Abstract for QNM Work Group Presentations
3 February 2009

Quasiperiodic Quasi-One-Dimensional Metallic Nano-Structures:
"Does the Da Vinci Code Hold the Key to Room Temperature Superconductivity?"

Paul M. Grant
Visiting Scholar, Stanford University

The year 1957 witnessed what might have been the most important theoretical advance in condensed matter physics of the past century. Bardeen, Cooper and Schreiffer[1] were able to show, based on an elegantly simple proof by Cooper, that the degenerate Fermi energy could be gapped by weak lattice vibration-mediated attractive electron-electron interactions, and that the transition temperature of superconductors could be semi-quantitatively given by the expression, $T_C = a\theta_D \exp(-1/\lambda)$. Here T_C is the critical temperature, θ_D the phonon Debye temperature, λ the dimensionless electron phonon coupling constant, and a a "gap scaling factor" of order 1-3. Strictly speaking, this simple "BCS relation" holds only for $\lambda < 1$, and $\lambda k\theta_D \ll E_F$, where E_F is the Fermi energy. However, Migdal and Eliashberg[2] later showed modifications of this relation that included higher order attraction terms as well as electron-electron repulsion could accommodate "strong coupling" values of λ in the range 1 – 2 and thus successfully account for the relatively high transition temperatures of the A15 compounds and perhaps the HTSC cuprates as well. The message of BCS is clear: a superfluid state is mediated by the pairing of fermions in a boson field, and its condensation temperature scales both with the characteristic temperature of the boson and the strength of its coupling to the fermions. It is possible that attempts to increase T_C by engineering a rise in the electron-phonon λ, given the known range of Debye temperatures available, may give rise to unphysical material constraints.[3] Even other possible "boson flavors," e.g., "magnons or "spin waves" or "resonating bonds," may not possess characteristic energies large enough to get T_C to room temperature with realistically achievable coupling constants.

On the other hand, various sorts of charge polarization bosons, such as excitons, have characteristic energies on the order of 1 eV and, in principle, could manifest in properly designed structures superconducting transition temperatures on the order of 300 K, even under extremely weak electron-exciton coupling. This opportunity did not go unnoticed and was suggested (before BCS!) by Fritz London[4] as perhaps possible in macro-organic molecules, and was subsequently analytically addressed post-BCS by Davis, Gutfreund and Little,[5] Ginzburg,[6] and Allender, Bray and Bardeen,[7] and was even the subject of a science fiction short story in 1998.[8]

In this talk, we will review the several model approaches taken in the past in light of their possible incorporation in modern density functional theory employing today's powerful and widely available computational hardware and software applied to novel structures, now accessible by "nano-assembly" and "nano-machining" technologies. We will address one of the "devils in the details" of all such models, the required spatial separation of electron transport from the polarization portions of any hypothetical material embodiment, which often contain quasi-one-dimensional metal chains subject to gapping of their Fermi through commensurate structural distortion. As the sub-title of this presentation, there may exist in the wisdom of the ancients some rituals to exorcise this devil!

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[1] J. Bardeen, L. N. Cooper and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).
[2] A. B. Migdal, Sov. Phys. JETP 5, 1174 (1958); G. M. Eliashberg, Sov. Phys. JETP 11, 1364 (1959).
[3] M. R. Beasley – This conference
[4] F. London, “Superfluids,” (John Wiley & Sons, London, 1950), pp. 8-9.
[5] D. Davis, H. Gutfreund and W. A Little, Phys. Rev. B13, 4766 (1976).
[6] V. L. Ginzburg, Sov. Phys. Usp. 13, 335 (1970).
[7] D. Allender, J. Bray and J. Bardeen, Phys. Rev. B7, 1020 (1973).
[8] P. M. Grant, Physics Today, May 1998.

Quasiperiodic Quasi-One-Dimensional Metallic Nano-Structures

Does the

DA VINCI CODE

Hold the Key to Room Temperature Superconductivity?

http://www.w2agz.com/rtsc07.htm

Paul M. Grant

Visiting Scholar, Stanford (2005-2008)

IBM Research Staff Member Emeritus

EPRI Science Fellow (Retired)

Principal, W2AGZ Technologies

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Talk delivered at Working Group Session

ICQNM Advanced Topics in QNM

Tuesday, 6:00 PM, 3 February 2009

NanoConcept

What novel atomic/molecular arrangement might give rise to higher temperature superconductivity >> 165 K?

New approach to materials design:

•Define desired goal, e.g., a superconductor with Tc > 200 K.

•What structural arrangement and combination of elements is likely to achieve this goal?

•Could involve study and construction of existing ideas, e.g., models of exciton-mediated superconductivity.

NanoBlueprint

- Model its expected physical properties using Density Functional Theory.

$$E_{\mathrm{LDA+U}}\left[n(\mathbf{r})\right] = E_{\mathrm{LDA}}\left[n(\mathbf{r})\right] + E_{\mathrm{HUB}}\left[\left\{n_m^{l\sigma}\right\}\right] - E_{\mathrm{DC}}\left[\left\{n^{l\sigma}\right\}\right]$$

