gg \Delta E_{IT > T_c})$



- clusters at various temperatures

e.g., Cd_{83} ($N=166$)

1) $T \ll T_c$; 2) $T > T_c$

\downarrow
 $h\omega_{\min.} \approx 34 \text{ meV}$;

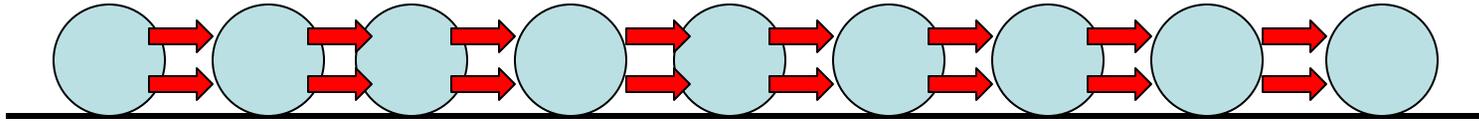
\downarrow
 $h\omega_{\min.} \approx 6 \text{ meV}$

- photoemission spectroscopy

odd-even effect

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

Bulk superconductivity ($R=0$)



Tunneling--> Josephson tunneling
(tunneling of the pairs)

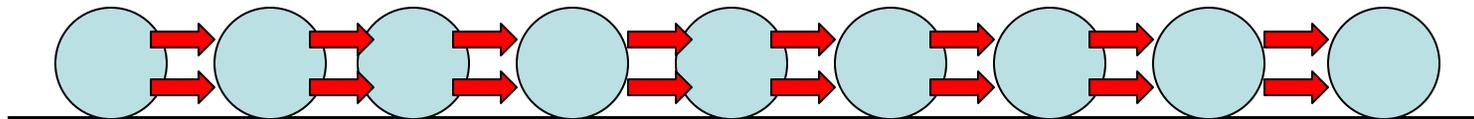


dissipationless macroscopic current ($R=0$)

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

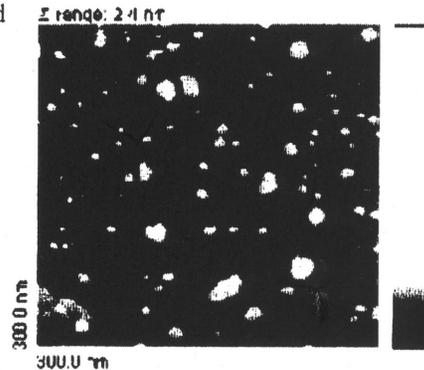
Individual (bi-)metallic clusters deposited on flat surfaces

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 couple 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 isolated nanoclusters :

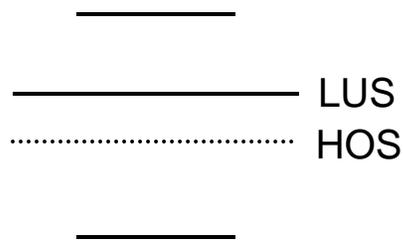
Proposed Experiments

Energy spectrum

experimentally measured excitation spectrum

(e.g. HOS – LUS internal (ΔE)) is temperature

dependent $(\Delta E_{IT \approx OK} \gg \Delta E_{IT > T_c})$



- clusters at various temperatures

1) $T \ll T_c$; 2) $T > T_c$

$h\omega_{\min.}(T \ll T_c) \gg h\omega_{\min.}(T > T_c)$

- photoemission spectroscopy

odd-even effect

the spectrum strongly depends on the number of electrons being

odd or even

Superconducting state of an isolated cluster

Experiments:

- Selection (mass spectroscopy; e.g., Ga₅₆)
- Cluster beams at different temperatures
($T > T_c$ and $T < T_c$)
- Spectroscopy (photoemission)
- Magnetic properties

Experiments:

- Selection (mass spectroscopy; e.g.,
 Ga_{56})
 - Cluster beams at different temperatures
($T > T_c$ and $T < T_c$)
 - Spectroscopy (photoemission)
 - Magnetic properties
- UVA** : 1), 2), 3), 4) (!)

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

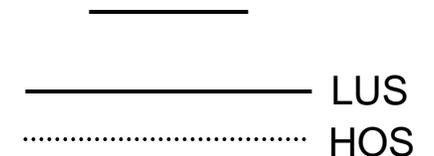
e.g., Ga₅₆ (N=168) : T_c ≈ 150K

Main factors:

- large degeneracy of the highest occupied shell (HOS); small HOS- LUS space

incomplete shell

small shape deformation



Manifestations of the pairing:

-temperature dependence of the spectrum:

$$\Delta E_{IT \approx 0K} \neq \Delta E_{IT > T_c}$$

- odd-even effect

- clusters with superconducting pair correlation are promising blocks for tunneling network.

Europhys J. B45, 5 (2005) ; B47, 333 (2005)

Phys.Rev.B 74,024514 (2006)

Small nanoclusters form a new family of high T_c superconductors

- *Cuprates*
- *Organics*
- *Heavy fermions*

- **Ruthenates**
- **MgB₂**
- **Fullerides**
- **Borocarbides**
- **Chloronitrides (e.g., Li(THF)HfNCL)**
- **WO₃ + Na**
- **Na_{0.2}CoO₂ * 1.3H₂O**

Superconductivity of a Crystalline Ga₈₄-Cluster Compound

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We report on magnetization and resistivity measurements of a cluster compound in which negatively charged Ga₈₄ entities are strongly bonded to organic ligands and confined in an ionic crystal structure. The macroscopic single crystals have a resistivity in the range of 100 Ω cm at room temperature with a semiconducting-like temperature dependence. They reveal a superconducting transition at $T_c \approx 7.2$ K and an upper critical field of $B_{c2} = 13.8$ T. The presence of the superconducting state in the regularly arranged Ga₈₄ clusters implies an electronic coupling between the individual clusters.

1. INTRODUCTION

The study of systems between the well-established regions of atomic or molecular species and condensed matter becomes increasingly important from a technological point of view and is equally interesting from funda-

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

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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 $Q_0 = C_g V_g$ 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 coefficient³ 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

$$E = \frac{(Q_0 - ne)^2}{2C_x} \equiv E_c \left(\frac{Q_0}{e} - n \right)^2. \quad (1)$$

Here $Q_0 = -C_g V_g + Q_{00}$ 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_x is the total capacitance of the island to the bias leads and the gate electrode, and $E_c \equiv e^2/2C_x$ 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 Nazarov⁴ 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 $\Delta(T^*) \approx \Delta(0) \gg k_B T$ and the material is still

Fluctuations

$$T \sim T_c$$



Ginzburg - Landau functional



δT_c (broadening of the transition)

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

$$T_c \approx \tilde{\Omega} e^{-1/\lambda}$$

$\tilde{\Omega}$ is the characteristic vibrational frequency ($\sim \Omega_D$)

λ is the coupling constant ($\lambda \ll 1$)

The expression for T_c can not be obtained with use of the perturbation theory

$f = e^{-1/x}$  can not be expanded in a Taylor series for small x