HIGHER SUPERCONDUCTIVITY FROM THE LOWER ELEMENTS:

...and from external pressure to 'chemical pressure'

(N.W.Ashcroft, Cornell University)

ROOM TEMPERATURE SUPERCONDUCTIVITY
(LOEN, MIDSUMMER, 2007)

"Masters, spread yourselves"*

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o Room temperature superconductivity (... which room?); constraints?

o Pairing interactions in a valence electron system: a revisit via the Kohn-Luttinger framework

o Systems with favorable dynamic energy scales AND electronic structures

o Lithium as a test case

o Higher transition temperatures in the light elements in combination

o 'Chemical pre-compression' and the high-hydrides

o Prospects

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* A Midsummer Night's Dream, (I, ii, [16])

THE DREAM OF HIGH T_c, AS IN CHAPTER 1 OF:

High-Temperature Superconductivity

Edited by

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The original Russian text, published by *Nauka* in Moscow in 1977, has been expanded and revised by the authors for the present edition. This translation is published under an agreement with VAAP, the Copyright Agency of the USSR.

PROBLEMA VYSOKOTEMPERATURNOI SVERKHPROVODIMOSTI
V. L. Ginzburg and D. A. Kirzhnits
ПРОБЛЕМА ВЫСОКОТЕМПЕРАТУРНОЙ СВЕРХПРОВОДИМОСТИ

- 1964 – W. A. Little, extended organic molecules

- 1964 – V. L. Ginzburg, excitonic mechanisms

- - - - -

- Chapters 6 and 8; emphasis on likely importance of layered systems

CONSTRAINTS OR LIMITATIONS ON THE SCALE OF T_c?*

- Temporal progression of theory: from the Cooper problem, to BCS mean-field, to the Eliashberg equations

- Then to approximate solutions of the Eliashberg equations:

-- MacMillan, Phys. Rev. 167, 331 (1968)

-- Kirzhnits, Maksimov and Khomskii, J. Low Temp. Phys. 10, 79 (1973)

- Suggestions of a possible bound on T_c from these approximate solutions (around 24-25K)

- Allen and Dynes (Phys. Rev. B 12, 905, (1975)):

  Eliashberg theory actually places no bounds on the values of T_c, within reasonable physical limits (e.g. stability limits of the systems that might be proposed)

- Existence of approximate bounds firmly dispelled in 1986; discovery of the class of high temperature superconductors

- Physical problem: the choice of systems manifesting the necessary sources of polarization (from all physically plausible mechanisms) and associated energy and length scales as input into the Eliashberg equations

- The role of dimensionality in accentuating these

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*General reference:

P. B .Allen and M.Mitrovic, "Theory of the Superconducting T_c" Solid State Physics, 37,1 (1982)

Periodic Table of Superconductivity

(dedicated to the memory of Bernd Matthias)

30 elements superconduct at ambient pressure, 22 more superconduct at high pressure.

Key:
- ambient pressure superconductor: T_c(K), T_c^{max}(K), P(GPa)
- high pressure superconductor: T_c^{max}(K), P(GPa)

H																	He
Li 0.0004 14 30	Be 0.026											B 11 250	C	N	O 0.6 100	F	Ne
Na	Mg											Al 1.14	Si 8.2 15.2	P 13 30	S 17.3 190	Cl	Ar
K	Ca 25 161	Sc 8.1 74.2	Ti 0.39 3.35 56.0	V 5.38 16.5 120	Cr	Mn	Fe 2.1 21	Co	Ni	Cu	Zn 0.875	Ga 1.091 7 1.4	Ge 5.35 11.5	As 2.4 32	Se 8 150	Br 1.4 100	Kr
Rb	Sr 7 50	Y 19.5 115	Zr 0.546 11 30	Nb 9.50 9.9 10	Mo 0.92	Tc 7.77	Ru 0.51	Rh .00033	Pd	Ag	Cd 0.56	In 3.404	Sn 3.722 5.3 11.3	Sb 3.9 25	Te 7.5 35	I 1.2 25	Xe
Cs 1.3 12	Ba 5 18	insert La-Lu	Hf 0.12 8.6 62	Ta 4.483 4.5 43	W 0.012	Re 1.4	Os 0.655	Ir 0.14	Pt	Au	Hg-α 4.153	Tl 2.39	Pb 7.193	Bi 8.5 9.1	Po	At	Rn
Fr	Ra	insert Ac-Lr	Rf	Ha													

La-fcc 6.00 13 15	Ce 1.7 5	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu 2.5 22
Ac	Th 1.368	Pa 1.4	U 0.8(β) 2.4(α) 1.2	Np	Pu	Am 0.79 2.2 6	Cm	Bk	Cf	Es	Fm	Md	No	Lr

J.S. Schilling, High Pressure Effects, Ch. 11 in *Handbook of High Temperature Superconductivity: Theory and Experiment,* editor J.R. Schrieffer, associate editor J.S. Brooks (Springer, Hamburg, 2007)

RECENT LOW TEMPERATURE SUPERCONDUCTOR :

SUPERCONDUCTIVITY AT LOW TEMPERATURES

The lowest T_c metal?

- **Formerly RHODIUM, [Kr] $4d^8$ $5s^1$; transition metal, FCC, one atmosphere, T_c ~ 0.5 mK. But role of magnetic impurities is crucial; lowering of T_c, 0.01-0.03 mK/ppm**

- **Recently, LITHIUM, [He] $2s^1$; alkali metal, the FIRST in the Periodic Table, BCC one atmosphere, T > 77K. But δ - Sm (9R), T > 77K (Martensite)**

  Tuoriniemi, *et al.*; Nature 447, 187 (2007); $T_c \lesssim 0.4$ mK

  -- an instructive balance!

- **(e), ^1H, ^2H, ^3H, ^3He, ^4He, …then ^6Li, ^7Li … A fundamental system. Large 2s density AT the Nucleus; nuclear-electronic coupling (hence coupling of nuclear ordering and electronic ordering?)**

- **And next ^9Be, also high valence electron density at the nucleus. $T_c = 0.026$ K ($T_D > 1000$ K).**

LETTERS

Superconductivity in lithium below 0.4 millikelvin at ambient pressure

Juha Tuoriniemi[1], Kirsi Juntunen-Nurmilaukas[1]†, Johanna Uusvuori[1], Elias Pentti[1], Anssi Salmela[1] & Alexander Sebedash[1]

Elements in the alkali metal series are regarded as unlikely superconductors because of their monovalent character[1,2]. A superconducting transition temperature as high as 20 K, recently found in compressed lithium[3–6] (the lightest alkali element), probably arises from pressure-induced changes in the conduction-electron band structure[6–12]. Superconductivity at ambient pressure in lithium has hitherto remained unresolved, both theoretically and experimentally[11–16]. Here we demonstrate that lithium is a superconductor at ambient pressure with a transition temperature of 0.4 mK. As lithium has a particularly simple conduction electron system, it represents an important case for any attempts to classify superconductors and transition temperatures, especially to determine if any non-magnetic configuration can exclude superconductivity down to zero temperature. Furthermore, the combination of extremely weak superconductivity and relatively strong nuclear magnetism in lithium would clearly lead to mutual competition between these two ordering phenomena under suitably prepared conditions[17,18].

The Fermi gas of conduction electrons in any metal is forced to a state with high energy content, of the order of thousands of kelvins, owing to the Pauli exclusion principle. The degenerate state is susceptible to symmetry breaking phase transitions lowering the ground state energy if even weak interactions exist between the electrons. Therefore, most metals develop either a magnetic or a superconducting state at low temperatures, usually at around the kelvin range. The alkali metals sustain the degenerate state to an exceptional extent, which stems from the nearly ideal character of these monovalent metals. As mutual interactions, no matter how weak, still exist in the condensed matter host, there is a possibility of testing the fundamental question: can any real conduction electron system remain degenerate to zero temperature?

Until now, no alkali metal was known to become superconducting in its bulk form at ambient pressure, but lithium was expected to be the best candidate in this group for showing such a phase change at a sufficiently low temperature[13,14]. Earlier experiments down to 4–5 mK failed to provide any indication of a superconducting state in lithium[15,16]. We cooled down our samples in an external field of less than 20 nT to a temperature of 0.1 mK by means of a copper nuclear demagnetization refrigerator[19]. Susceptibility measurements showed superconducting transitions in several bulk lithium samples below 0.4 mK at ambient pressure. The set-up for the sample environment and the susceptibility measurement is illustrated in Fig. 1.