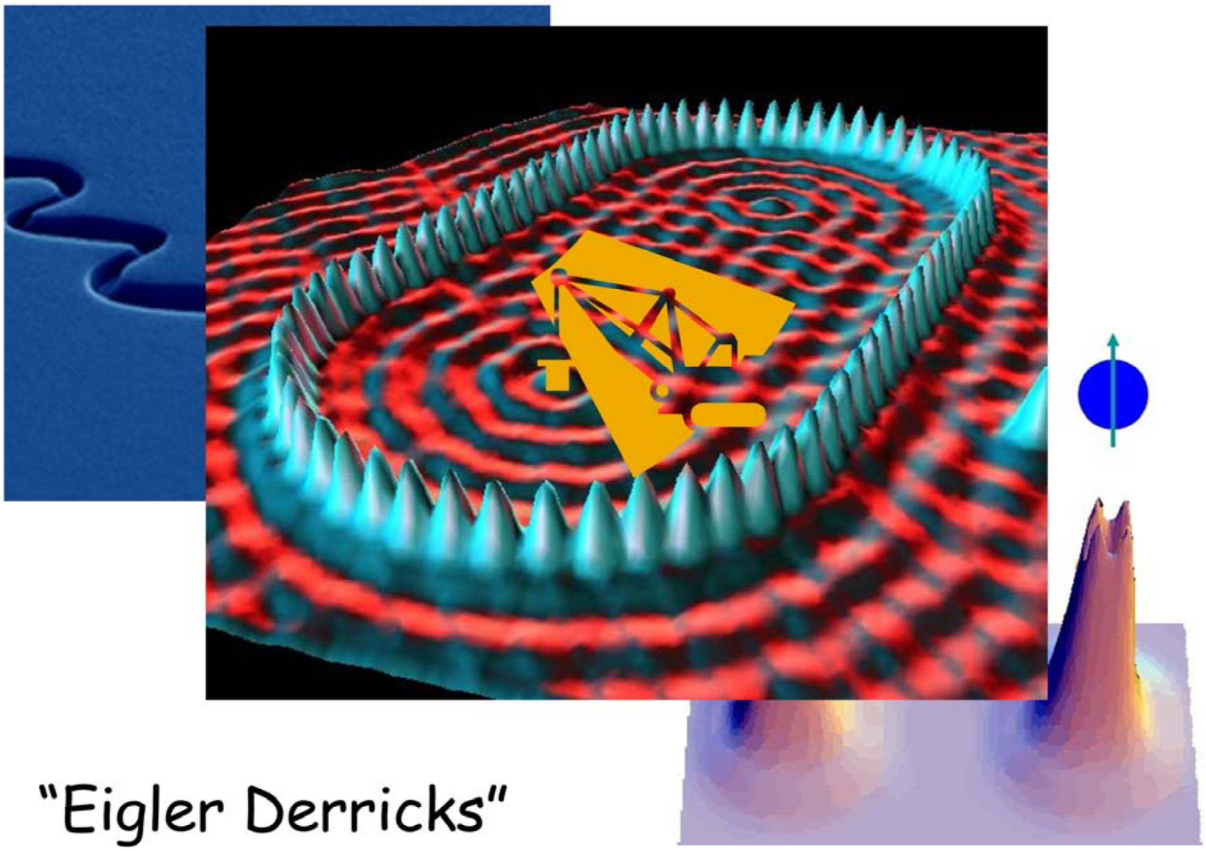
  - DFT is a widely used tool in the pharmaceutical, semiconductor, metallurgical and chemical industries.
  - Gives very reliable results for ground state properties for a wide variety of materials, including strongly correlated, and the low lying quasiparticle spectrum for many as well.
- This approach opens a new method for the prediction and discovery of novel materials through numerical analysis of “proxy structures.”

<u>Use Density Functional Theory to test efficacy of promising “proxy structures:”</u>

•E.g., ways to stabilize the metallic state against charge density wave instabilities (Peierls-Froehlich) in low dimensional conductors.

•Induction of Cooper pairing with bosonic states available within the structure, e.g., phonons, excitons, spin waves, magnons, plasmons, etc.

NanoConstruct



"Eigler Derricks"

<u>Assemble substructure (Examples shown above):</u>

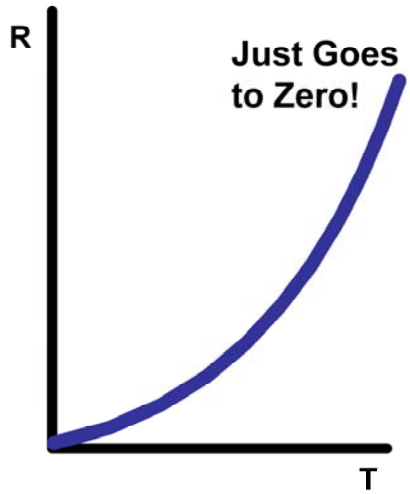
•"Scribing" or "trenching" graphene sheet, then backfilling with sulfur.

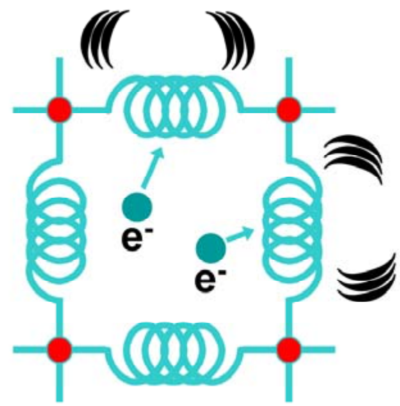
•Selectively locating directed spins via spin-polarized STM tips.

•Building extended periodic and possibly aperiodic structures ("Quantum Corral" shown above) on appropriate substrates using an STM ("Eigler Derricks").

Models of Electrical Conductivity 1900

One Idea:





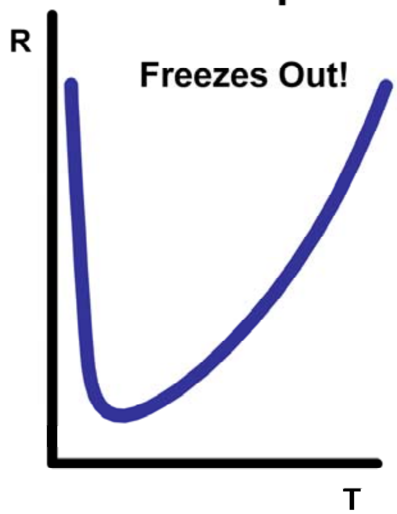
<u>Brief Tutorial on Superconductivity I:</u>

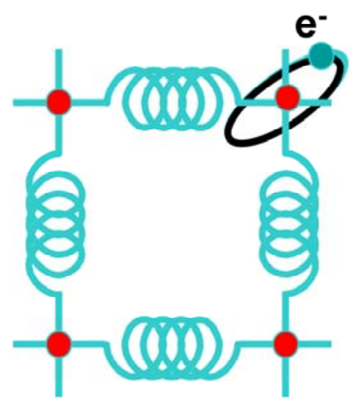
•Prior to 1900, electrical conductivity thought to be dominated at all by scattering off lattice vibrations.

•Thus, as T -> 0, R -> 0 algebraically.

Models of Electrical Conductivity 1910

The Most Popular:





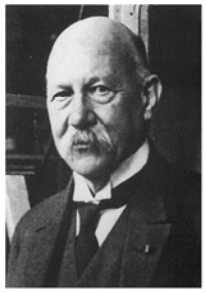
Brief Tutorial on Superconductivity II:

•After 1900, Bohr picture of atom theory revealed localized orbital nature of electron states.

•Thus, as T -> 0, R -> infinity due to “freeze out” of conducting electrons on lattice atoms.

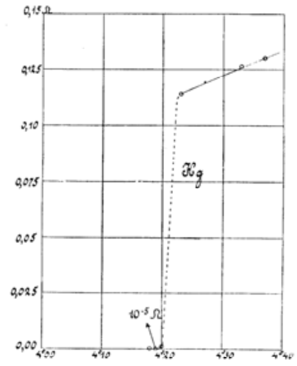
•However, lack of a suitable cryogen and a pure material made measurements of R < 20 K (liquid hydrogen) made accurate measurements difficult.

1911: A Big Surprise!



