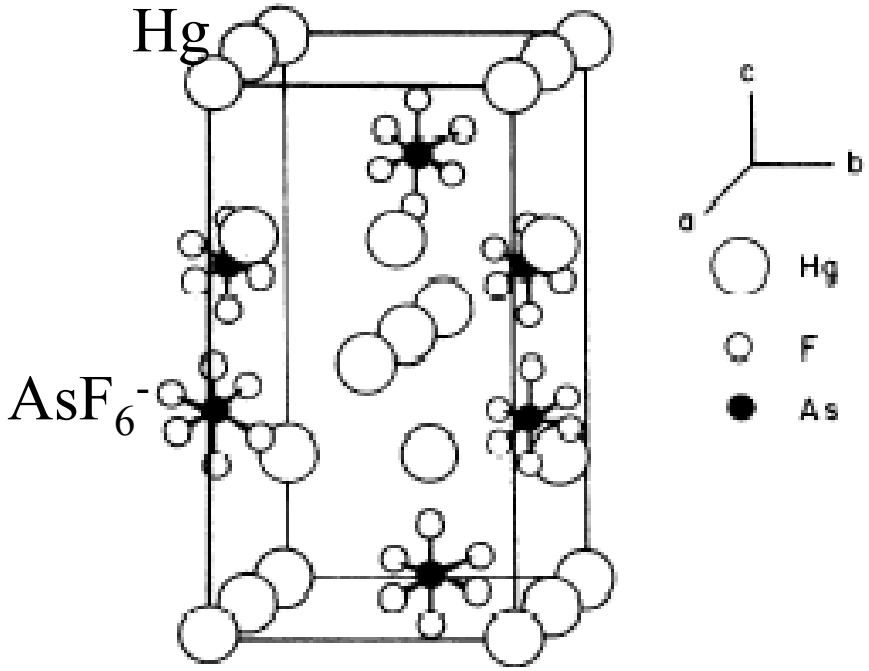
Alchemist's Gold:
The Remarkable One-dimensional Hg Chain Compound

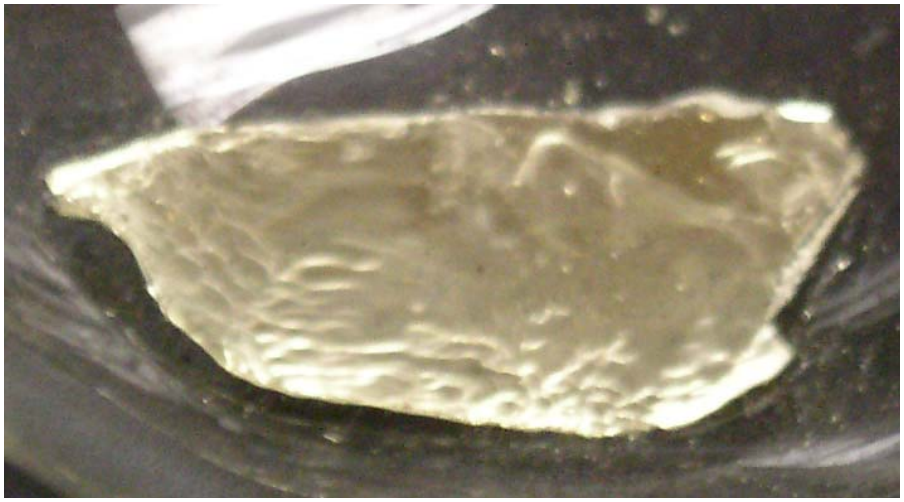
$Hg_{3-\delta}AsF_6$



Time Period: 1977-1979

Acknowledgement: Gen Shirane
Vic Emory
Arnold Denenstein

The Hg chains are metallic



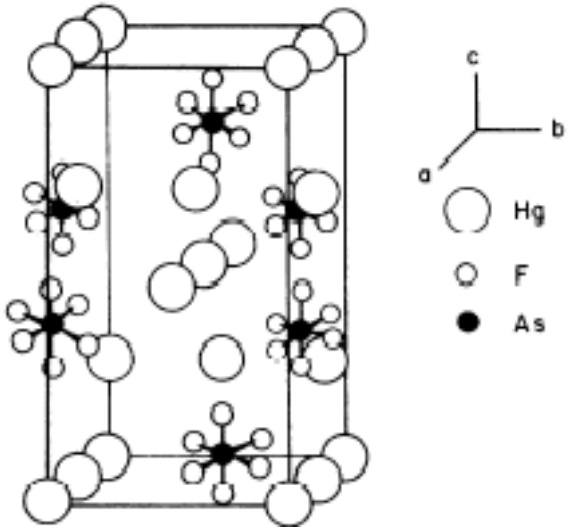
Looks like a metal ----

d = 2.64 Å

<< distance between Hg atoms in liquid Hg = 3.0 Å

The Remarkable 1d Hg Chain Compound

$Hg_{3-\delta}AsF_6$



* Tetragonal unit cell

  a = b = 7.54 Å , and c = 12.34 Å

* Spacing between Hg atoms (at all temperatures)

  d = 2.64 Å

Thus: a/d = 2.856 implying $Hg_{2.86}AsF_6$

The Hg chains are incommensurate with the lattice!

Note that $d(T) = 2.64$ Å, independent of temperature.

Thus, the Hg – Hg interatomic potential is harmonic ---

Fourth order terms are sufficiently small that there is no thermal expansion or contraction of the Hg – Hg spacing .

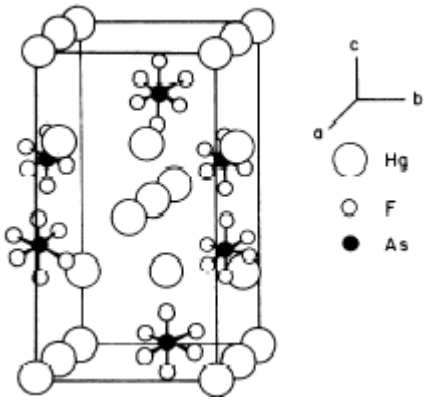
However, the lattice constants that define the unit cell with the $(AsF_6)^-$ ions exhibits thermal expansion and contraction --- as is typical of most solids.

Therefore, in $Hg_{3-\delta}AsF_6$, $\delta(T)$ is a function of the temperature.

As a result, Hg is reversibly excluded from the crystal and can be seen as small drops on the a-c and b-c surfaces of the crystal.

The Remarkable One-dimensional Hg Chain Compound

$Hg_{3-\delta}AsF_6$



- Hg chains are incommensurate with the tetragonal lattice of $(AsF_6)^-$ ions.

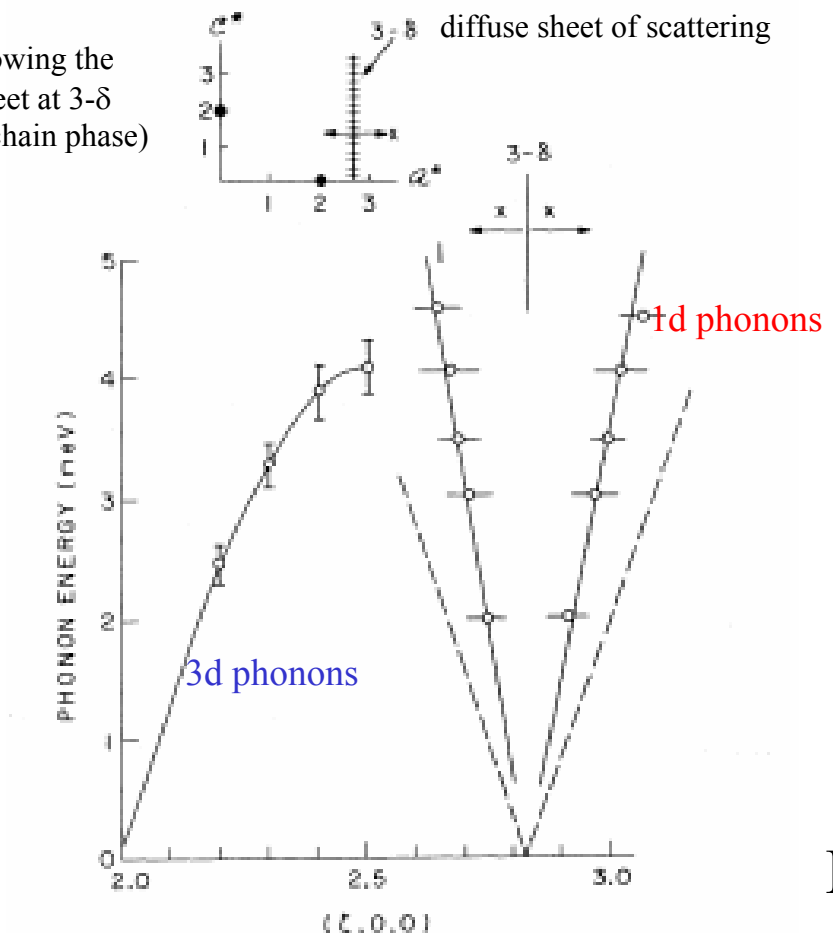
  Result: 1d lattice dynamics

- Very weak interchain electronic coupling

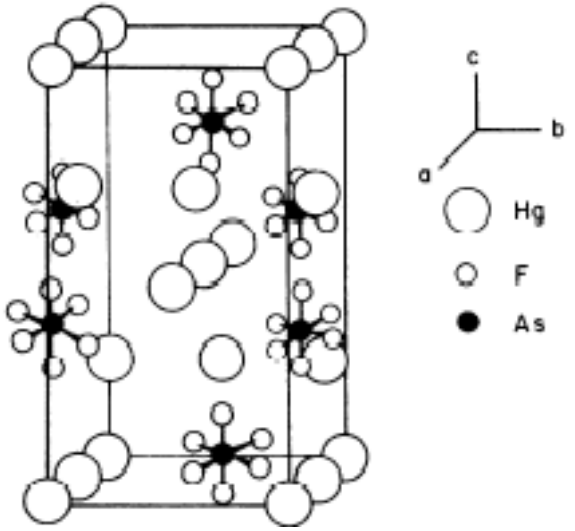
  Result: 1d electronic structure with many interesting features.