Two conditions are required—in addition to a sufficiently low temperature—to bring about a superconducting state with an extremely low superconducting transition temperature, T_c. First, the sample material must be sufficiently clean with respect to magnetic impurities, as they easily disturb the electron pairing necessary for superconductivity. The exact relation between the impurity concentration and the suppression of T_c depends on the host and on the impurity, but as a rule of thumb one may assume that T_c is lowered of the order of 0.01–0.03 mK per p.p.m. of impurity. Note that this effect is independent of the absolute magnitude of T_c. Thus, as little as 10 p.p.m. of iron, for example, could seriously shift the transition in relative terms for a metal with a low T_c to begin with. The manufacturer of the raw lithium we used (Alfa Aesar, Johnson Matthey GmbH) stated a maximum magnetic contamination of 4 p.p.m. for this particular batch. For more details on the purity, see ref. 18.

The second imperative is that of good shielding from any ambient magnetic field, as a low T_c is also bound up with a low critical magnetic field. Furthermore, owing to supercooling of the normal state, a

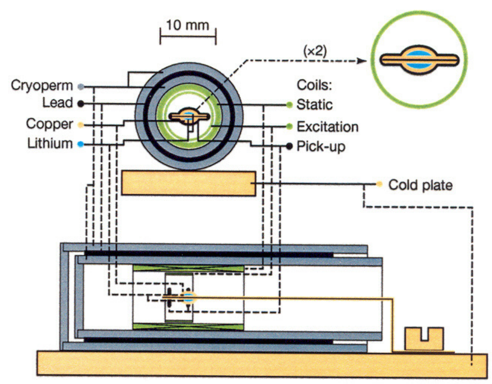


Figure 1 | Diagrams of a lithium sample pair, magnetic shields and the measuring coil system. The arrangement is shown looking along the axis (upper left) and as a section from the side (below). Pieces of lithium metal were encapsulated into pockets of thin copper foil, which also made the thermal link to the refrigerator cold plate. Handling of lithium was performed in an argon glove box, taking precautions to avoid any contamination of the sample material. A pick-up coil for a SQUID susceptometer was wound directly on a pair of two identical samples (see the magnified view at upper right), which were then placed into the cylindrical shields and solenoids. The magnetic shields consisted of two layers of high-permeability material (Cryoperm 10) with a superconducting lead cylinder in between to give nearly total immunity to external fields. The SQUID detection was made with very small excitation amplitude (some nanoteslas) at frequencies 3–17 Hz. A static field for the measurement could be created by another solenoid inside the shields. The assembly was cooled down with three different pairs of samples to about 0.1 mK, having a field less than 20 nT inside it.

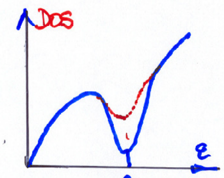
[1]Low Temperature Laboratory, Helsinki University of Technology, PO Box 2200 FI-02015 TKK, Finland. †Present address: Philips Medical Systems, Äyritie 4, FI-01510 Vantaa, Finland.

Improve T_C by alloying?

❖ BCS formula

$$T_c = 1.13\Theta_D \exp(-1/g_o V)$$

$$\exp(-1/g_o V) = \frac{T_c}{1.13\Theta_D} = 2.3 \times 10^{-5}$$



❖ **If $g_o V$ increases:** $g_o' V' = \alpha g_o V$

$$T_c' \simeq T_c \frac{(2.3 \times 10^{-5})^{\frac{1}{\alpha}}}{2.3 \times 10^{-5}}$$

[eg $\alpha = 3$
$T_c' \sim 70K$]

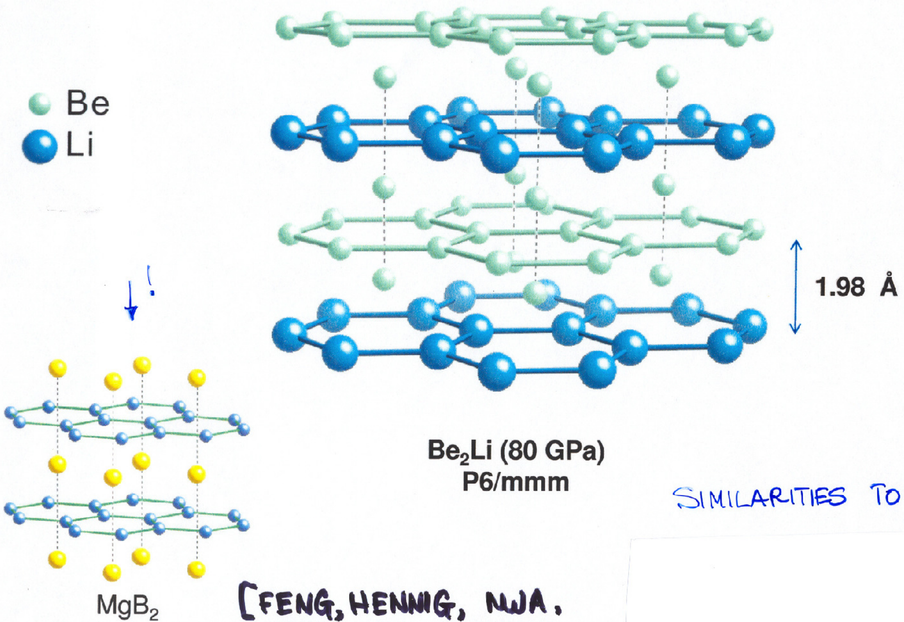
❖ Alloying with lithium?

- Light, metallic (electropositive)

FROM:
Ji FENG (CORNELL U)

[Be-Li structures:
Feng, Hennig, NWA, Hoffmann; submitted to Nature.]

The most competitive Be_2Li structure



Be_2Li (80 GPa)
P6/mmm

SIMILARITIES TO: MgB_2.

[FENG, HENNIG, NWA, HOFFMANN, NATURE 2007]

PROSPECTS

- Metallic systems with light elements; high dynamic scales for conventional phonon mechanism

- Groupings of other constituents in highly polarizable arrangements

  Benefit; presence of quantized waves of polarization, or even of quadrupole excitations

  Observation; the polarizabilty of O_2 groupings in the cuprate superconductors is around 30 cubic Bohrs.

  Examples of both: Metal ammines

  $Li(NH_3)_4$ is already a metal
  SiH_4, under compression
  (presence of hydrogen, important)

- Systems of light elements, but in complex multi-atom unit cells

  Benefit; proliferation of Umklapp (interband) processes

  Example: MgB_2, 8 atoms/cell

  'Bad conductors are often good superconductors'

  Hence....

- Systematic survey of the inter-metallics

  Especial physical guide: the appearance of layered systems (the important role of dimensionality)

- The use of chemical pre-compression for systems revealed by pressure to be possible candidates for high temperature superconductivity.

EINSTEIN'S 1922 VIEW OF SUPERCONDUCTIVITY

(FROM HIS SOLE PAPER ON THE SUBJECT)

. Though a quite frequent visitor to Leiden, Einstein wrote but a single paper on the theoretically challenging problem of superconductivity, and this for a volume commemorating the lengthy career of H. Kamerlingh Onnes

. An English translation of Einstein's paper apparently first appears in 2005*, and Einstein's concluding comment (on 'phantasizing' and theory) still has a certain ring of conviction about it, some 85 years later, in Mid-summer, 2007

. Thus … to conclude …

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* ArXiv: Physics/0510251 (October 27, 2005)
Translation; Dr Bjoern Schmekel (Cornell/ UCB)

EINSTEIN'S OBSERVATIONS ON THE PROBLEM OF SUPERCONDUCTIVITY (1922)

FROM: "Theoretische Bemerkungen zur Supraleitung der Metalle."