Thus the mercury at 4.2 K has entered a new state, which, owing to its particular electrical properties, can be called the state of *superconductivity*

<u>H. Kamerlingh-Onnes (1911)</u>



<u>Brief Tutorial on Superconductivity III:</u>

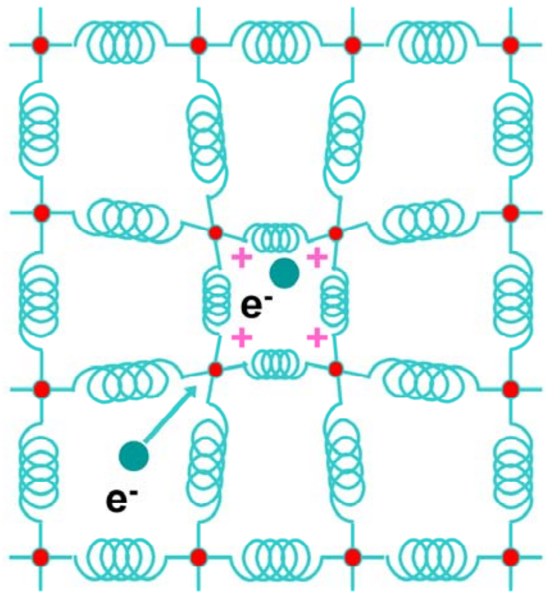
•The successful liquifaction of He (4 K) and the purification of Hg by distillation led to the astounding discovery that its resistance completely disappeared below 4.2 K in Kammerlingh Onnes' laboratory in Eindhoven in 1911.

•It was recognized that this new state was not merely low resistance, but "perfect resistance," a state which Onnes defined as "superconductivity."

•Throughout the following decades it was found by Meissner and Oschenfelder that a magnetic field contained within a superconductor was completely expelled on entering the superconducting state.

•Moreover, the discovery that the onset of a second order phase transition when entering the superconducting state, suggested a discrete energy difference, or gap, existed between the superconducting and metallic states.

Physics of Superconductivity (Carriers Pair Off)



Brief Tutorial on Superconductivity IV:

•These mysterious properties of superconductivity were not qualitatively understood until the 1940s and 1950s.

•The discovery that the transition temperature of a given superconductor depended upon the mass of its constituent atoms (the “isotope effect”) strongly suggest lattice vibrations were fundamentally involved.

•Careful measurements of the electrical charge transported inferred from the magnetic field a closed loop of superconductor produced that it flowed in units of 2e, or a bound pair of electronic charges.

“Bardeen-Cooper-Schrieffer”

$$T_C = a\Theta e^{-\frac{1}{\lambda-\mu^*}}$$

$$\lambda k\Theta << E_F$$

Where

Θ = Debye Temperature (~ 275 K)

λ = Electron-Phonon Coupling (~ 0.28)

μ^* = Electron-Electron Repulsion (~ 0.1)

a = “Gap Parameter, ~ 1-3”

Tc = Critical Temperature (9.5 K “Nb”)

Brief Tutorial on Superconductivity V:

•These observations were brought together in the 1950s by Walter Bardeen, Leon Cooper and J. Robert Schrieffer summarized in the above equation, the “BCS equation.”

•The numbers shown are those of Nb, whose Tc = 9.5 K. The effect of lattice coupling is represented by the Debye temperature and the electron-phonon coupling constant, the two numbers the most important in determining the overall superconducting properties of a given material.

•This equation applies in the weak coupling limit subject to the inequality shown, the so-called “Migdal Criterion,” requiring the reduced Debye temperature to be much less than the Fermi energy.

•Note the BCS equation is, in principle, quite general, describing the pairing of two fermions mediated by a boson field. An example is Color Superconducting exhibited in neutron stars, the fermion field being quarks and the bosons gluons, and the resulting Tc around 10^9 K (or C).

Electron-Phonon Coupling
a la Migdal-Eliashberg-McMillan

(plus Allen & Dynes)

$$H_{el-ph} = \sum_{\mathbf{k}\mathbf{q}\nu} g^{\mathbf{q}\nu,mn}_{\mathbf{k}+\mathbf{q},\mathbf{k}}\, c^{\dagger m}_{\mathbf{k}+\mathbf{q}} c^{n}_{\mathbf{k}}\, (b^{\dagger}_{-\mathbf{q}\nu} + b_{\mathbf{q}\nu}) \qquad (1)$$

First compute this via DFT…

$$\alpha^2 F(\omega) = \frac{1}{N(\varepsilon_F)} \sum_{mn} \sum_{\mathbf{q}\nu} \delta(\omega - \omega_{\mathbf{q}\nu}) \sum_{\mathbf{k}} |g^{\mathbf{q}\nu,mn}_{\mathbf{k}+\mathbf{q},\mathbf{k}}|^2 \times \delta(\varepsilon_{\mathbf{k}+\mathbf{q},m} - \varepsilon_F)\delta(\varepsilon_{\mathbf{k},n} - \varepsilon_F), \qquad (2)$$

$$\lambda = 2 \int \frac{\alpha^2 F(\omega)}{\omega} d\omega = \sum_{\mathbf{q}\nu} \lambda_{\mathbf{q}\nu}, \qquad (3)$$

$$\lambda_{\mathbf{q}\nu} = \frac{2}{N(\varepsilon_F)\omega_{\mathbf{q}\nu}} \sum_{mn} \sum_{\mathbf{k}} |g^{\mathbf{q}\nu,mn}_{\mathbf{k}+\mathbf{q},\mathbf{k}}|^2 \times \delta(\varepsilon_{\mathbf{k}+\mathbf{q},m} - \varepsilon_F)\delta(\varepsilon_{\mathbf{k},n} - \varepsilon_F). \qquad (4)$$

Then this…

Quantum-Espresso (Democritos-ISSA-CNR)

http://www.pwscf.org Grazie!