Lattice dynamics of one-dimensional chains

a*-c* plane showing the expected 1d sheet at 3-δ (Random interchain phase)



Two independent Phonon dispersion curves



$Hg_{3-\delta}AsF_6$

Different slopes

$v_s(3d) = 2.2 \times 10^5$ cm/s

$v_s(1d) = c = 4.4 \times 10^5$ cm/s

The Hg chains are incommensurate with the lattice

There is no long range order in 1d systems:

Landau and Lifschitz "Statistical Physics" --- last page

Example: 1d ferromagnet (Ising model)

"Ground state": --- ↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑ ---

Defect state: --- ↑↑↑↑↑↑↑↑↑↓↓↓↓↓↓↓↓↓↓ ---

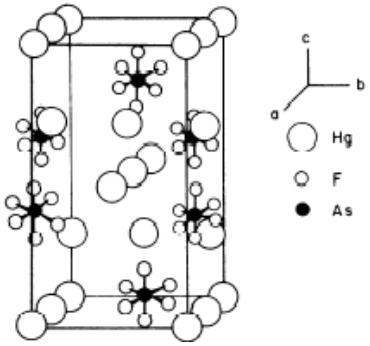
Free Energy = $J - k_B T \ln N$

Long correlation length ~ "a"$\exp(J/k_B T)$

For N large, many such defects at random sites

----- No long range order in 1d.

No Long range order in 1d chains -----
Therefore, the Hg atoms in the 1d chains must be a liquid!



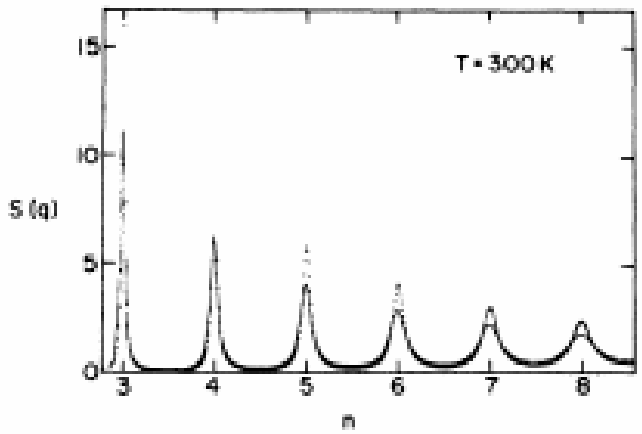
Note: Detailed studies show that the chains do not buckle!
(Chains are linear to within approx 2%)

Liquid structure factor for 1d chains can be solved exactly:

R. Spal, C.-E. Chen, T. Egami, P. J. Nigrey and A. J. Heeger, Phys Rev. B 21, 3110 (1980)

$$S(q) = \frac{\sinh \frac{1}{2}\sigma^2 q^2}{\cosh \frac{1}{2}\sigma^2 q^2 - \cos qd},$$

where $\sigma^2 = d^2(k_B T/Mc^2)$



Solid curve: Harmonic potential: $V(x) = (1/2)Mc^2(x/d)^2$

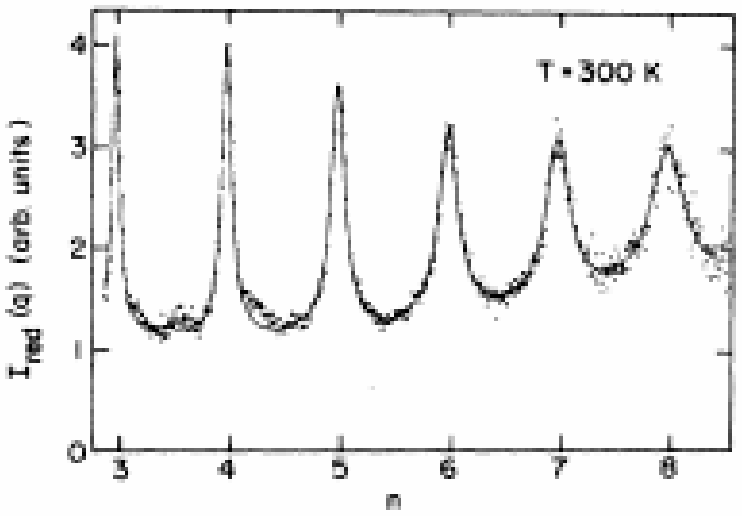
Dashed curve: $V(x) = (1/2)Mc^2(x/d)^2 + \text{const}(x/d)^4$

"Sheet" scattering at (001), (002), (003) ---------- (008) ---

Energy dispersive X-ray diffraction:

Use continuous part of the emission from an X-ray tube rather than the line spectrum. Different energies correspond to different wavelengths and different q-values.

- Capable of measuring S(q) out to high q-values.
- Perfect for measuring the 1d structure factor.



"Sheet" scattering at (100), (200), (300) ---------- (800) ---

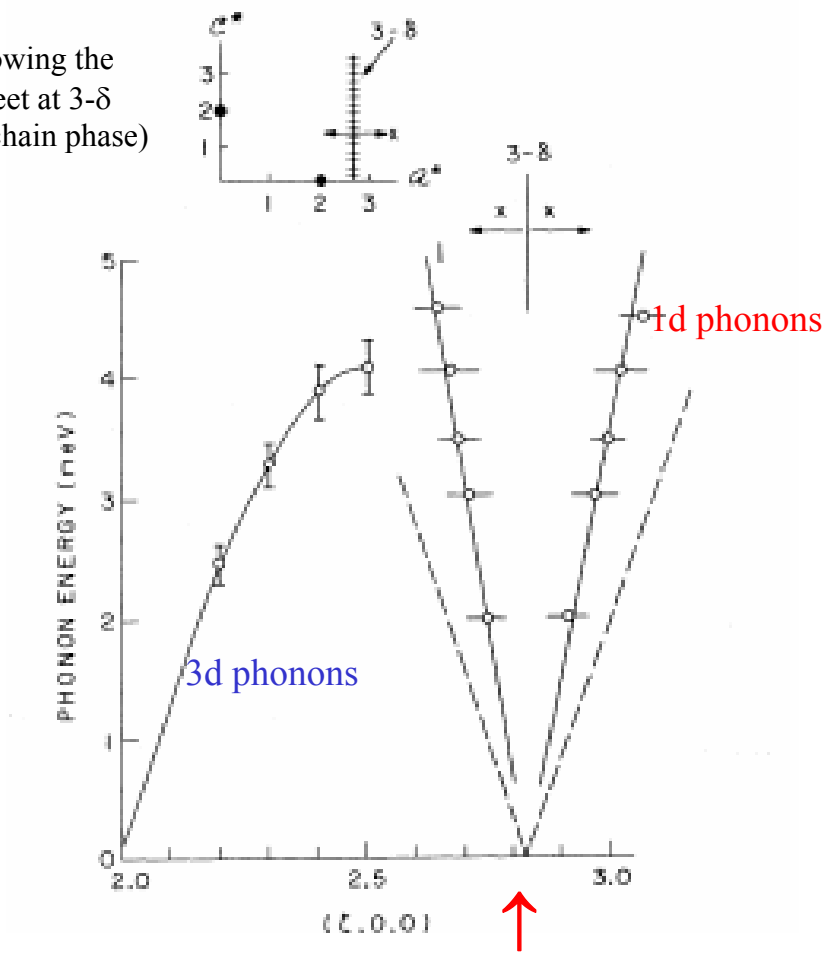
Dotted curve: X-ray Data
Solid curve: Fit of the predicted S(q)

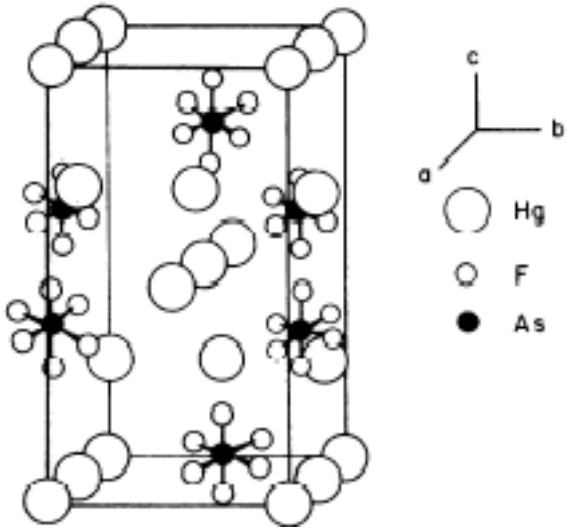
For details of both the theory and experiments:

R. Spal, C.-E. Chen, T. Egami, P. J. Nigrey and A. J. Heeger, Phys Rev. B 21, 3110 (1980).

Conclusion: **Hg chains are 1d liquids**.

a*-c* plane showing the expected 1d sheet at 3-δ (Random interchain phase)





$Hg_{3-\delta}AsF_6$

No elastic scattering Bragg peak; the scattering observed by the X-ray "diffraction" arises completely from inelastic scattering by the 1d "phonons". (No energy resolution in X-ray detector)