Gedenkenboek aangeb. aan H. Kamerlingh Onnes, enz. Leiden, E. IJdo, 1922, page 429.
[Translation: Bjoern Schmekel, Cornell University]*

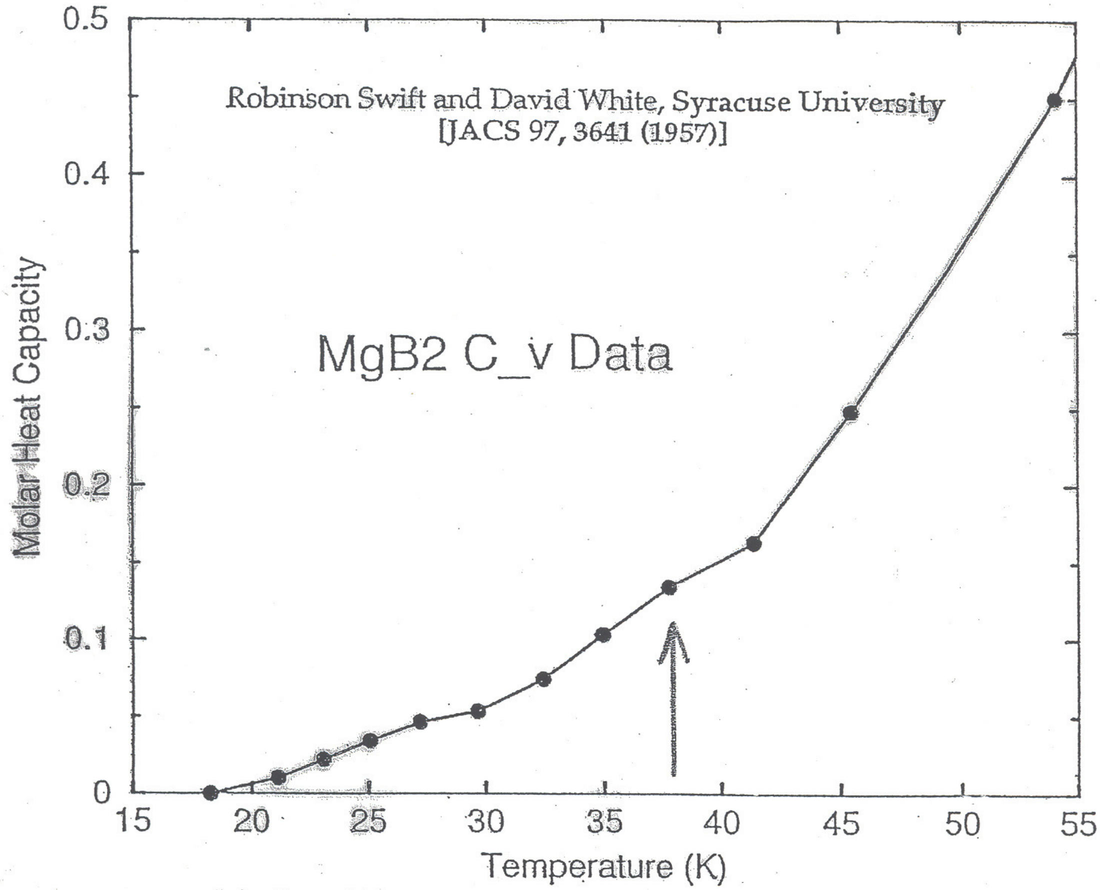
- "In this paper I want to focus on the fate of theories concerning metallic conductivity and on the revolutionary influence which the discovery of superconductivity must have on our ideas of metallic conductivity."
- "If one wanted to explain superconductivity by the presence of free electrons one would have to view them as agitation-free…"
- "It seems unavoidable that superconducting currents are carried by closed chains of molecules (conduction chains) whose electrons endure ongoing cyclic exchanges." (Ampere's molecular currents)
- "… conduction chains can only carry currents with a finite value…"
- "It is not too far stretched to assume that conduction chains can be destroyed by magnetic fields."
- "Phantasizing can only be excused by the momentary quandary of theory."

* ArXiv: Physics/0510251 (Oct 27, 2005)

RECENT (?) HIGH TEMPERATURE SUPERCONDUCTOR

BORON IN COMBINATION WITH MAGNESIUM: 1957

- Heat capacity data



- A curious conjunction: 1957 is also the year of the BCS theory
- If MgB_2 had been recognized at the time as a superconductor what likely impact on theory?
- WHAT ABOUT B?

PAIRING PHYSICS AND PHONONS: FROM BCS TO STRONG COUPLING TO INTRINSIC

- Isotope effect (Fröhlich → BCS): $T_c \sim M^{-1/2}$
  But . . .

  * Osmium (less compressible than diamond, energetic phonons): small

  * Ruthenium: none

  * Pd (H, D, T): **inverse isotope effect,** . . . . . etc.

- Eliashberg (1961): extension of pairing theory to strong coupling (large electron–phonon coupling)

- Approximate solutions to Eliashberg theory (e.g. McMillan)

$$k_B T_c = \langle \hbar\omega \rangle \exp\{-1.04(1+\lambda)/(\lambda - \mu^*(1+0.62\lambda))\}$$

associations	λ	$\rightarrow \hat{H}_{el-ph}$	electron – phonon coupling
	μ^*	$\rightarrow \hat{H}^c_{el}$	'Coulomb – pseudopotential'
	$\langle \hbar\omega \rangle$	$\rightarrow \hat{H}_{ph}$	mean phonon energy

- But, there is a clear hierarchy in energetics

$$\hat{H}^c_{el} > \hat{H}_{el-ph} > \hat{H}_{ph}$$

leading eventually to the Kohn–Luttinger question:

- **What are the electronic ground states of the static lattice problem**

$$\mathbf{\hat{H} = \hat{H}^c_{el}} \qquad \textbf{alone?}$$

EARLY (AND CONTROVERSIAL) REPORT OF HIGH TEMPERATURE: SUPERCONDUCTIVITY IN A LIGHT ELEMENT SYSTEM: [HYDROGEN RICH...]

[R.A. Ogg, Phys. Rev. **69**, 243 (1946)]

Bose-Einstein Condensation of Trapped Electron Pairs. Phase Separation and Superconductivity of Metal-Ammonia Solutions

RICHARD A. OGG, JR.
Department of Chemistry, Stanford University, California

March 2, 1946

" In all probability such solid solutions remain superconducting up to the melting point, i.e., to absolute temperatures of the order of 180 to 190 degrees.

The probable explanation of the above phenomena is to be found in the behavior of trapped electron pairs*, recently demonstrated[1] to be a stable constituent of fairly dilute metal-ammonia solutions."

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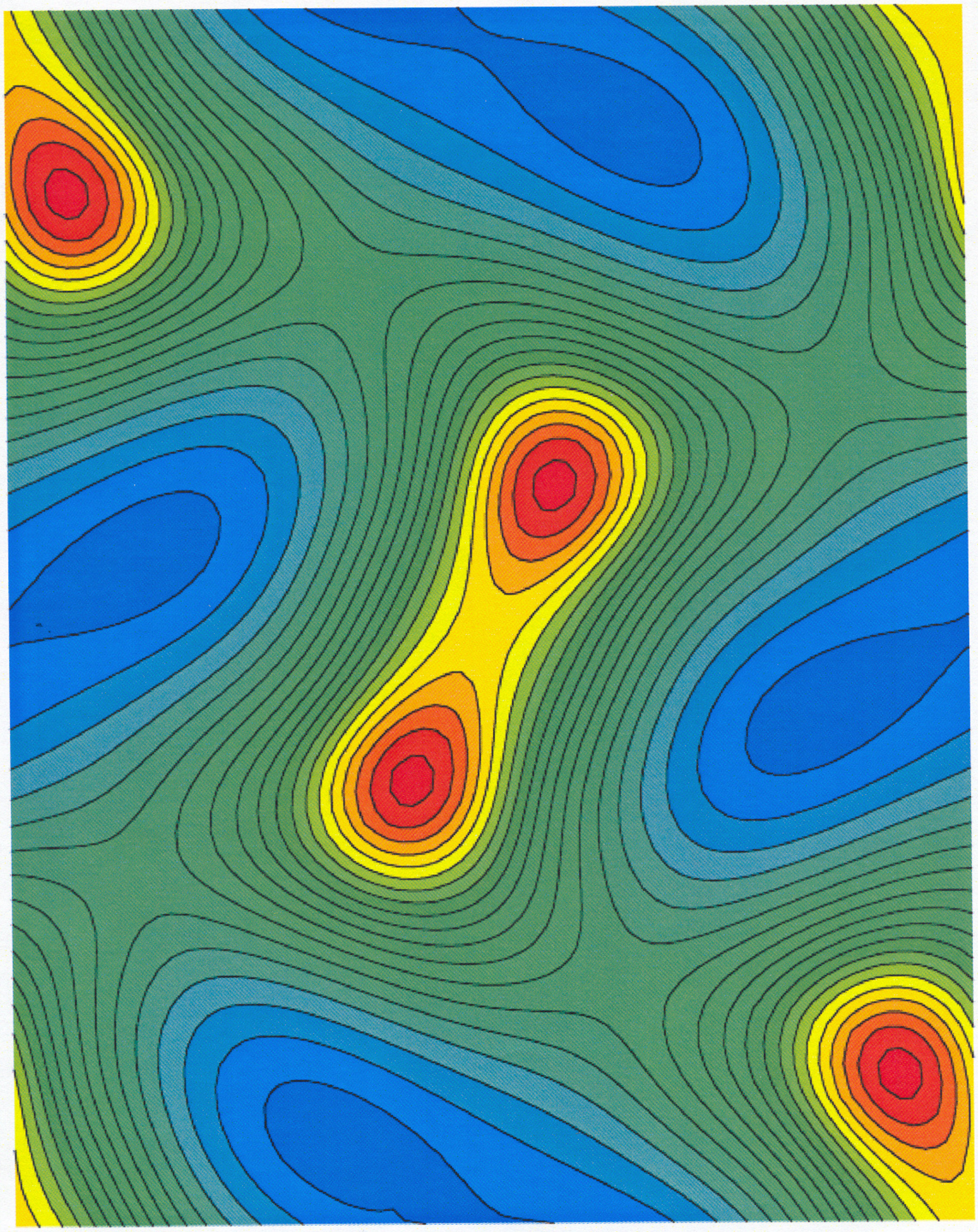
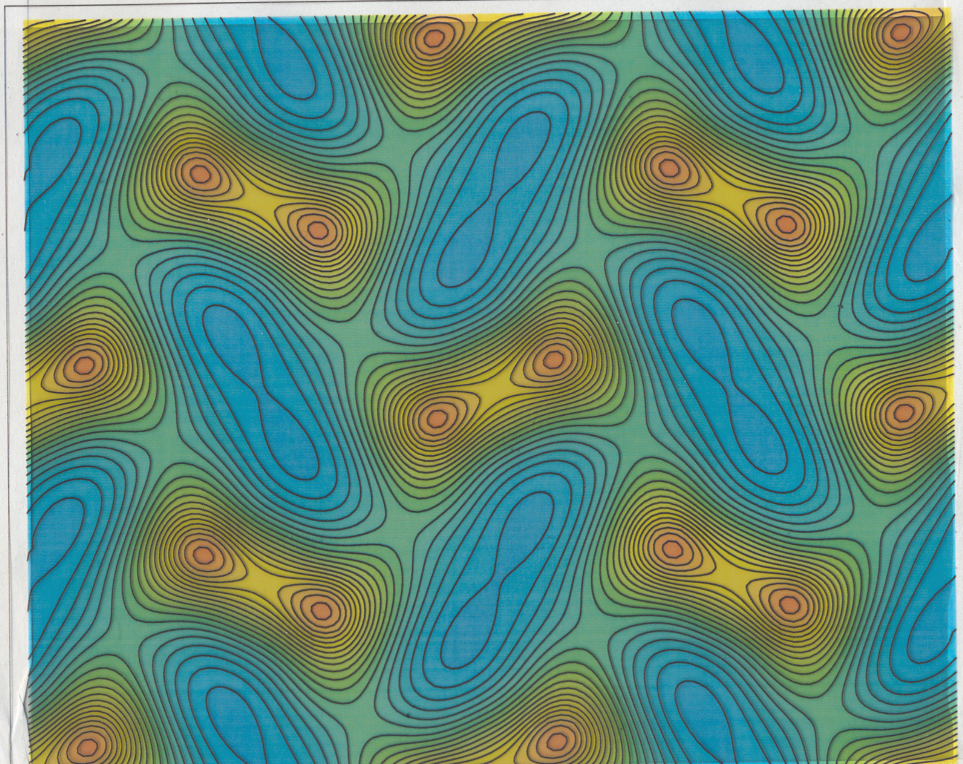
(1) R.A. Ogg, Jr., J. Chem. Phys. **13**, 533 (1945)