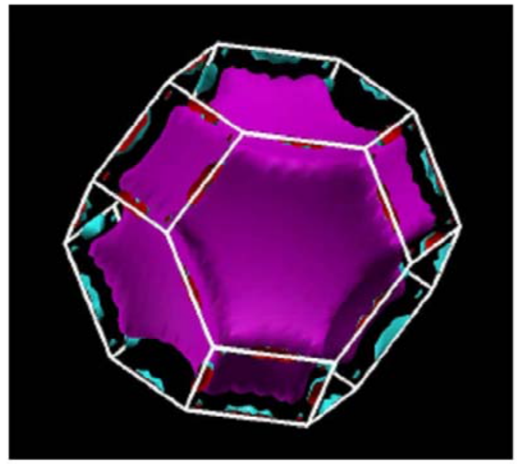
<u>Brief Tutorial on Superconductivity VI:</u>

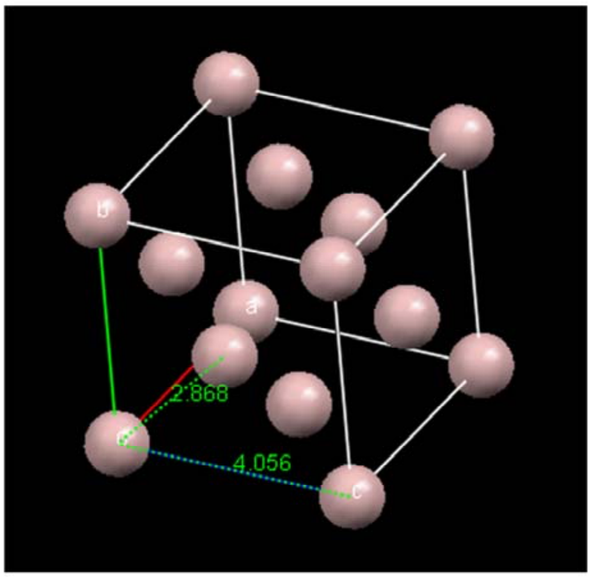
•Quantum mechanical description of electron-phonon interaction constant.

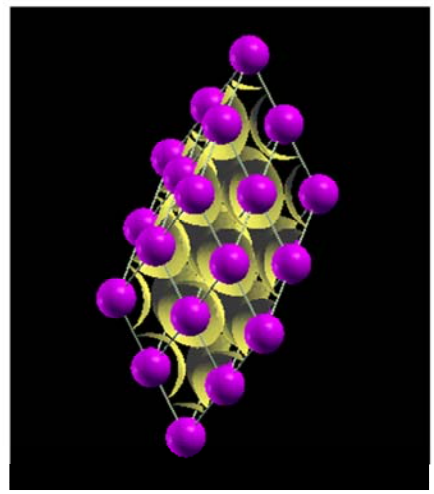
•Computable via DFT techniques.

•Can predict superconducting properties of simple systems, e.g., Al.

“3-D”Aluminum
T_C = 1.15 K

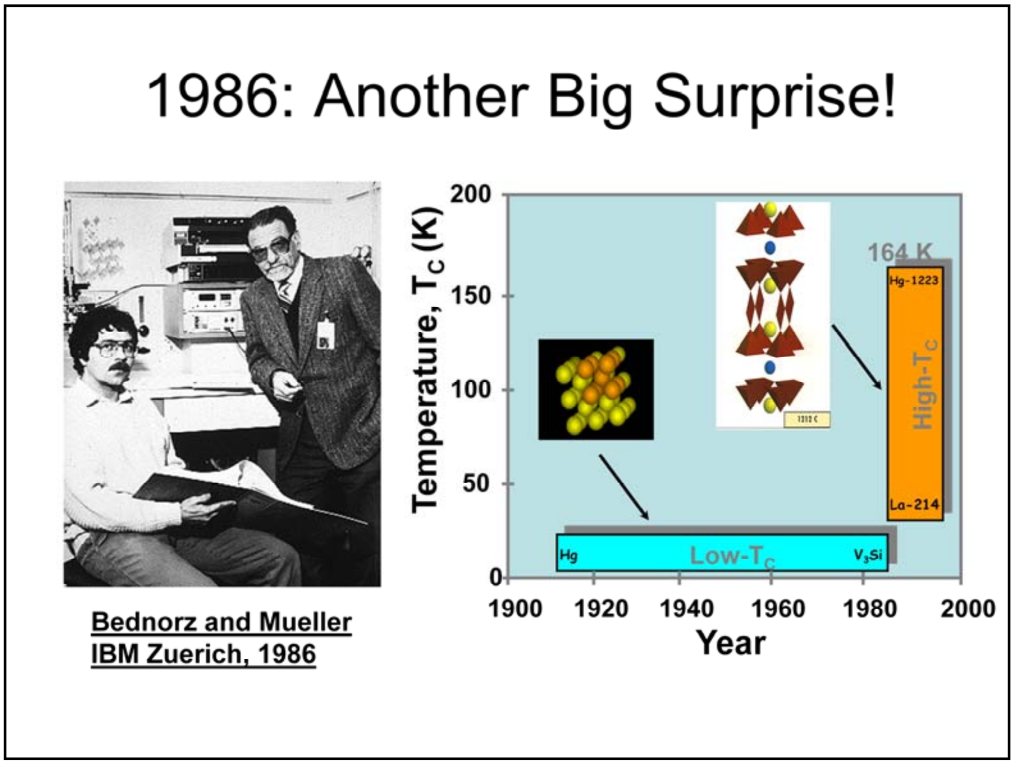






<u>Typical Structure of a Low Temperature Superconductor</u>

- •High symmetry, cubic
- •However, has Fermi surface topology with large “quasi-flat” regions which promote “nesting” and enhance e-p coupling.
- •Too much coupling will gap the Fermi surface and yield an insulator instead.



Discovery of High Temperature Superconductivity - 1986

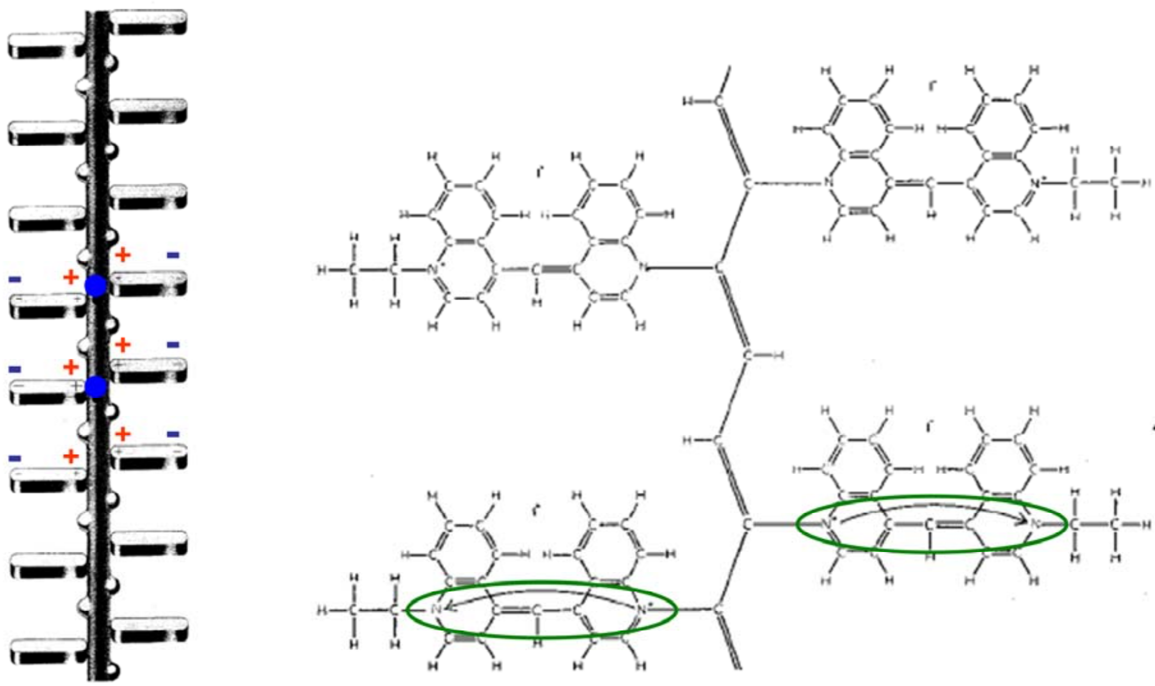
•Doped layered copper oxide perovskites were discovered at IBM Zurich to be superconducting at 40 K, increasing rapidly to 164 K by 1993.