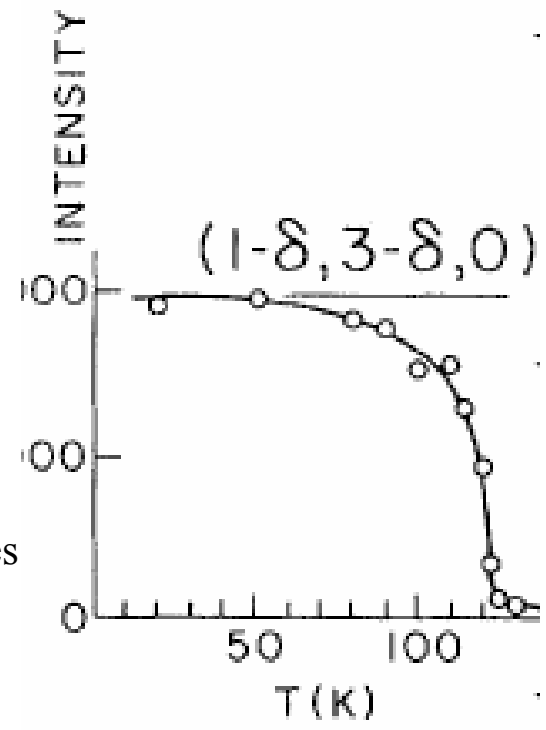
"Phase Ordering" Phase Transition in $Hg_{3-\delta}AsF_6$

At 120K, the chains phase- lock into a "phase ordered" 3d structure

Order parameter Intensity of new satellite Bragg peaks at

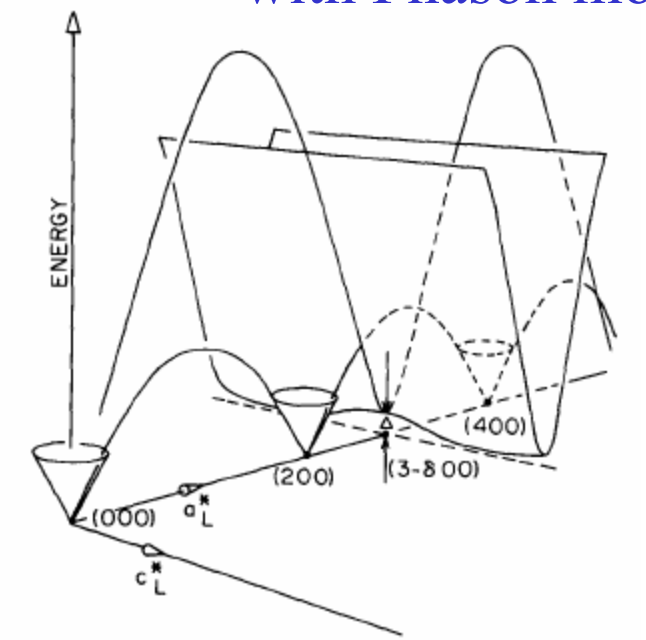
$(1\pm\delta, 3-\delta, 0)$

Scattering in the sheets collapses into Bragg peaks.

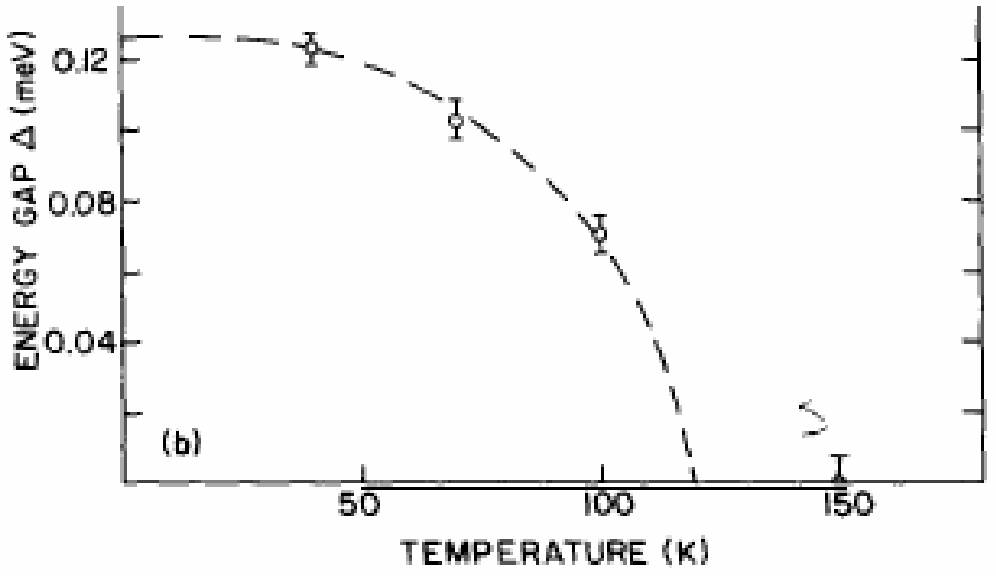


Long range order; successive chains are out-of-phase.

Phonon dispersion relation with Phason mode



T-dependence of the phason mode



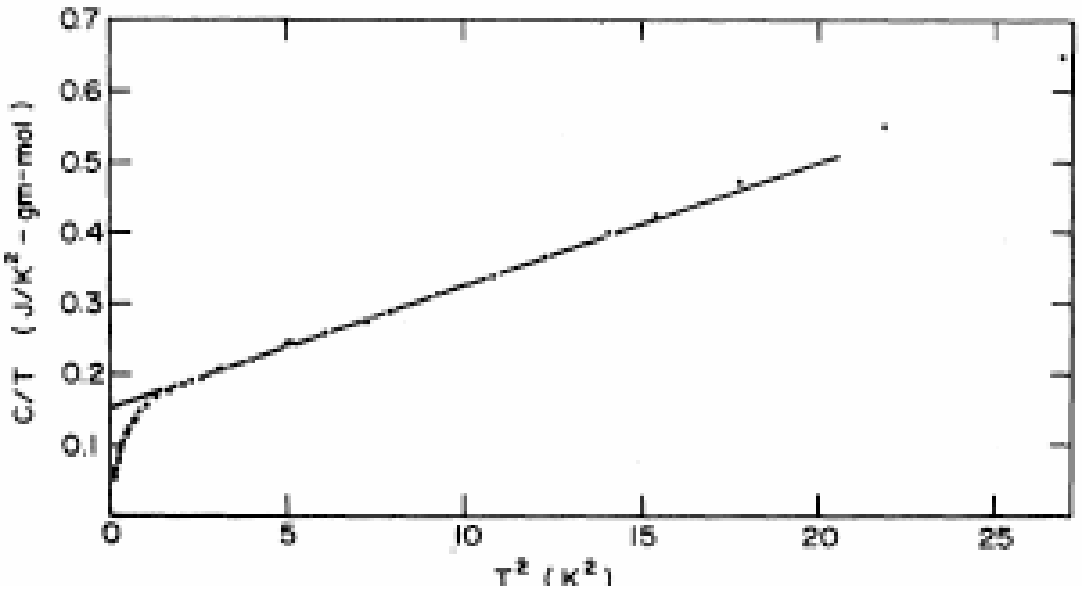
Phason "gap" due to out-of-phase excitations:
At low T ----- phason gap = 1.2×10^{-4} eV = 1.5 K

Note: T_c >> phason gap ------ long coherence length above T_c
characteristic of very weakly coupled chains where $T_c \sim [J_{intra} J_{inter}]^{1/2}$

J.M. Hastings, J. P. Pouget, G. Shirane, A. J. Heeger, N. D. Miro and A. G. MacDiarmid,PRL 39 1484 (1977)

Low Temperature Specific Heat

α large $= \rightarrow$



C/T vs T^2

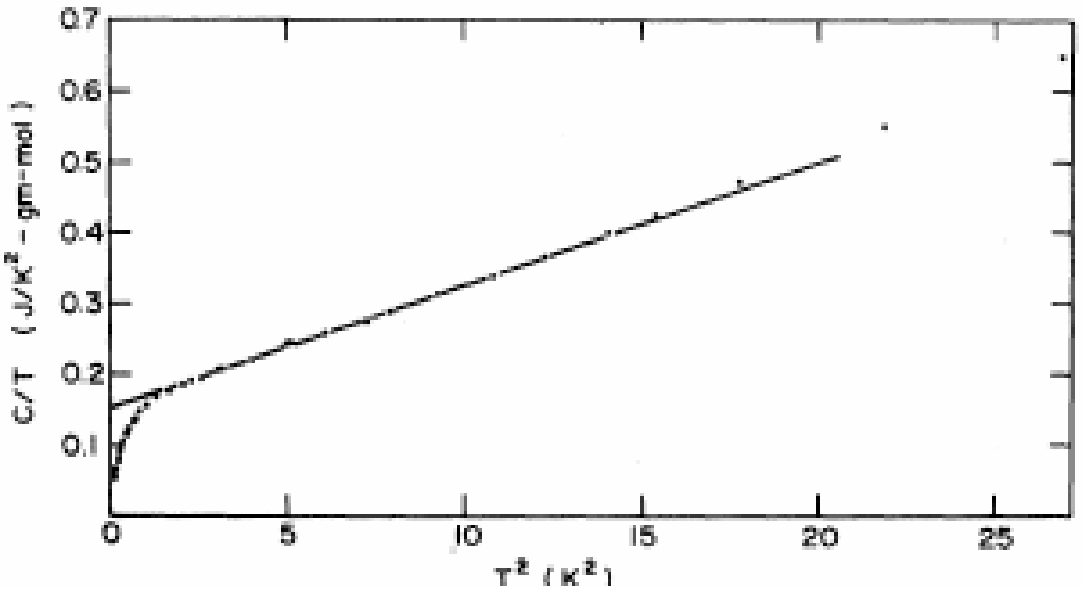
$$C = \alpha T + \beta T^3$$

Linear term: Electronic origin?? Hg chains are metallic.