- See `The Ogg Saga' in P.P. Edwards, Journal of Superconductivity **13**, 933 (2000)
- In retrospect, these systems are characterized by high dynamic energy scales, (but probably low electronic densities of states)

* OGG'S DI-ELECTRON





• LITHIUM , Z=3

LETTERS

Superconductivity in lithium below 0.4 millikelvin at ambient pressure

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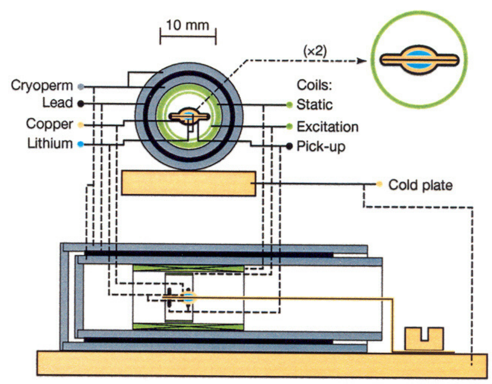

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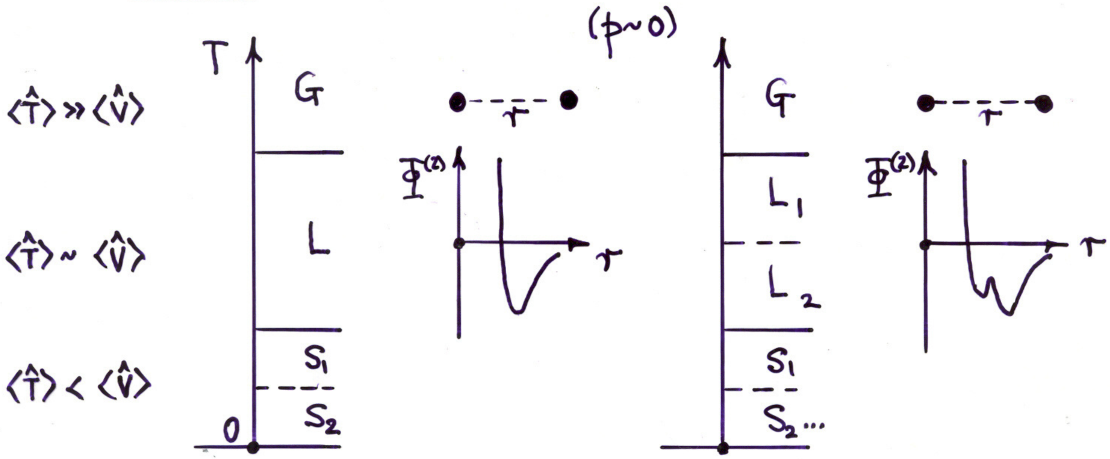
LIQUID-LIQUID INSTABILITIES

Many particle systems; common phases

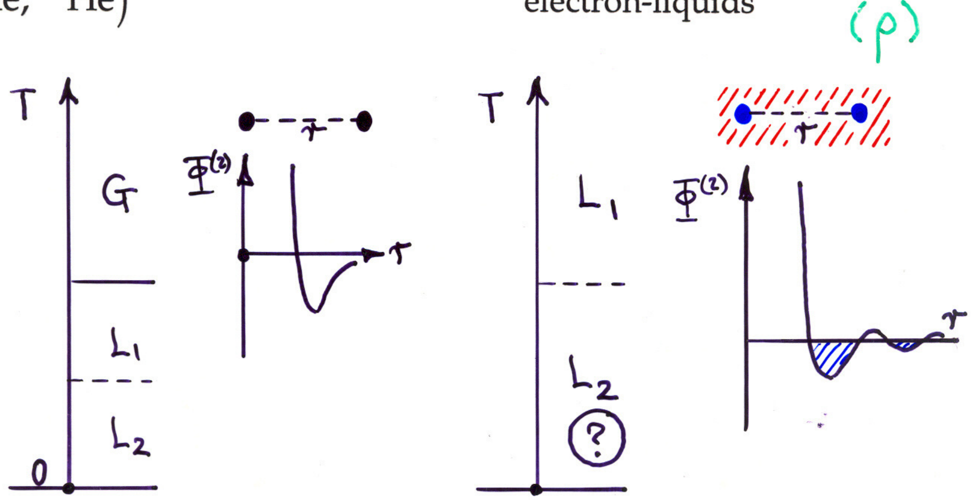
- **Classical**



- **Quantum**

The neutral permanent Liquids $(^3He,\ ^4He)$

Neutral **homogeneous** electron-liquids



L_2 : Superfluids

L_2 : Superconductor

PAIRING INSTABILITIES IN ELECTRON SYSTEMS: ROUTE TO T_c (ALLEN/MITROVIC, SSP, 1982)

(From the Cooper problem to BCS/Eliashberg/Nambu/Anderson approaches.)