•All HTSC compounds are highly anisotropic.

•Superconductivity is of the BCS type, but the nature of the mediating pairing boson is still unclear (2009), but evidence is that it is likely to be a magnetically enhanced phonon interaction…or maybe not!

•Practical applications exist in power technology…cables, transformers, FCLs…but presently very expensive.

Little, 1963



Diethyl-cyanine iodide

<u>Room Temperature Superconductivity</u>

•As pointed previously, the BCS formalism allows in principle all types of bosons to pair electrons into a superconducting state.

•In 1963, William “Bill” Little of Stanford University, suggested that a conducting polymer surrounded by stacks of high polarizable molecules might allow pairing electrons on the polymer chain mediated by excitons thereon to sustain very high superconductivity, perhaps at room temperature.

•However, two problems arise:

- The low dimensionality of the conducting polymer chain will likely lead to dimerization and destruction of the metallic state.
- Leakage of electronic charge density from the chains onto the polarizable molecule stack may screen the creation of excitons.

•Little conjecture is quantified on the next slide.

"Bill Little's BCS"

$$T_C = a\Theta e^{-\frac{1}{\lambda - \mu^*}}$$

Where $\cancel{\lambda k\Theta << E_F}$

Θ = Exciton Characteristic Temperature (~ 22,000 K)

λ = Fermion-Boson Coupling Constant (~ 0.2)

μ^* = Fermion-Fermion Repulsion (?)

a = "Gap Parameter, ~ 1-3"

Tc = Critical Temperature, ~ 300 K

<u>BCS "a la Little"</u>

•Note the coupling constant is weak…on the order for electron-phonons.

•The scaling is driven by the high characteristic energy of the exciton (22,000 K) compared to phonons (200-300 K).

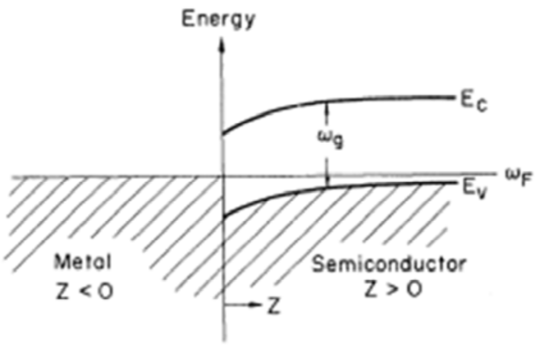
•However, the Migdal Theorem is violated. This is discussed shortly.

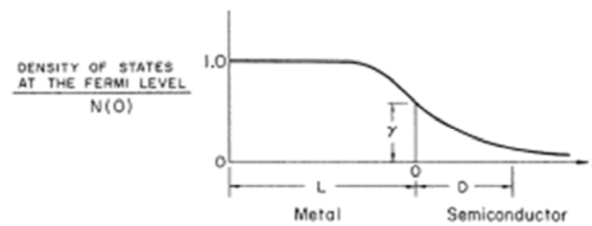
Allender-Bray-Bardeen (1973)

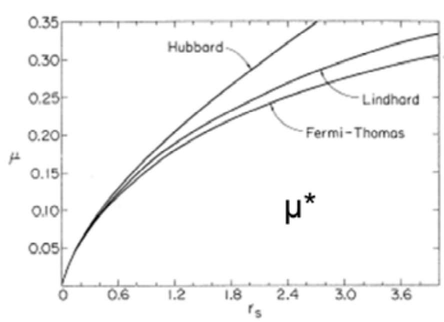
PHYSICAL REVIEW B VOLUME 7, NUMBER 3 1 FEBRUARY 1973

Model for an Exciton Mechanism of Superconductivity*

David Allender,† James Bray, and John Bardeen
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801
(Received 7 August 1972)







<u>Allender-Bray-Bardeen (1973)</u>

•ABB proposed a Little-configuration suggested high-Tc might be achieved by depositing a film of Nb (Tc = 9 K) on a polarizable semiconductor like Ge.

•So far, despite a number false alarms, such an effect has not been observed to date.

•Note the value of μ*, the higher the more deleterious to the occurrence of superconductivity, depends on how effectively the mutual coulomb repulsion of the electrons is screened, the optimum being Thomas-Fermi in the case for an interacting free electron gas.

Davis – Gutfreund – Little (1975)

PHYSICAL REVIEW B VOLUME 13, NUMBER 11 1 JUNE 1976

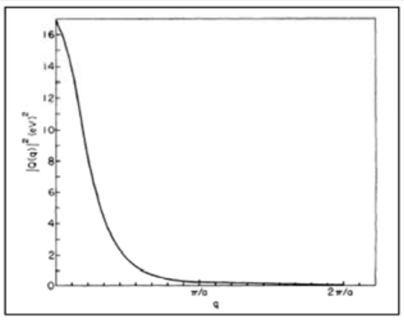
Proposed model of a high-temperature excitonic superconductor*

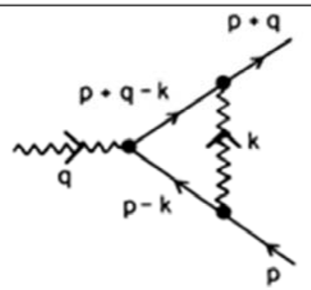
D. Davis,† H. Gutfreund,‡ and W. A. Little
Physics Department, Stanford University, Stanford, California 94305
(Received 16 October 1975)

$$g_{\mathbf{k+q,k}}^{\mathbf{q}\nu,mn} \longrightarrow$$

$$\phi^*(r_1 - R_j)\,\phi(r_1 - R_h)e^{i[kR_h-(k-q)R_j]}V(r_1r_2)\sum_{m,l,\nu}\left[u_{\alpha l}^{\nu}(q) + i v_{\alpha l}^{\nu}(q)\right]e^{-iqR_l}\,\Psi_\nu^*(R_{ml})\Psi_{00}$$

$$Q_\alpha(q) = \frac{1}{N^{3/2}}\int\sum_{j,k}\phi^*(r_1 - R_j)\,\phi(r_1 - R_h)e^{i[kR_h-(k-q)R_j]}V(r_1r_2)\sum_{m,l,\nu}\left[u_{\alpha l}^{\nu}(q) + i v_{\alpha l}^{\nu}(q)\right]e^{-iqR_l}\,\Psi_\nu^*(R_{ml})\Psi_{00}\,d^3r_1 d^3\tau$$





Migdal Issues:

- Only small exciton q's, $v_q > v_f$, couple to the electrons.
- Thus vertex corrections are of order λ^2/θ and we're OK.
- DGL claim this is NOT the case for ABB.
- IMHO, this is an item amenable to numerical analysis.