No --- Knight shift (NMR) data yield $D(E_F) \approx 0.08$ states/eV/Hg atom.
Thus, C_{el} < 2% of the observed linear term.

D. Moses, A. Denenstein, A. J. Heeger, P. J. Nigrey and A. G. MacDiarmid, PRL 43 369 (1979)

Low Temperature Specific Heat



$C = \alpha T + \beta T^3$

↑1d ↑3d

C/T vs T^2

Phonon contributions ($\propto T^{\text{dimensionality}}$)

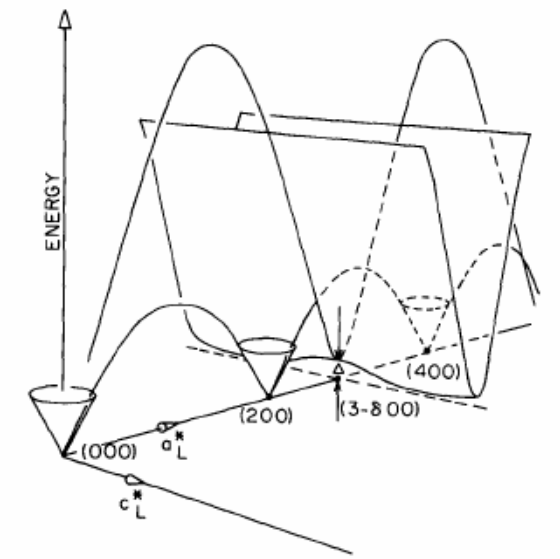
$C_L(1d) = (\pi^2/3)Nk_BT/\Theta_1$ where Θ_1 is the 1d Debye temperature.

$\Theta_1 = 540$ K

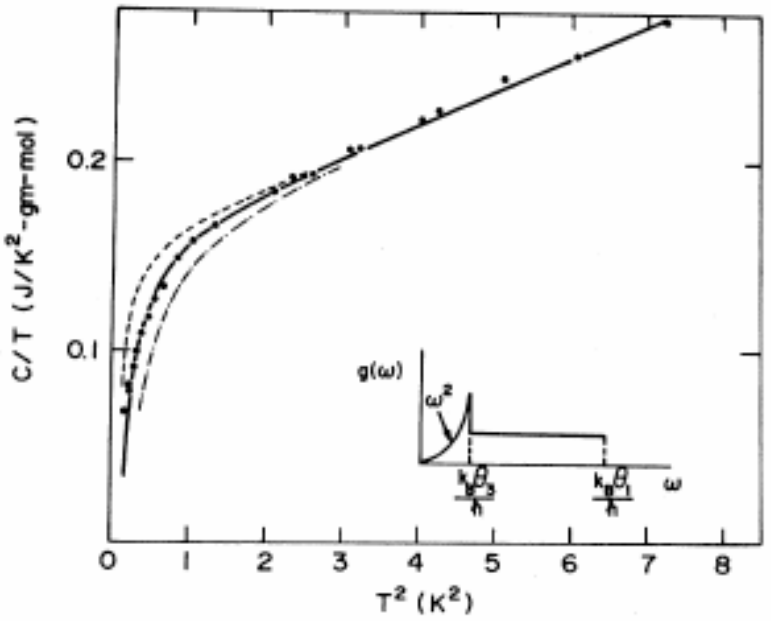
$v_s = \Theta_1 a k_B/\pi\hbar = 6\text{x}10$ cm^5/s (OK re neutron data)

D. Moses, A. Denenstein, A. J. Heeger, P. J. Nigrey and A. G. MacDiarmid, PRL 43 369 (1979)

At low temperatures (Below 1.5K) the phason gap dominates the Specifc heat because of the interchain phase ordering ----
1d contribution crosses over to 3d.



This implies that the contribution from the phase-ordered Hg chains becomes 3d at low T (At lowest T, slope increases and becomes T^3)

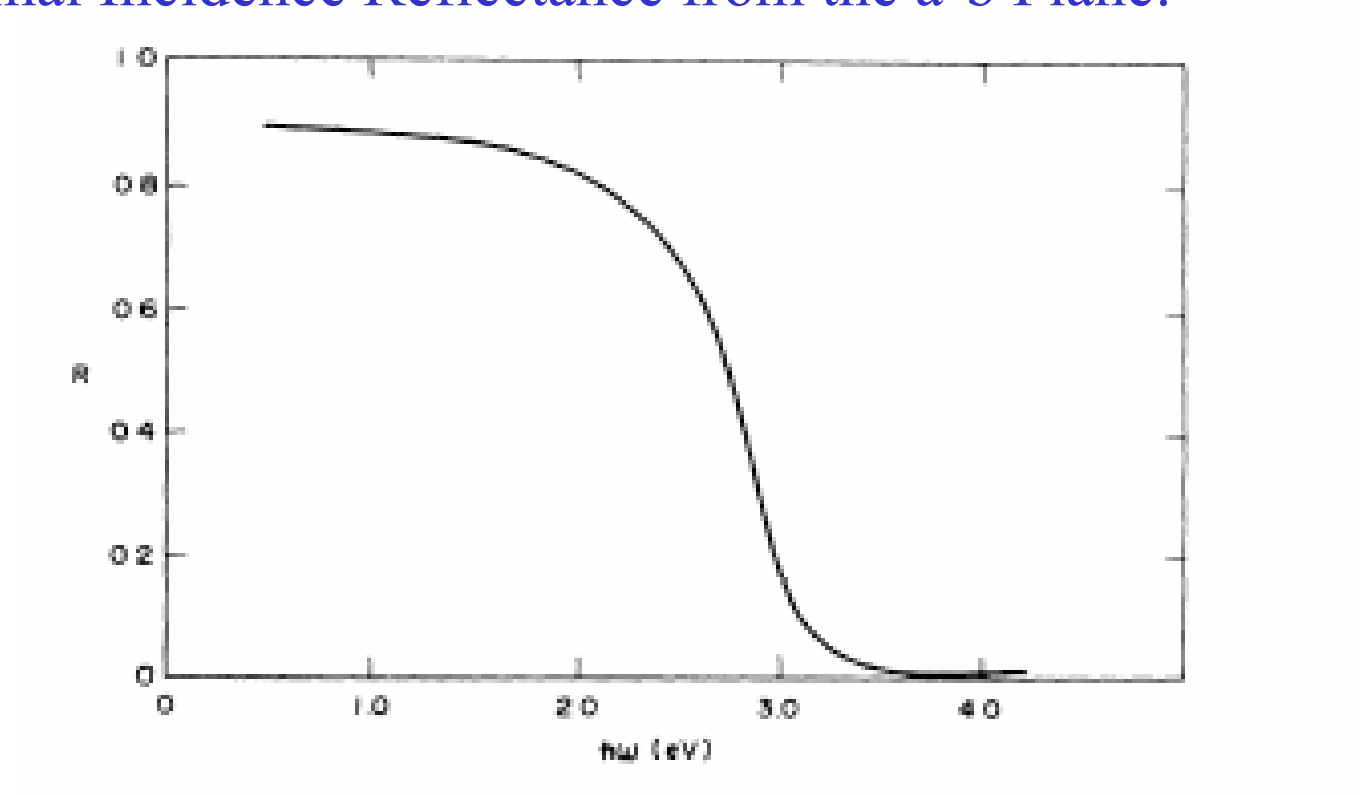


Best fit to the data yields a phason gap of 1.5K, in agreement with that found from inelastic neutron studies.

Optical reflectance measurements and their implications

Looks like a metal ----

Normal Incidence Reflectance from the a-b Plane:

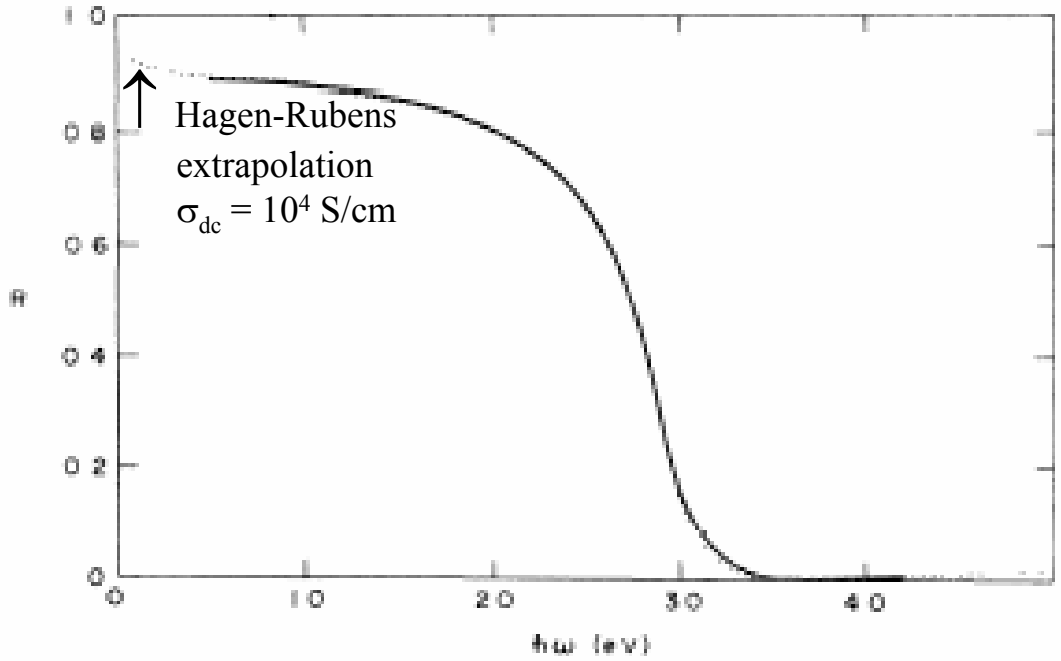


Plasma edge in reflectance like that of a simple free electron metal

D. L. Peebles, C. K. Chiang, M. J. Cohen, A. J. Heeger, N. D. Miro and A. G. MacDiarmid, Phys. Rev. B 15 4607 (1977)

Drude Theory --- Free Electron Theory --- Fit to R(ω)

$$\mathcal{R} = \frac{|\epsilon| + 1 - [2(|\epsilon| + \epsilon_1)]^{1/2}}{|\epsilon| + 1 + [2(|\epsilon| + \epsilon_1)]^{1/2}} ,$$