- **Cooper** $k_B T_c \sim \langle \hbar\omega \rangle \exp\left(-1/N_o V\right)$, (attractive V)

- **BCS** $\Delta_k = \sum_{k'} \left(V_{k,k'} \Delta_{k'} / 2E_{k'}\right) \tanh\left(E_{k'}/2k_B T\right)$

$$k_B T_c \sim 1.13\, \hbar\omega_D \left(-1/N_o V\right)$$

$$\Delta = 3.52\, k_B T_c \qquad \text{(Gap function)}$$

- **Eliashberg...**

$$\Phi_\ell(k, i\omega_n) = -k_B T \sum_{\omega_{n'}} \int_o^\infty dk' K_\ell(k, i\omega_n; k', i\omega_{n'}) \Phi_\ell(k', i\omega_{n'})$$

K_ℓ contains the **effective electron-electron interaction**, all sources

- Sources: (i) electron-phonon coupling
  (ii) electron-electron interactions
  (valence + core)

EFFECTIVE ELECTRON-ELECTRON INTERACTIONS AND T_c

* Standard separation of energies for dynamic crystals

$$H = H_{ee} + H_{e\text{-}ph} + H_{ph}\,, \qquad \text{where}$$

H_{ee} (electronic problem) >> H_{ph} (phonon problem)

> $H_{e\text{-}ph}$ (el-phonon problem)

- Standard (historic) approximations treat $H_{e\text{-}ph}$ fairly accurately but H_{ee} rather poorly:

  Examples: BCS, hardly at all,

  MacMillan approximation

$$T_c = (T_D/1.45) \exp[-1.04(1 + \lambda)/(\lambda + \mu(1+0.62\lambda))],$$

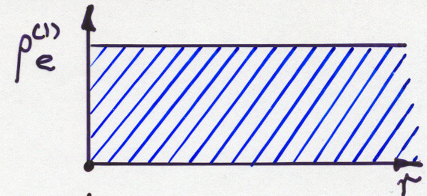
λ : manifestation of $H_{e\text{-}ph}$

μ: manifestation of H_{ee} (usually ignoring bands)

(and leads to a predicted maximum in T_c!)

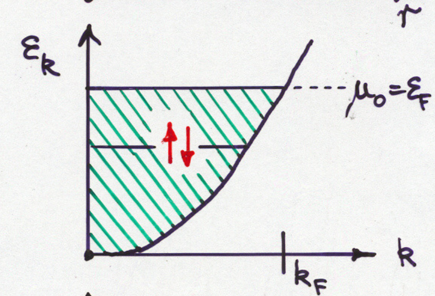
ELECTRONIC STRUCTURE AND PAIRING (I)

- THE KOHN-LUTTINGER PROPOSITION

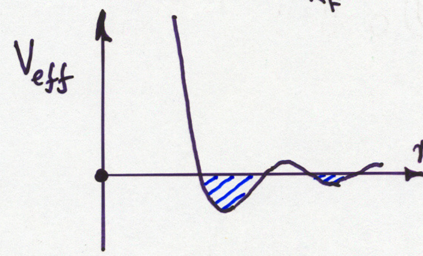


  - Homogeneous interacting electron gas (single band)

    $\hat{H} = \hat{H}_e$



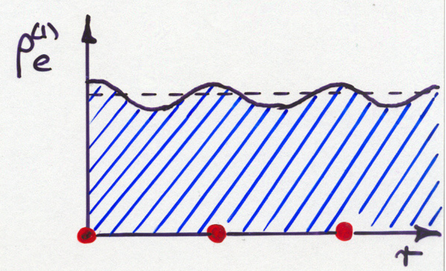
  - Attractive regions in dynamically screened effective electron-electron interaction: $\left(V_{eff}(r)\right)$



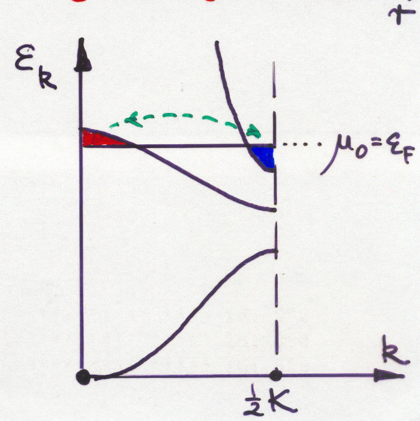
  - Ground state: paired *

- Extension to multiple-bands:

  $\hat{H} = \hat{H}_e^c$



  - Further attractive contributions to $\left(V_{eff}(r)\right)$
  - Ground state: paired



* RENORMALIZATION GROUP APPROACH
R. SHANKAR, RMP 66, 129 (1994)

TOWARDS ROOM TEMPERATURE SUPERCONDUCTIVITY: WORDS OF ENCOURAGEMENT

" ...room temperature superconductivity (regardless of a thousand statements by theorists and an equal number of theories) is in my opinion – pure science fiction.

...

I can think of no other field in modern physics in which so much has been predicted without producing a single experimental success."

B.T. Matthias, Physics Today **24,** (#8), 21 (1971)

"... Ginzburg [g], Schneider [s] and Ashcroft [a] have predicted superconductivity in metallic hydrogen at astronomic pressures, at astronomic temperatures, found only at astronomic distances"

B.T. Matthias, Comments on Solid State Physics, **3**, 93 (1970)

Observations:

- T_c seems to have been rising of late with the number of elements present in metallic compounds (the dark hand of complexity?)
- There are 90+ elements
- "... [Volte face?]... The field of ternary superconductors is still comparatively new and there is still some hope."
  B.T. Matthias, September 1980, in "Ternary Superconductors" (Ed, Fradin)
  - Acknowledging complexity in the electronic domain?

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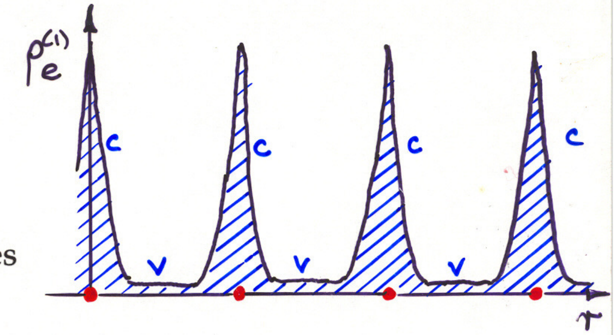
[g] V.L. Ginzburg, Contemp. Phys. **9**, 355 (1968)
[s] T. Schneider, Helv. Phys. Acta **42**, 957 (1969)
[a] N.W. Ashcroft, Phys. Rev. Letts. **21**, 1748 (1968)

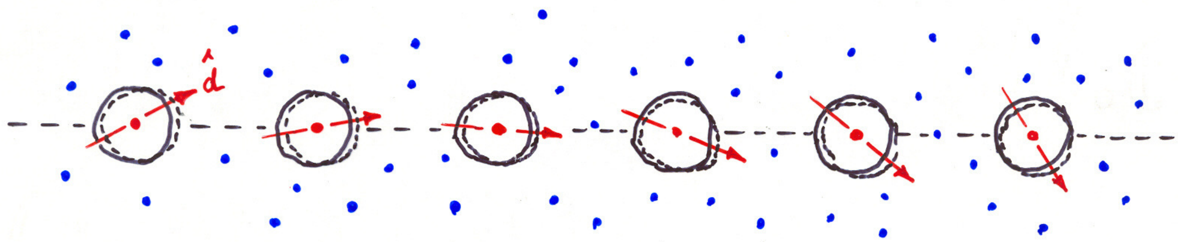
ELECTRONIC STRUCTURE AND PAIRING (II)

- Extension to rigid, but electronically polarizable, **ions**, and valence electrons



  - Collective (coupled dipolar) excitations; polarization waves (*pw*)

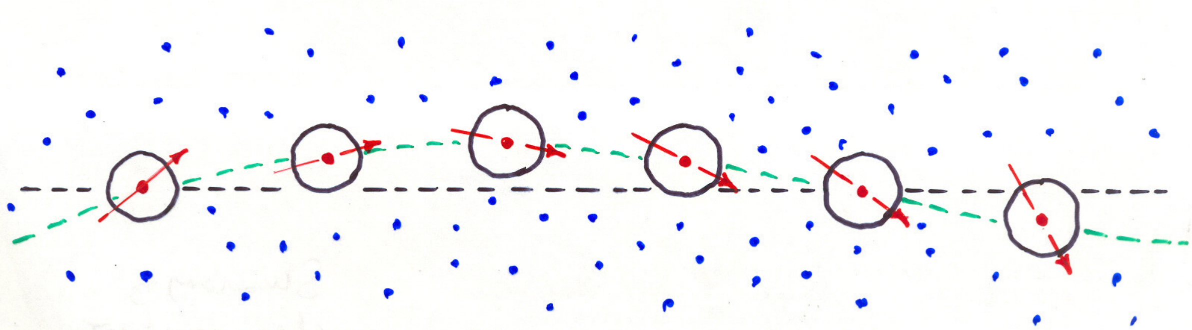
$$\hat{H} = \hat{H}_e^c + \hat{H}_{e,\,pw}$$



- Extension to dynamically displacive (and electronically polarizable) **ions**, and valence electrons