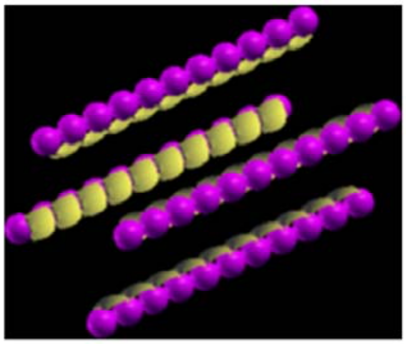
<u>Davis-Gutfreund-Little (1975)</u>

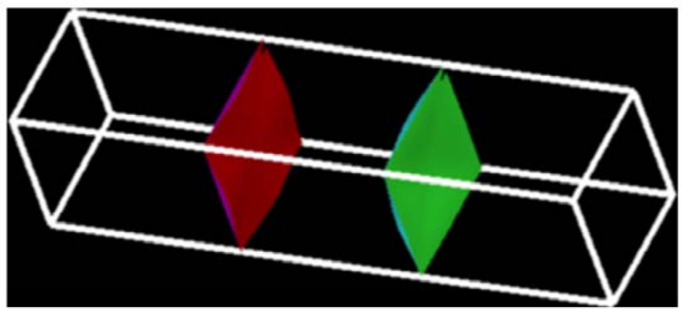
•DGL proposed a quantitative formalism of Little's Model quite similar to that of Migdal-Eliashberg-McMillan discussed earlier.

•This formalism in principle could be studied by DFT techniques, but to date, the code to do so has not been written.

•The problem of instability of the metallic state in one dimension, however, must be addressed first.

Al Chain Supercell:
c* = c,   a*, b* ~ 3 x c*





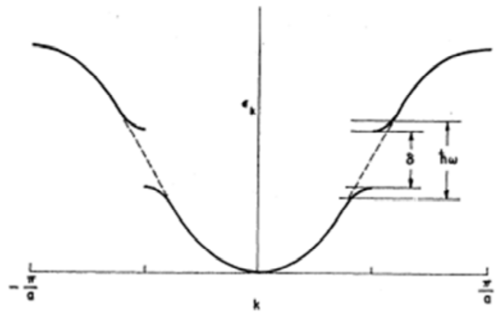
<u>Fermi Surface of Quasi-1D-Supercell</u>

•Simulation of metallic Al chain by stretching cubic cell along the c-axis.

•Note the appearance of near-planar Fermi surfaces subject to CDW nesting and FS gapping.

Al Chain Supercell:
$c^* = c$, $a^*, b^* = >10 \times a$

- Periodic Al chain unstable – dimerizes!
- Fermi surface is totally gapped!
- However…



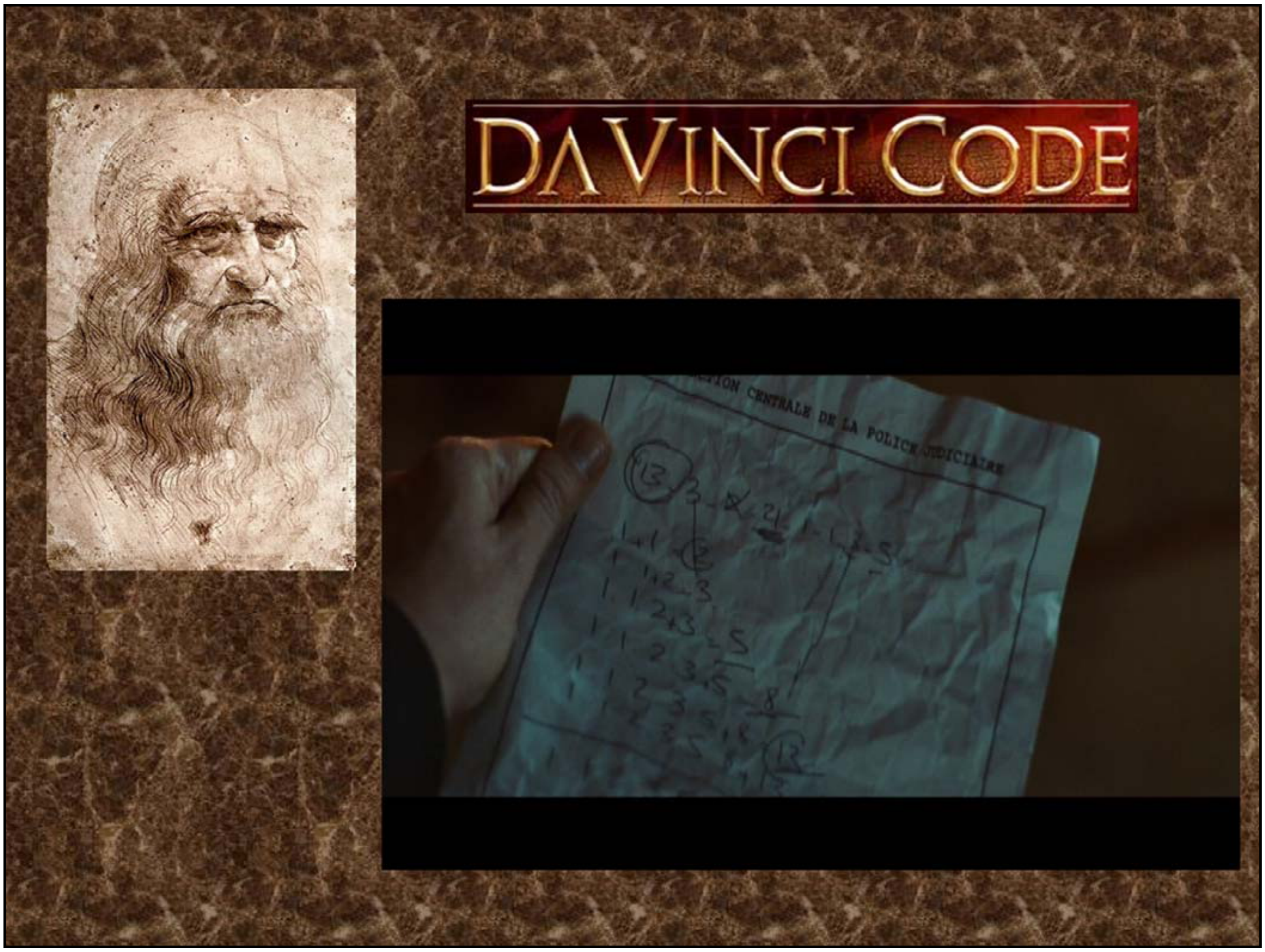
…could still give a BCS HTSC if $h\omega >> \delta$!