$\hbar\omega_p = 4.8$ eV

$\hbar/\tau = 0.27$ eV

$[\hbar\omega_p/\varepsilon_\infty]^{1/2} = 2.9$ eV

$\varepsilon_\infty = 2.7$

$$\epsilon_{ob}(\omega) = \epsilon_\infty - \omega_p^2/(\omega^2 + i\omega/\tau) ,$$

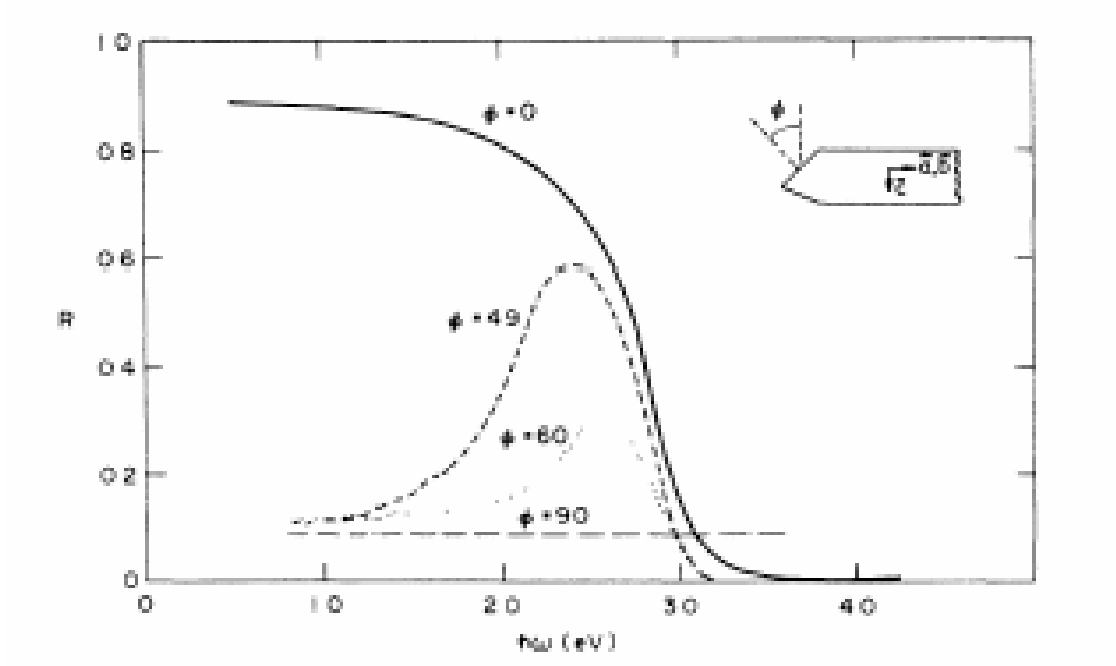
$$\epsilon_c(\omega) = \epsilon_\infty ,$$

$\sigma_{opt} = (1/4\pi)\omega_p^2\tau = 1.2 \times 10^4$ S/cm

$\sigma_{dc} = 10^4$ S/cm

Anisotropy in the Reflectance

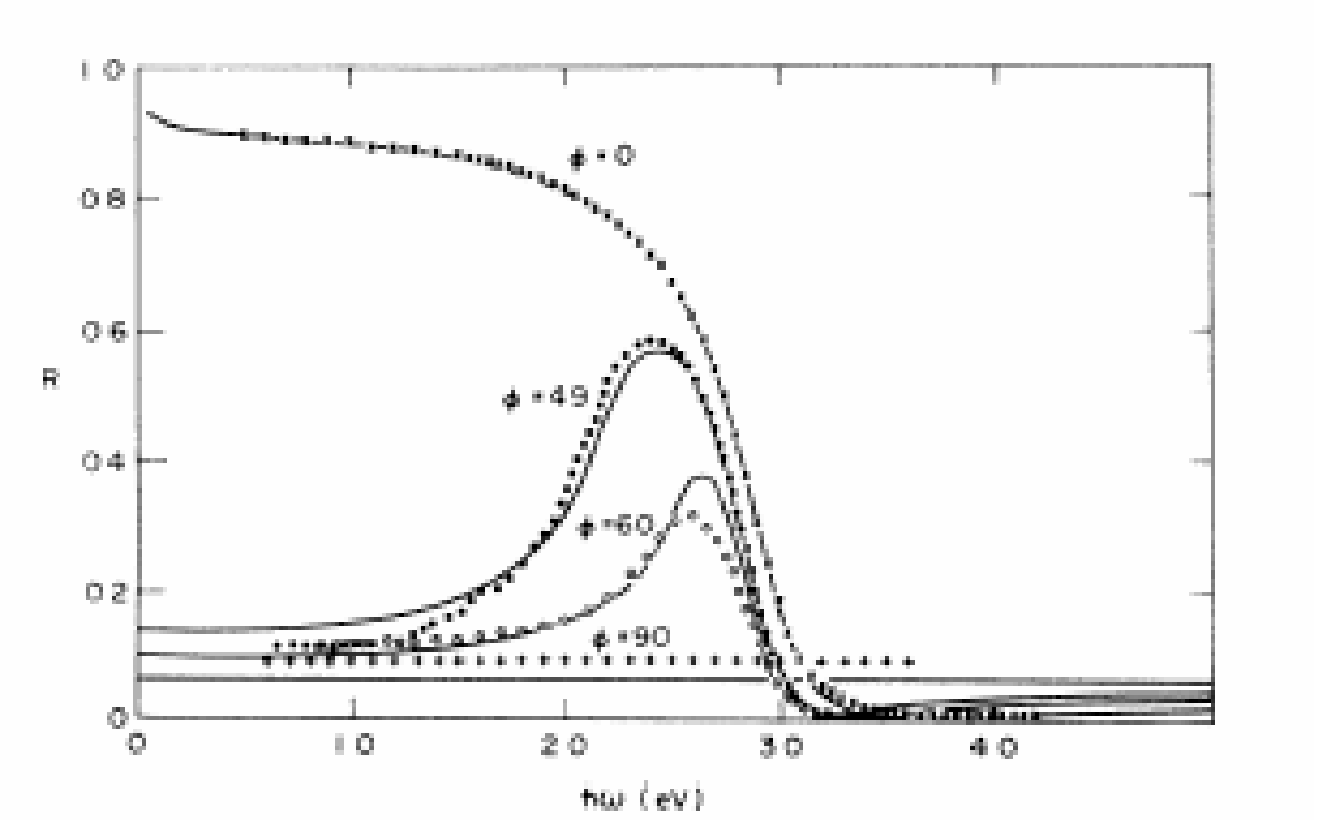
Normal Incidence Measurements from Different Crystal Facets at Angles with respect to a-b plane



Conclusion: One dimensional chains ---Metallic parallel to the Hg chains
Not metallic perpendicular to Hg chains.

$$\mathfrak{R}_{(\varphi,\omega)} = \left|(n_{(\varphi,\omega)} - 1)/(n_{(\varphi,\omega)} + 1)\right|^2$$

$$n^2(\cos^2\varphi/\epsilon_{ab} + \sin^2\varphi/\epsilon_c) = 1$$



Excellent fits to the anisotropic Reflectance;
No adjustable parameters (all obtained from φ = 0)

Transport measurements and their implications

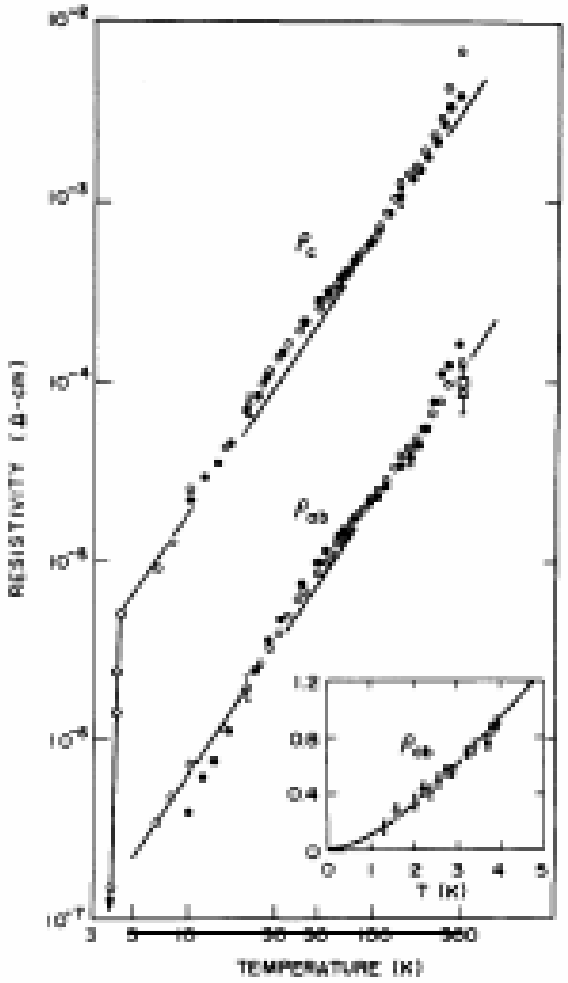
Resistivity vs temperature: $\rho_{||}(T)$ and $\rho_{\perp}(T)$

Magnetic field dependence of the resistivity: $\rho_{||}(H,T)$

In a-b plane: Electrical Conductivity of a Metal

At 300K, $\rho_{\|} = 10^4$ S/cm

(4-probe measurements; Montgomery method)



- $\rho_{\|} \propto T^{3/2}$ between 300K and 30K.
  No sign of residual resistivity!
  See inset in Figure.