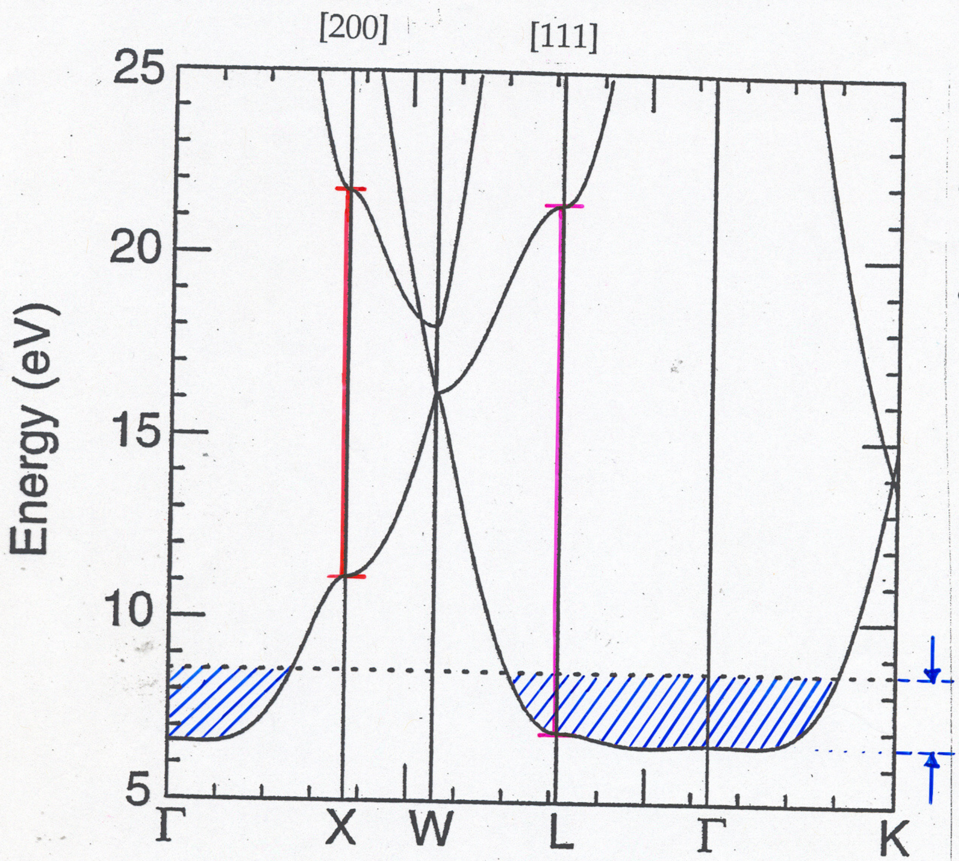
  - Collective (coupled 'monopolar') phonons (*ph*)

$$\hat{H} = \hat{H}_e^c + \hat{H}_{e,\,pw} + \hat{H}_{e,\,ph}$$



'SIMPLE' METALS AT HIGHER DENSITIES: SIGNIFICANT SHIFTS AWAY FROM NEARLY–FREE ELECTRON BEHAVIOR

- Example: Li FCC Bands at ~ 4–fold compression*



- Band width ~ 2.1 eV
- Expected (r_s~ 2), NFE ~ 12.5 eV

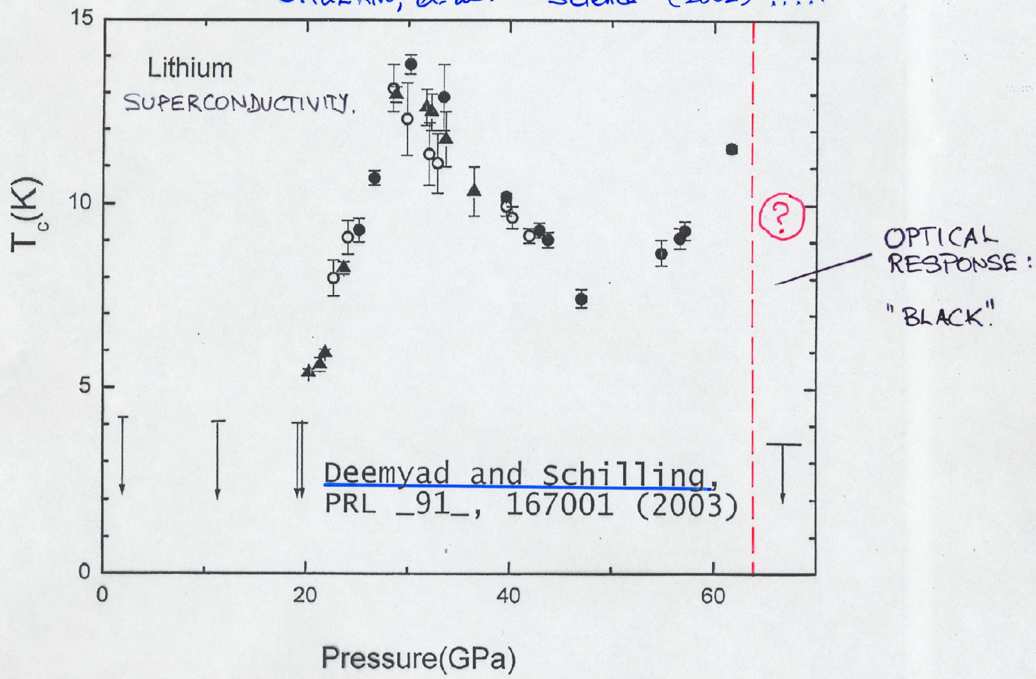
Reason: Interstitial localization by core orthogonali –zation

- Consequences of band–narrowing: high density of states
- Inference from increase in gaps: large electron ion interaction hence large electron–phonon interaction
- Expectations: – structural transitions (charge–density–waves) – **superconductivity**
- Pairing (μ^*): most favorable for non–Bravais lattices

* J. B. Neaton, NWA: Nature, 400, 141 (1999)

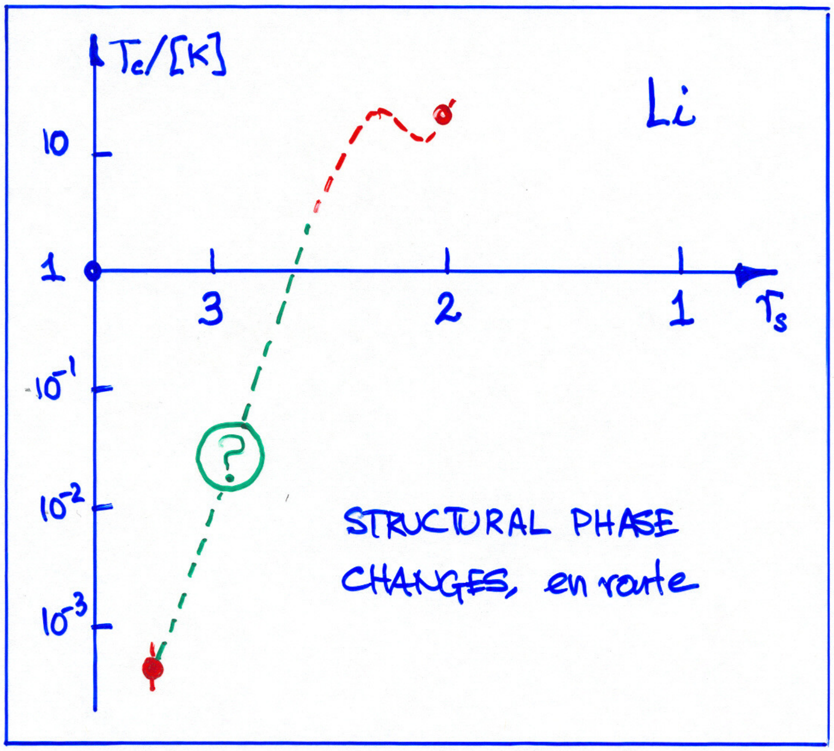
Experimental Progression:

- Shimizu, et. al Nature (2002)
- Struzkin, et. al. Science (2002) ....



LITHIUM ($Z_a = 3$) AS A TEST CASE

- EXPERIMENTAL / THEORETICAL OPPORTUNITY



- Also: $^6Li \leftrightarrow {}^7Li$
- Insight into relative roles of el-ph, el-el effects in a "simple" system.