<u>Al Periodic Chain Dimerizes</u>

•Using DFT to relax the quasi-1D Al chain, we see it dimerizes into an insulator.

•However, could still result in an excitonic superconductor according to the conditions shown.

•New ideas are needed!



<u>Quasiperiodicity: The Secret Behind the DaVinci Code</u>

•In the film, The DaVinci Code, the number sequence written behind the Mona Lisa contain the first few digits of a Fibonacci series, a clue to the combination opening a Swiss back vault containing Knights Template documents authenticating the lineage of the descendants of Jesus of Nazarath.

•A Fibonacci sequence is an example of an “almost periodic” function whose properties we describe on the next slide.

“Not So Famous Danish Kid Brother“

Harald Bohr

Silver Medal, Danish Football Team, 1908 Olympic Games

Harald Bohr, Kid Brother of Niels

•Niels Bohr referred to his younger brother as the “truly brilliant one” in the family and maybe he was right.

•Harald Bohr extended the theory of analytic functions to include “Fourier series” whose trigonometric terms contained irrational arguments.

Almost Periodic Functions

"Electronic Structure of Disordered Solids and Almost Periodic Functions,"

P. M. Grant, **BAPS 18**, 333 (1973, San Diego)

Definition I: Set of all summable trigonometric series:

$$f(x) = \sum_n A_n e^{i\lambda_n x}$$

where $\{\lambda_n\}$ are denumerable.

Type (1) Purely Periodic: $\lambda_n = cn$, n = 0, ±1, ±2, ...

Type (2) Limit Periodic: $\lambda_n = cr_n$, $r_n \in$ {rationals}

Type (3) General Case: One or more λ_n irrational

===

Definition II: Existence of an infinite set of "translation numbers," $\{\tau_\varepsilon\}$, such that:

$$| f(x+\tau_\varepsilon) - f(x) | \le \varepsilon; \quad -\infty < x < \infty$$

where $\varepsilon \ge 0$.

===

Parseval's Theorem:

$$\sum_n | A_n |^2 = \lim_{L\to\infty} \frac{1}{2L} \int_{-L}^{L} | f(x) |^2 \, dx$$

Mean Value Theorem:

$$\int_{-\infty}^{\infty} f(x) e^{i\lambda x} dx = A_n \delta(\lambda - \lambda_n)$$

$$\text{Example} : f(x) = \cos x + \cos\sqrt{2}x$$

Almost Periodic Functions

•Defined as a subset of the total class of denumerable (countable, or "discrete") trigonometric series…note this definition excludes "continuous" or integrable trigonometic functions such as those defined by Fourier transforms.

•An alternative definition is a function defined by a set of translation vectors with a given range.

•Both exclude a trigonometric series with "nesting periodicity" and thus APFs may be an appropriate basis to describe electronic order not susceptible to CDW instabilities.

APF “Band Structure”

“Electronic Structure of Disordered Solids and Almost Periodic Functions,”
P. M. Grant, **BAPS 18**, 333 (1973, San Diego)

<u>Band Structure Resulting From a Simple Almost Periodic Potential</u>

•We envision a “fundamental” periodic cosine of wave vector K= 1 and amplitude U_1 modulated by another periodic potential of wave vector ΔK = (√2)/8 (~2) and amplitude U_2, resulting in the almost periodic function shown.

•Note the quasi-momentum dependence of E(k) contains “gaplets” which diminish the tendency for a given “Fermi sheet” to nest and result in a gap.

•Because the number representation of a digital computer is by necessity rational, we can only approximate numerically an APF by a “limit periodic series.” However, if we approximate a given irrational by a long enough rational, we can observe that in the limit, the tendency to nest will fade.

Fibonacci Chains

"Monte-Carlo Simulation of Fermions on Quasiperiodic Chains,"
P. M. Grant, **BAPS March Meeting** (1992, Indianapolis)

$$G_n \equiv G_{n-1} \mid G_{n-2}, \quad n = 3, 4, 5, \ldots, \infty$$

Where $G_1 = a, \; G_2 = ab$

And $\lim\limits_{n \to \infty} N_a(G_n) / N_b(G_n) \equiv \tau = (1 + \sqrt{5}) / 2 \approx 1.618\ldots$

Example: $G_6 = abaababaab \; (N = 13)$

Let $a = c\tau b$, subject to $\langle a, b \rangle$ invariant,

And take a and b

to be "inter-atomic n-n distances,"

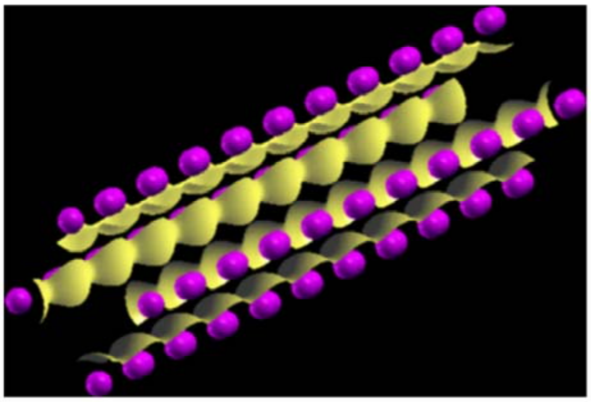
Then $b = \tau \langle a, b \rangle / \left[(1 + c)\tau - 1\right]$.

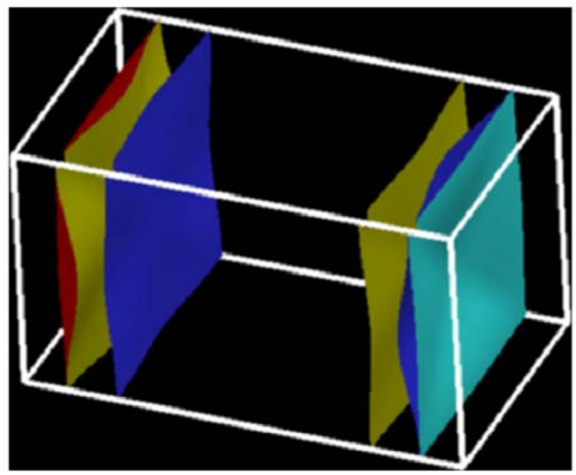
Where c is a "scaling" parameter.