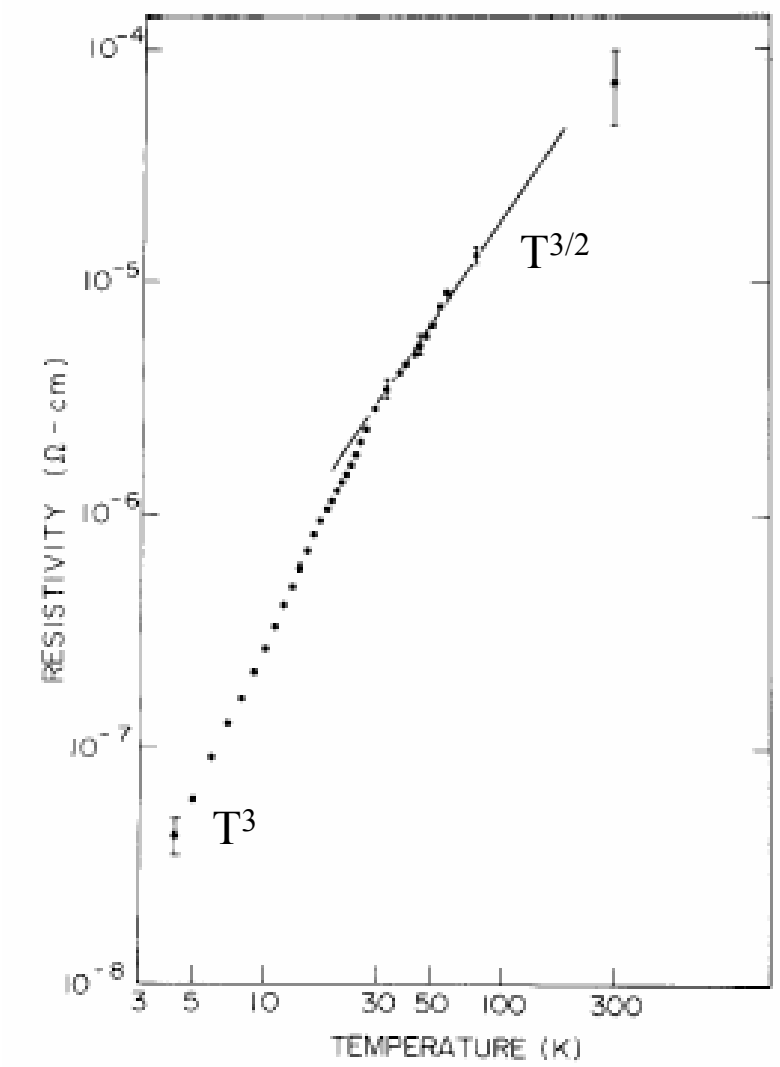
- $\rho_{\perp}$ has same T-dependence
  Therefore, probably not intrinsic:
  $(\rho_{\perp} / \rho_{\|}) >> 10^2$

- At 4.1K, $\rho_{\perp}(T)$ drops abruptly to ZERO.

C. K. Chiang, R. Spal, A. Denenstein, A. J. Heeger, N. D. Miro and A. G. MacDiarmid, Solid State Commun. 22 293 (1977)

In a-b plane: Electrical Conductivity of a Metal

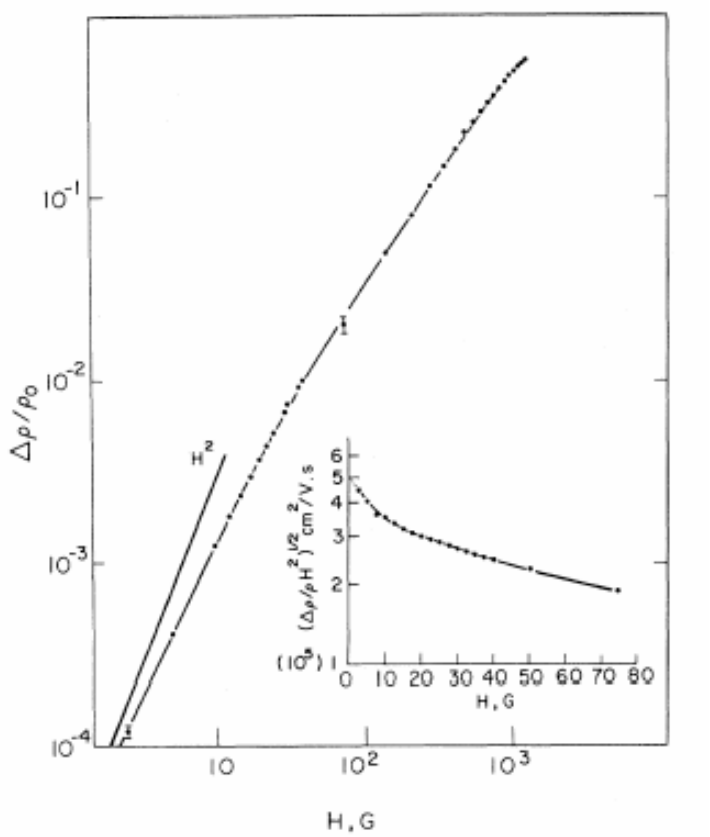
At 300K, $\rho_{||}$ = 104 S/cm
(contactless ac method)



- Above 30K, $\rho_{||}(T) \propto T^{3/2}$
- Below 30K, $\rho||(T) \propto T^3$

- At lower T, the T-dependence is even stronger (T^3).

- No sign of the residual resistivity expected from scattering by defects, imperfections and impurities.



$\Delta\rho/\rho_o$ vs H at 4.2 K on a log-log scale. The line represents an H^2 dependence. The data approach H^2 dependence only for H < 1 gauss.

From this low field data, one can calculate the mobility using the Hall relation:

$$\mu_{eff} = (\Delta\rho/\rho_o H^2) = 5 \times 10^5 \text{ cm}^2/\text{Vs}$$

From dc resistivity ------ $\sigma = 1/\rho = ne\mu$ yields $\mu = 5 \times 10^4$ cm^2/Vs.

Using $\mu = 5 \times 10^4$ cm^2/Vs, one estimates electronic mean free path of 50 μm.

Resisitivity data imply electron mean free path of
50 - 500 μm at low temperatures.

Remarkably perfect crystal !!????

However, chemical analysis, structural data and density measurements indicate 3:1 stoichiometry for Hg : AsF_6.

Thus --- $Hg_{2.82}(AsF_6)_{0.94}$ --- implies 6% charged defects.

The absence of residual resistivity is interesting and difficult to understand ---- especially in a quasi-one-dimensional system where back-scattering causes localization.

Magnetic Field Induced Residual Resistivity in $Hg_{3-\delta}AsF_6$

(contactless ac technique)

T-dependence of $\rho_{||}(T)$

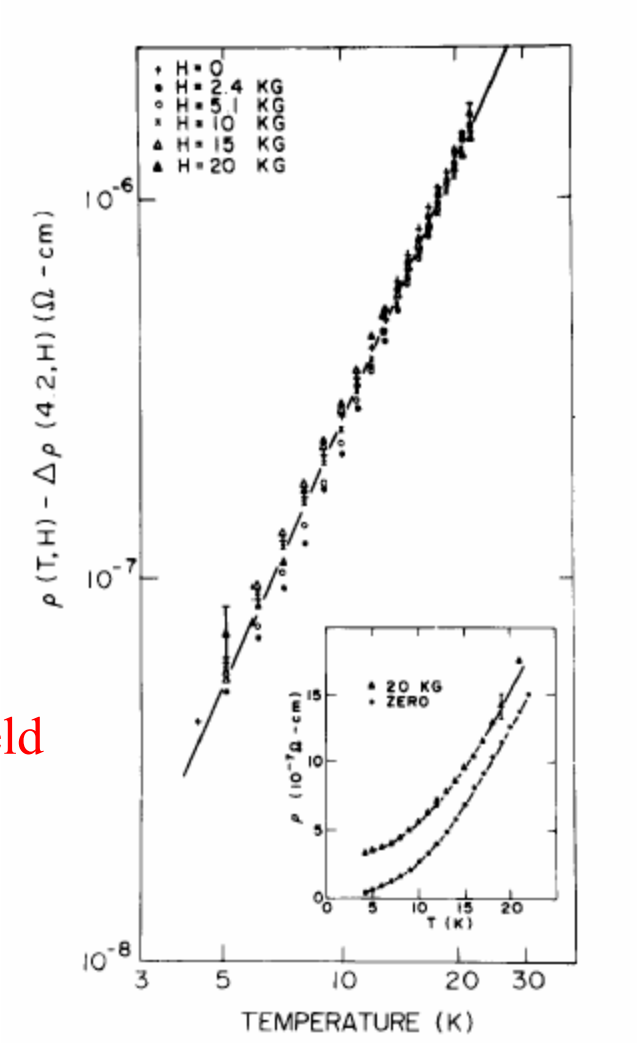
(a-b plane)

Magnetic Field Dependence

$\rho_{||}(H,T) = \rho_o(H) + \rho_1(T)$

Residual resisitivity is magnetic field dependent ---

$\rho_o(H)$ approaches zero as H approaches zero!