SUPERCONDUCTIVITY IN METALLIC HYDROGEN

I. As a Monatomic Crystalline Metal

. Proton Mass - 1836 electron masses; lightest of the nuclei

. High dynamic energy scales, large electron-proton interaction, large electron-phonon coupling

. High superconducting transition temperatures indicated via BCS theory (~ 100 K)

[see, for example, NWA, PRL **21**, 1748 (1968)]

II. As a Paired Crystalline Metal

. Additional pairing strength from correlated electron-hole fluctuations indicated by an Eliashberg approach. Transition temperatures still in ~100 K range

[C.F.Richardson and NWA, PRL **78**, 118 (1997)]

III. As a Low Temperature Liquid Metal

. With the emerging possibility of a ground state liquid for metallic hydrogen, direct solution of the Eliashberg equations continue to indicate high superconducting transition temperatures

[J.Jaffe and NWA, PRB **23**, 6176 (1981)]

IV. As a Dual Fermionic Paired System

. Pairing at low temperatures in both protonic and electronic degrees of freedom. Novel vortex structures arising with associated failures of London and Onsager-Feynman laws indicating direct tests of the ground-state liquid proposition

[E.Babaev and NWA, Nature Physics **3**, 530 (2007)]

High pressures still required; are there 'en route' possibilities involving 'alloys' of metallic hydrogen and setting in at lower pressures?

EN ROUTE TO METALLIC HYDROGEN: HIGH HYDRIDES OF LIGHT ELEMENTS

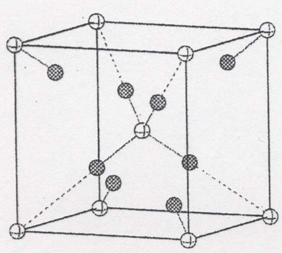
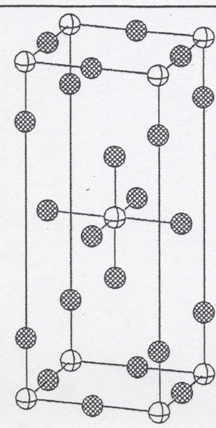
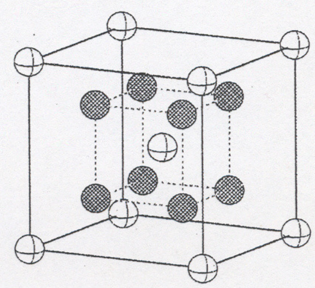
(NWA, PRL **92**, 187002 (2004))

- Concept: 'doping' of metallic hydrogen with multi-valent light elements

- Reduction in pressure via 'chemical pre-compression'

Example: SiH_4

Examination of high-pressure structures via total-energy calculations (Feng, Grochala, Jaron, Hoffman, Bergara, NWA, 2004)

 A	 B	 C
$I\bar{4}3m$ (No. 217)	I4/mmm (No. 139)	I432 (No. 211)

"SnF_4"

• SUPERCONDUCTIVITY ?

INSULATOR-METAL TRANSITION IN GROUP IVa HYDRIDES

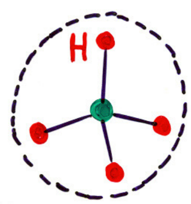
- **Consider as wide band systems**

    - Pb H_4
    - Sn H_4
    - Ge H_4
    - Si H_4
    - CH_4

∗ Pb, Sn : strong-coupling superconductors $(p = 0)$

∗ Ge, Si : superconductors at high pressure

- **First, as molecules**

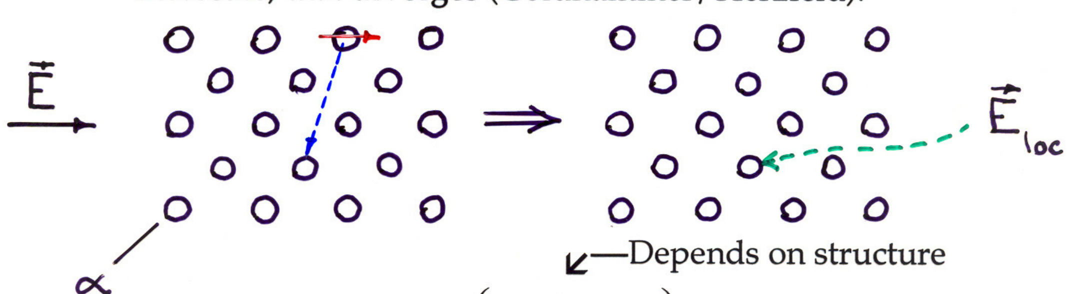


Measure of internal fluctuational physics: - dipole polarizability α

- **Next, in a crystalline state:**

Q: At what density, ρ_m, is a band-view (wide) appropriate?

A: (Approximate; —from polarization catastrophe). When an external field **E** leads to a local-field $\mathbf{E}_{loc}$, at a molecule, that **diverges** (Goldhammer / Herzfeld).



↙—Depends on structure

$$\mathbf{E}_{loc} = \mathbf{E} \Big/ \left(1 - \frac{4\pi}{3} \rho_m \alpha \right)$$

(Luttinger-Tizsa)

AN EXAMPLE: GERMANE $\{GeH_4\}$

- Average electron density (8 electrons) at one-atmosphere is already higher than the average valence electron density of all alkali – and alkaline-earth-metals

$$r_s\,? \quad \frac{4\pi}{3} r_s^3 a_o^3 = \frac{1}{\rho_{e,v}} = \frac{V}{N_V}$$

$$r_s = 2.53$$

- Free GeH_4 molecule has a linear dipole polarizability of

40.2 au

- Onset of a polarization divergence is expected at a relative compression of

3.2

(in hydrogen, more than a factor of 10)

- Characteristic phonon energies: Acoustic longitudinal plasmon energy

$$4120 / r_s^{3/2}\ \mathrm{K}$$

(high; at the insulator-metal transition, $r_s \sim 1.71$)

- A test of strong-coupling (Eliashberg) theory can follow from measurements of transition temperatures in:

GeH_4, $GeDH_3$, GeD_2H_2, GeD_3H, and GeD_4

EARLY (AND CONTROVERSIAL) REPORT OF HIGH TEMPERATURE: SUPERCONDUCTIVITY IN A LIGHT ELEMENT SYSTEM: [HYDROGEN RICH...]

[R.A. Ogg, Phys. Rev. **69**, 243 (1946)]

Bose-Einstein Condensation of Trapped Electron Pairs. Phase Separation and Superconductivity of Metal-Ammonia Solutions

RICHARD A. OGG, JR.
Department of Chemistry, Stanford University, California
March 2, 1946

" In all probability such solid solutions remain superconducting up to the melting point, i.e., to absolute temperatures of the order of 180 to 190 degrees.

The probable explanation of the above phenomena is to be found in the behavior of trapped electron pairs*, recently demonstrated[1] to be a stable constituent of fairly dilute metal-ammonia solutions."