Quasiperiodic Fibonacci Chains

- This slide presents the recursion algorithm used to generate a classic Fibonacci set. Note that the Fibonacci set is only strictly almost periodic in the limit of n $\rightarrow\infty$.
- In what follows we will impose almost periodicity on a linear chain of Al atoms by assuming a, b to be two different, but physically reasonable, interatomic nearest neighbor distances, subject to the invariance relation shown.
- We then use DFT to calculate the one-dimensional bandstructure and Fermi surfaces of such a chain.

Al Fibonacci Chain Supercell: $c^* = G_3(2.862|4.058)$, $a^*, b^* \sim 2 \times c^*$





<u>Al Fibonacci Chain of Length Generation 3</u>

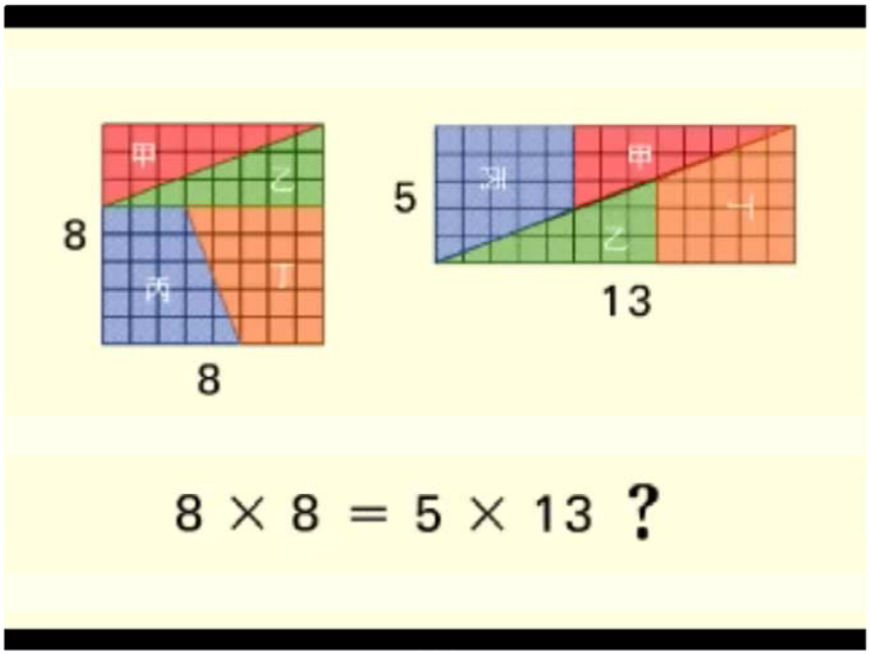
•Shown are the “unit cell” and Fermi surface features of such a chain as computed using DFT.

•a* and b* are chosen roughly 2 times c* to reduce the interchain coupling, but note there is still some as seen by the slight warping of the Fermi sheets.

•Note that because we have truncated the Fibonacci chain, so the 1D system is not strictly almost periodic , but rather limit periodic, so eventually nesting will occur, but will require a long range distortion, resulting in a small gap as shown in slide 22.

•The Fibonacci generating sequence 2.862|4.058 represents the diagonal Al-Al interatomic distance in angstroms followed by the cube edge value. Note this choice is not necessarily physically realistic.

64 = 65



<u>64 =65 ?</u>

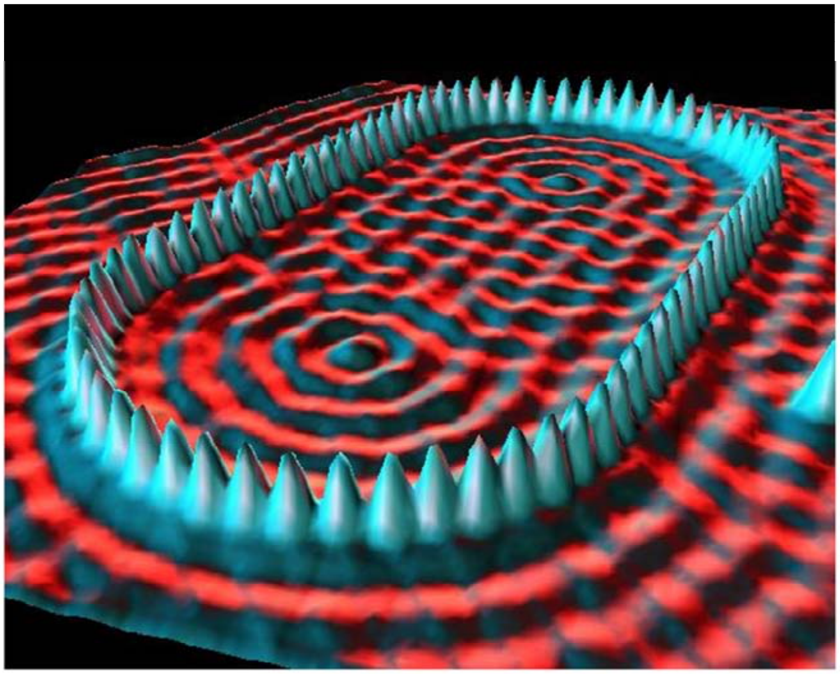
•This cartoon illustrates the "geometric puzzle" that almost periodicity can create. It appears paradoxical that an apparently trivial rearrangement of the four-colored, quadrahedral objects comprising the square on the left into the rectangle on the right, apparently violating the most fundamental axiom of arithmetic, that of superposition!

•The clue to the dilemma lies in the slight excess thickness of the diagonal of the rectangle with respect to the unit grid representing a small "incommensurate shift" of the four quadrahedra to make the edges align.

•Mathematicians call this a "Fibonacci Bamboozlement," in that the intersection of the rectangular diagonal generates a Fibonacci sequence.

•Suppose we have as a substrate the 100 face of some cubic crystal, say silicon, and then atomically scribe at some arbitrary angle, and then decorate that line with Al atoms resulting in a Fibonacci chain…

•How?



WITH EIGLER DERRICKS!

Fast Forward to 2028

•Several of the ideas put forward in this talk are derived from a Physics Today article written in honor of the 50th anniversary of its initial publication…go to http://www.w2agz.com/Documents/PTMay98_B&W.pdf

•I hope to live long enough to see the fulfillment of the dream…after all, it's only 20 years off!