D. Chakraborty, R. Spal, C.Chiang, A. Denenstein, AJH and A. MacDiarmid, Sol St Com. 27. 849 (1978).

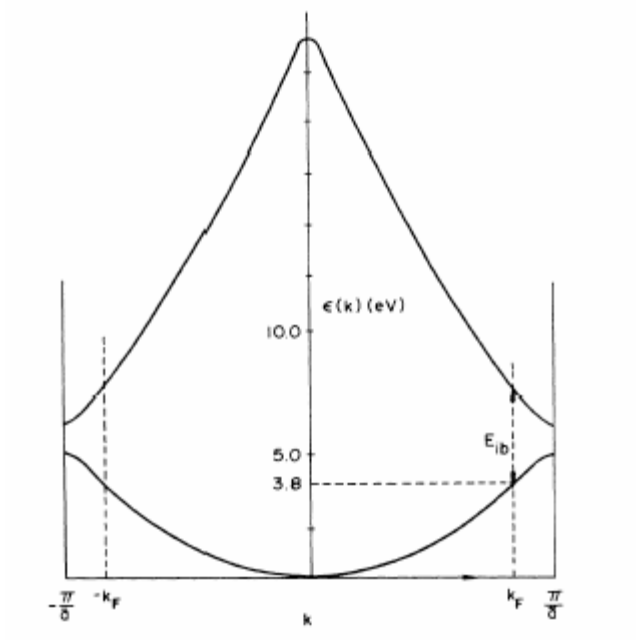
Resistivity data summarized by

$$\rho_{||}(H,T) = \rho_o(H) + \rho_1(T).$$

??? Why no residual resistivity despite clear evidence of defects ???

??? What is the mechanism responsible for the field dependent "residual resistivity" ???

Electronic Structure

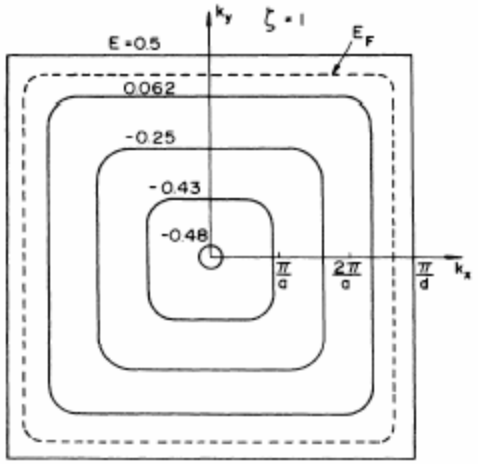


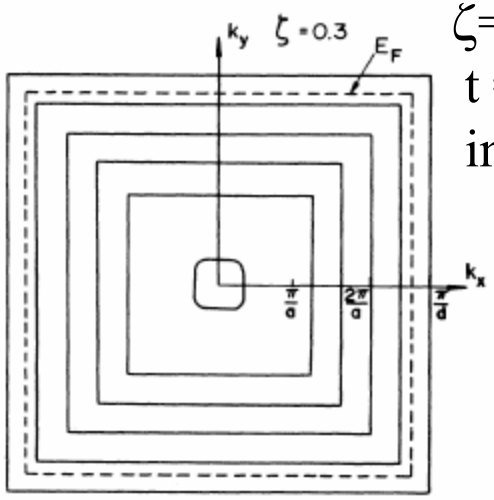
5 electrons/chain in the unit cell

$\hbar\omega_p = 4.43\ (m/m^*)^{1/2}$ eV

$\hbar\omega_p(\text{exp}) = 4.8 \pm 0.3$ eV

Thus: $m/m^* \approx 1.2$

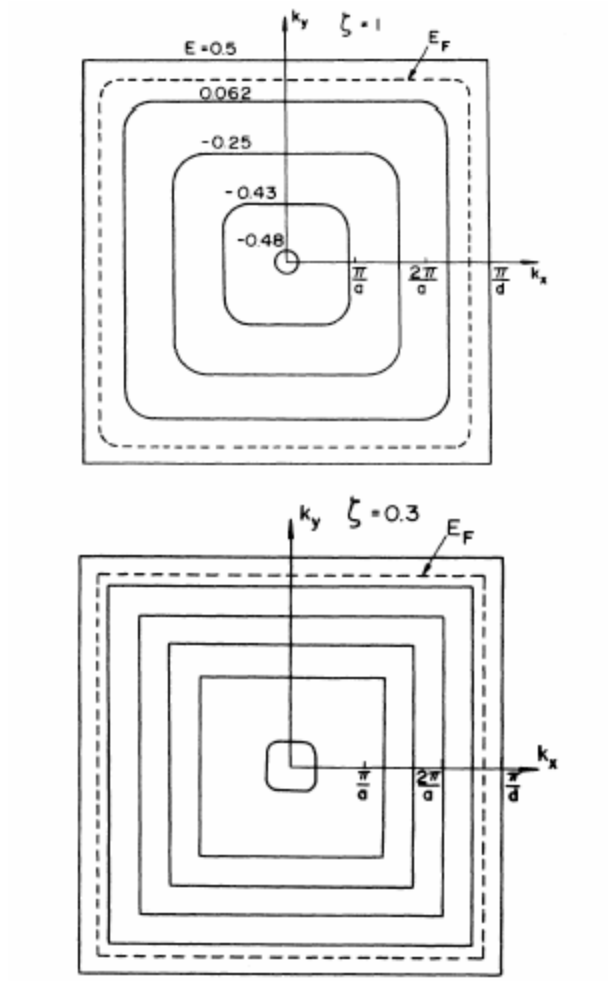




$\zeta = (2td/a)(\hbar^2\pi^2/2md^2)$
t = inter-family transfer integral (t=0 is 1d limit)

Fermi surface: Square cylinders with slightly rounded corners

Note that in k-space, the Lorentz force from the magnetic field along c-axis causes carriers to move around the cylinders



Phenomenological Model

Assumptions:

Defects and impurities ineffective on the planar sections of the Fermi surface giving a long scattering time, τ_p.

Defects and impurities are fully effective on the corners of the Fermi surface giving a short scattering time, τ_c.

For H=0, the planar and corner sections act in parallel; $\rho(T)$ is dominated by the planar sections with τ_p and no residual resistivity.

$$\rho(T) = (m/ne^2)[x\,\tau_c + (1-x)\,\tau_p] \approx (m/ne^2)\tau_p \quad \text{for } x<<1.$$

For H>0 (and parallel to c-axis), Lorentz force transfers all carriers into the corners where they are rapidly scattered by defects and impurities, etc.

Hence, Field dependent residual resistivity.

But why no scattering on planar sections???

Suggestion (Conclusion??):

1d chains with attractive el-el interactions

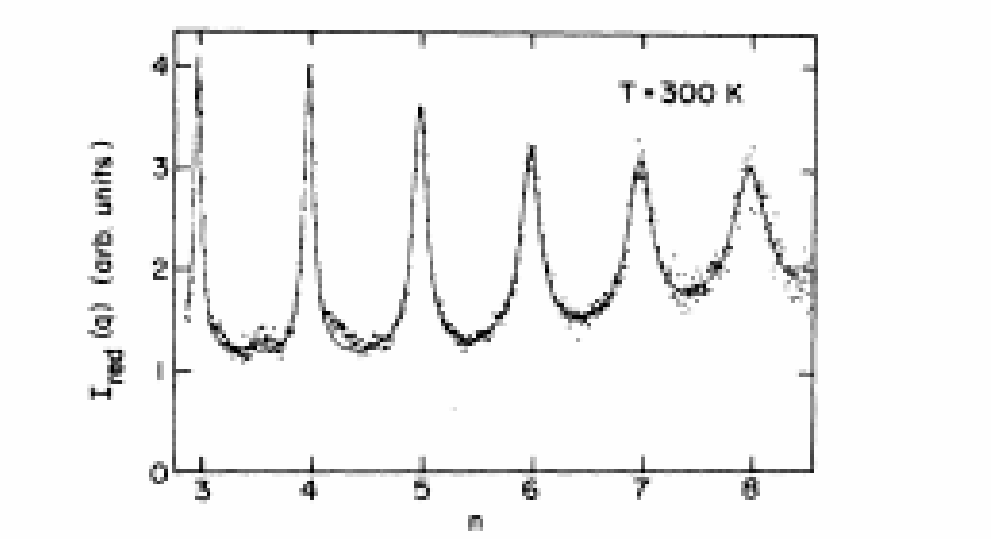
For 1d chains with attractive interactions

- Resistivity goes to zero at T = 0 K.
- Localization characteristic of 1d is avoided.
- Peierls instability (metal-insulator transition) is avoided.