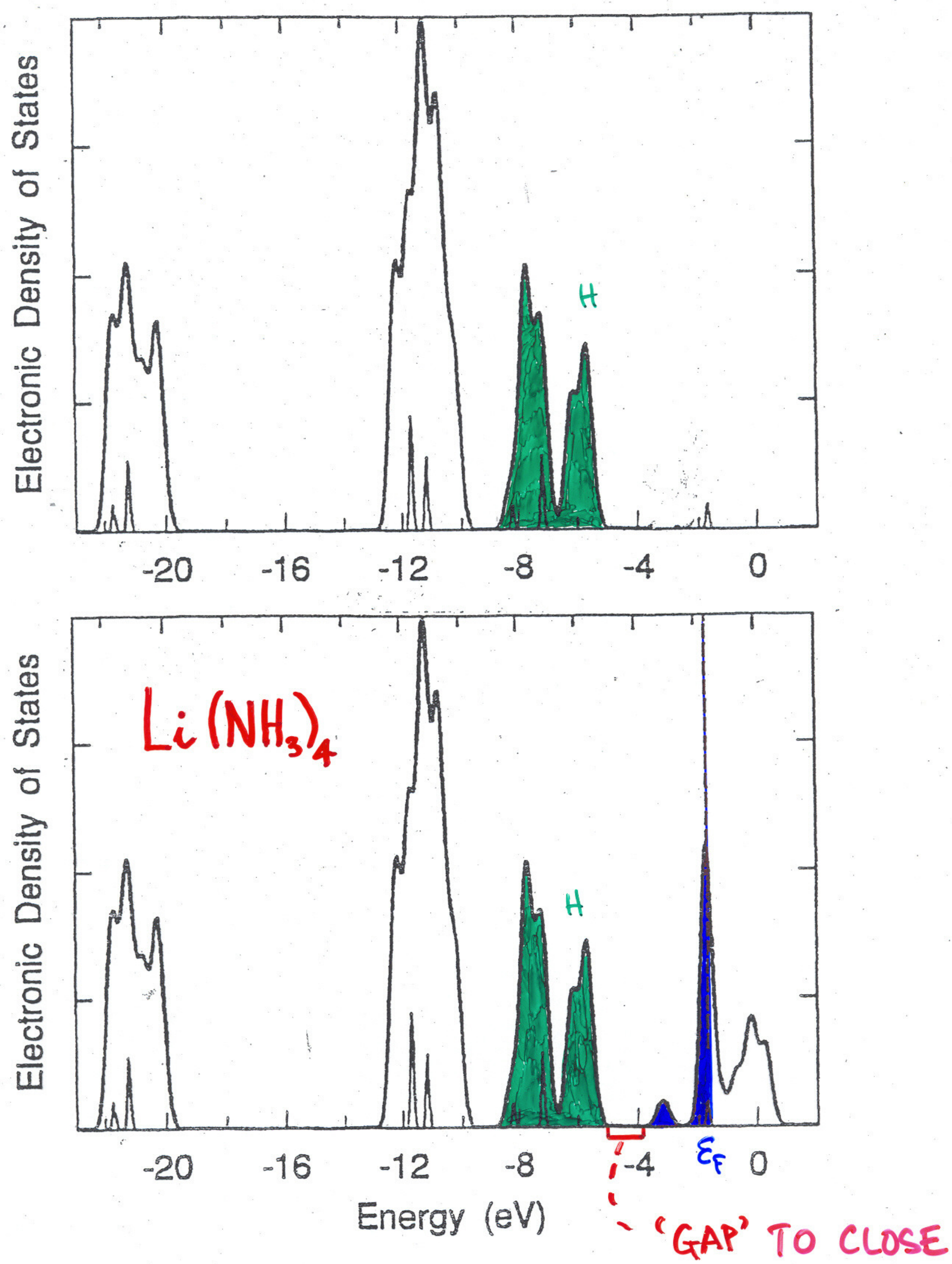
---

(1) R.A. Ogg, Jr., J. Chem. Phys. **13**, 533 (1945)

- See `The Ogg Saga' in P.P. Edwards, Journal of Superconductivity **13**, 933 (2000)
- In retrospect, these systems are characterized by high dynamic energy scales, (but probably low electronic densities of states)

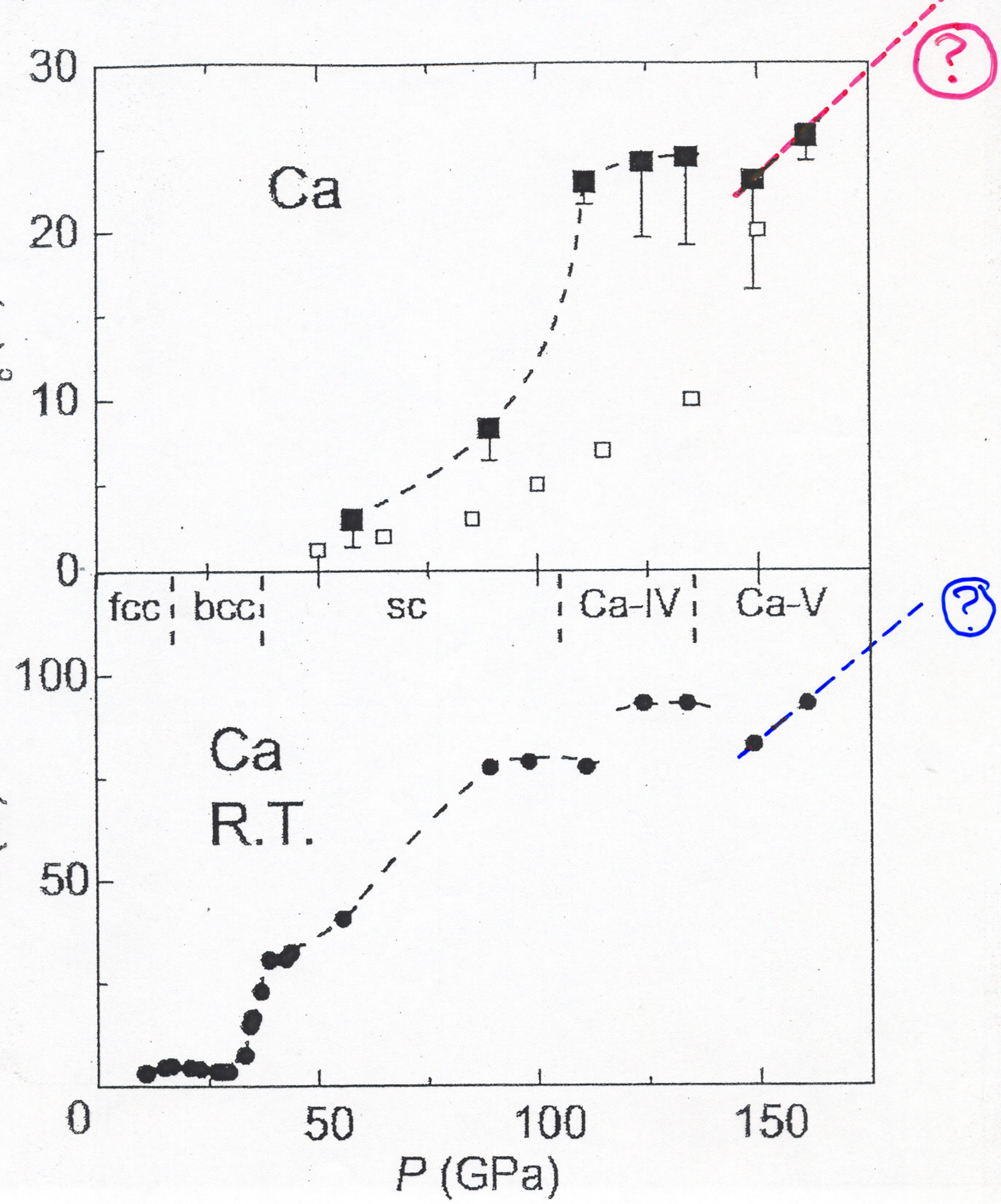
* OGG'S DI-ELECTRON

Hydrogen-Rich Systems That Already Are Metallic:



[Kohanoff et al, Phys Rev lett _73_, 3133 (1994)]

A RECENT RESULT... AND AN INTERMETALLIC EXTENSION



- T. YABULUCHI et. al JPSJ AUGUST 2006 75, 083703.
- Li/Ca in combination?

THE INTERMETALLICS: A VAST AREA

- Stoichiometric arrangements of the type

$$A_m B_n$$

  m, n integers; light elements A, B offer interesting prospects (quantum behavior)

- Emerging view; even though A and B may be drawn from the simple elements, the intermetallics may be far from simple.

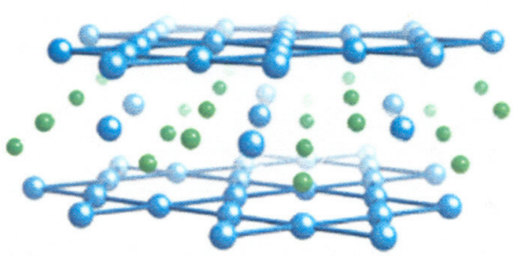
- Example: *Ca* is not a superconductor at ordinary pressures, to quite low temperatures. High pressures, T_c reaches $25K$. *Li*; presently 'newsworthy' at one atmosphere

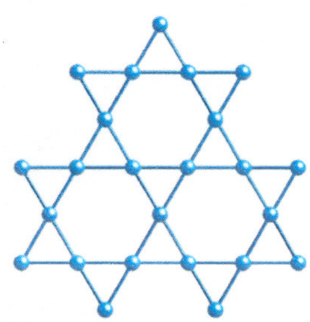
  Predicted to be a superconductor at higher density, now found to have a T_c as high as $16K$.

- Possible intermetallic arrangements? Hume-Rothery argument, *Ca Li2*

  Remarkably 'un'- free electron like under compression. [J. Feng, R. Hoffmann, NWA, 2007]

- Structure: Layered, not unlike MgB_2, *Li* layers are Kagome nets.

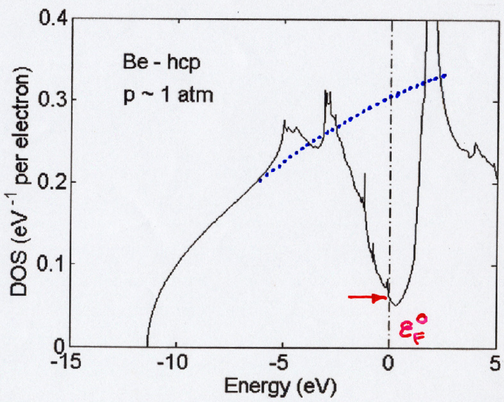




- Superconductivity? Phonons not unusual, but the electronic structure, and hence the 'Coulomb pseudopotential' is.

The beryllium story

- Elemental beryllium:
  - Highest Debye temperature among metallic elements
  - Superconducting transition $T_C = 0.026$ K
  - Because Be is barely a metal



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