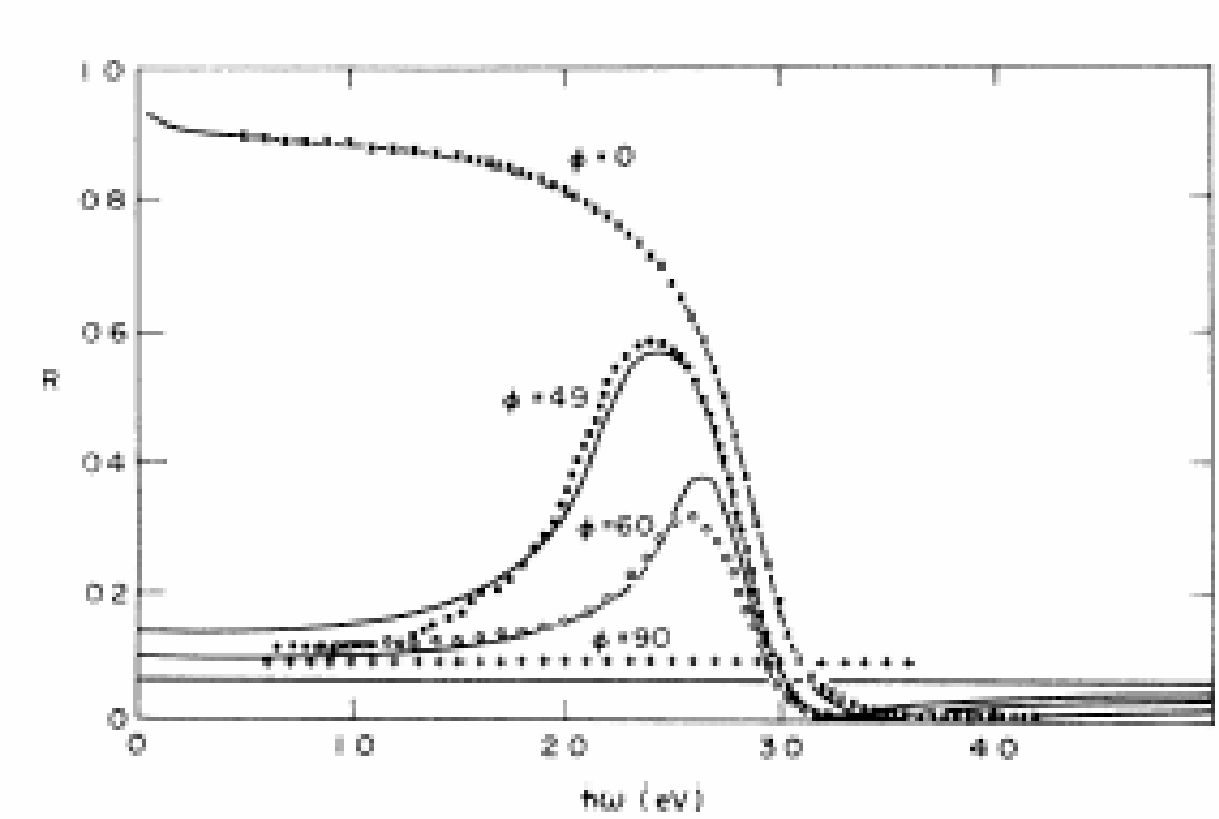
N. Menyard and J. Solyom, J. Low Temp. Phys. 12, 529 (1973)

Summary

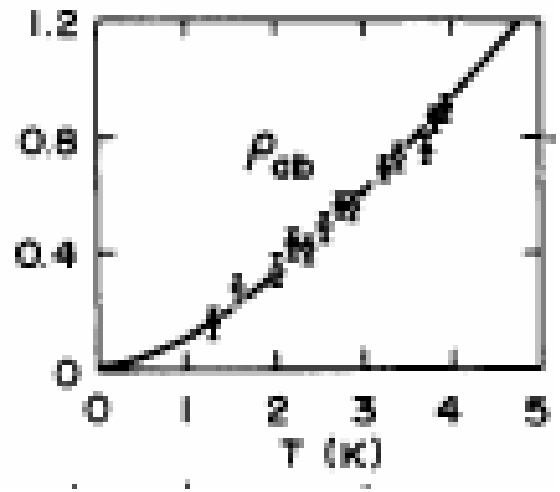
1d lattice dynamics --- the only known example.



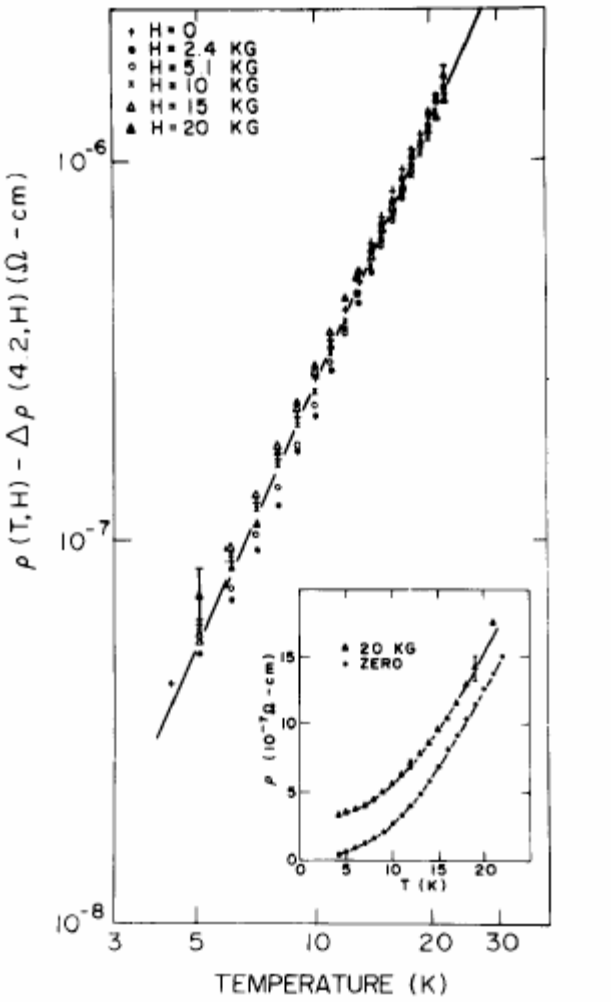
1d metallic chains

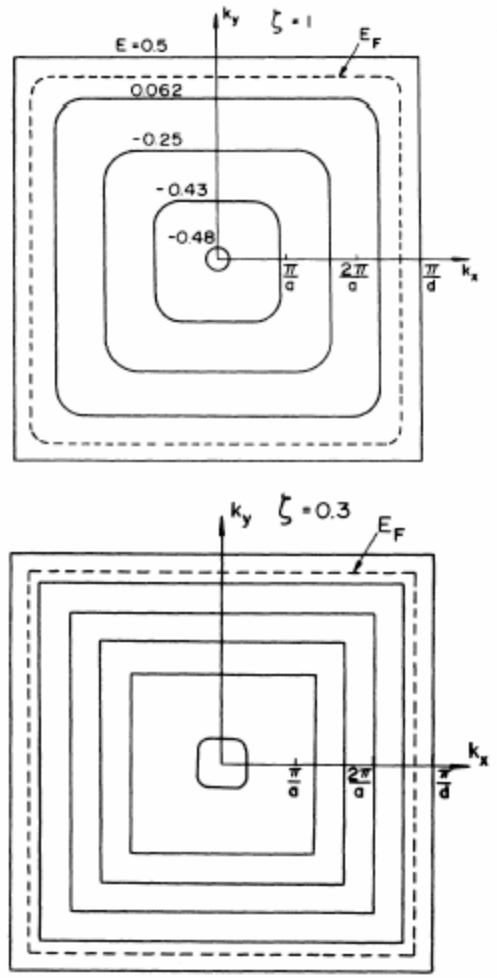


Resisitivity measurements provide evidence of attractive electron-electron interactions ---
Superconductivity in 1d at T = 0 K (?)



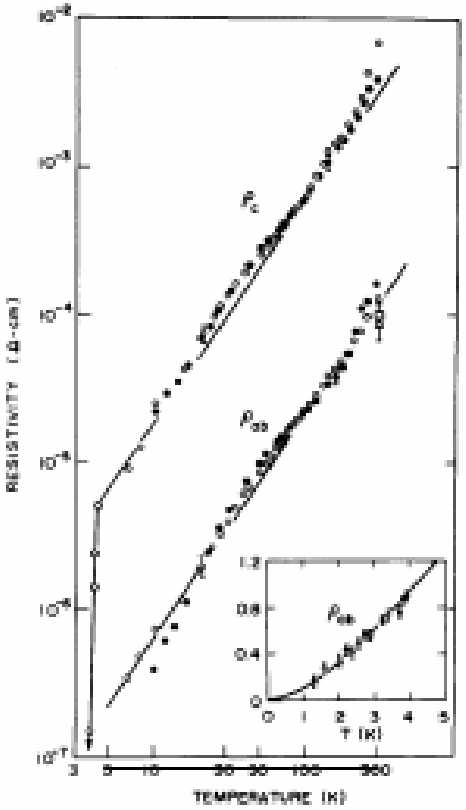
Magnetic field dependent residual resistivity that arises from the Fermi surface of the weakly coupled chains





Anisotropic superconductivity: $\rho_{\perp}(T)$ drops to zero at 4.1K

Intrinsic phenomenon ---
or
Hg excluded from the chains on the b-c and a-c planes ???



Note: Anisotropic Meissner effect

R. Spal, C.K. Chiang, A. Denenstein, A.J. Heeger,
N.D. Miro and A.G. MacDiarmid,
Phys. Rev. Lett. 39 650 (1977).

Thanks for listening!

Research done in 1977-1979 (during the period of initial work on semiconducting and metallic polymers)

Not my most cited work ---

But perhaps the best fundamental work ever done on one-dimensional phenomena in solids.

Acknowledgement:

Gen Shirane
Vic Emory
Arnold Denenstein

Meir Weger
Mark Azbel
Alan MacDiarmid

Richard Spal
Dan Moses
KiBong Lee

Andrew McGhie