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SPRING COLLEGE IN CONDENSED MATTER
ON
'PHYSICS OF LOW-DIMENSIONAL SEMICONDUCTOR STRUCTURES'
(23 April - 15 June 1990)

ELECTRON PROPERTIES OF LOW DIMENSIONAL ORGANIC CONDUCTORS

John R. COOPER
University of Cambridge
Cavendish Laboratory
Interdisciplinary Research Centre in Superconductivity
West Cambridge Site
Madingley Road
Cambridge CB3 0HE
United Kingdom

Electronic Properties of low dimensional organic Conductors

(J. R. Cooper)

Lecture 1 - Introduction

Since early 1970's single crystals of many new materials have been synthesised that have metallic conductivity (σ) ($d\sigma/dT < 0$) and large electrical anisotropy. $\sigma_{\parallel} \simeq 10^2 - 10^4$ (ohm cm)$^{-1}$ at 300 K and $\sigma_{\parallel}/\sigma_{\perp}$ 10 – 10^4. Low dimensional or quasi-one-dimensional conductors.

Inorganic – usually chains of transition metal atoms with unfilled d-orbitals

e.g. Potassium tetracyanoplatinate $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$ KCP (Figure 1)

Niobium triselenide $NbSe_3$ (Figures 6a – 6e)

Tantalum trisulphide TaS_3, Blue bronze $K_{0.3}MoO_3$, $(TaSe_4)_2I$, $(NbSe_4)_{10/3}I$ etc.

Organic conductors (lecture 2 onwards)

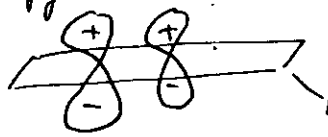
TTF-TCNQ - tetrathiafulvalene tetracyanoquino-dimethane

$(TMTSF)_2X$ – Bechgaard salts \ also superconductors

$(BEDT\text{-}TTF)_mX_n$ or 'ET' salts /

all composed of large planar molecules

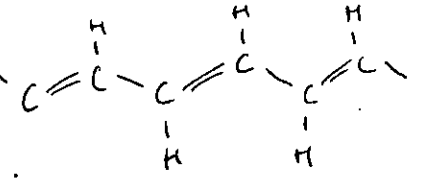
Highest energy electron orbitals have "π" symmetry



Molecules stack face to face in columns. Good electron overlap along the stacks - very weak overlap in two perpendicular directions hence electrical conductivity of single crystals can be highly anisotropic.

Conducting polymers

e.g. polyacetylene $(CH)_x$



not dealt with here but they also have some one dimensional properties.

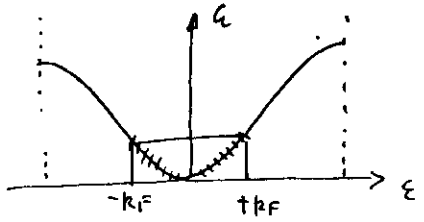
Peierls transition

Peierls (Ann. Phy. 4, 121 (1930) and "Quantum Theory of Solids" Oxford University Press (1955) p. 108) first showed that a one-dimensional metal has a tendency to undergo a metal - semiconductor transition associated with a periodic lattice distortion – the Peierls distortion

Nice treatment given by G. A. Toombs in review "Quasi-one-dimensional Conductors" Physics Reports 40, 181-240 (1978) (Ref. 1)

see also article by A. Bjeliš in "Low Dimensional Conductors ... " NATO ASI Series. Plenum (1987)

Free electrons in one dimension



Apply a periodic perturbation $\phi_q e^{-iqx}$ or $\phi_q \cos qx$

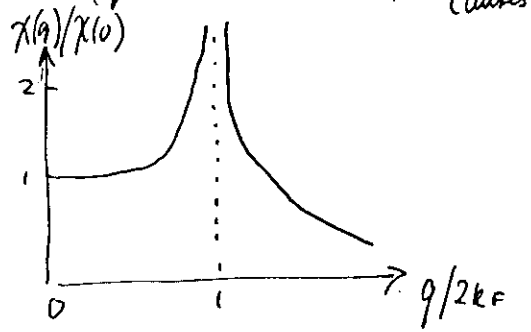
Then induced charge density $\rho_q = \chi(q)\,\phi_q$

where $\chi(q) = \sum_k \dfrac{f_k - f_{k+q}}{\varepsilon_k - \varepsilon_{k+q}}$ ..... (1)

$\chi(q)$ is density response function or dielectric response function. f_k is Fermi factor $\dfrac{1}{(\exp \beta\varepsilon_k + 1)}$

$\beta = \frac{1}{kT}$, ε = electron energy (see. eg. Ziman "Introduction to the Theory of Solids")

as $T \to 0$ $\chi(q = 2k_F)$ diverges logarithmically (also causes phonon softening Figure 5b)



If lattice distorts to give a $2k_F$ potential (V_{2kF} opens at Fermi level.

Energy gained by electrons $- \chi(2k_F)|V_{2kF}|^2$ always exceeds energy needed to distort the lattice. Peierls instability.

Mean field theory - phase transition when

$$\lambda\,\chi(2k_F)/N(0) = -\lambda \ln k_B T / 1.14 \cdot 2\varepsilon_F \geq 1 \quad \text{..... (2)}$$

i.e. $$T_p \simeq T_F \exp -\frac{1}{\lambda} \quad \text{..... (3)}$$

where T_F is the Fermi temperature and λ is the dimensionless e-ph. coupling constant $\lambda = I^2 N(0)/M\omega^2$. I is the electron-phonon matrix element, M is the ionic mass and ω is the 'bare' phonon frequency at $2k_F$.

According to the argument of Landau strictly speaking there are no phase transitions in a 1D system, at least for finite range forces. For example a chain of spins with nearest neighbour exchange interaction J

..... ↑ ↑ ↑ ↑ ↑ ↑ ↑ .....

will always tend to break up into domains with different spin directions. If there are N sites the free energy gain on reversing the spins after any one site is $\Delta F = 2J - kT \ln N$ ..... (4)

However there will be short range order over a correlation length $\xi_{11}(T) \simeq a \exp(2J/kT)$ (obtained by setting $\Delta F = 0$ in equation 4). This correlation length diverges as $T \to 0$. In real quasi-1D systems, a divergence of ξ_{11} will lead to long range 3D order even for very weak

A specific example for a magnetic system the $S = \frac{1}{2}$ Heisenberg chain is given in Figure 3 taken from Ref. 3. The total spin entropy is $k_B \ln 2$ per site. The specific heat measurements in Figure 3 show that as T is lowered most of this entropy is frozen out because of the on-chain interaction $J_{\parallel}$ which gives short range order and a broad peak in specific heat. A sharp peak (corresponding to 3D order) is only obtained at low temperatures. Note that the transition temperature $T_c \sim \frac{1}{k_B}\sqrt{J_{\parallel} J_{\perp}}$ - because as the on chain correlation length grows the effective interchain interaction increases.

It is believed that similar effects occur for Peierls transitions in quasi one dimensional conductors. As first discussed in ref. 4. a Peierls gap will develop on the conducting chains at temperatures $T \simeq T_P^{MF}$ - the mean field transition temperature given by eq. 3. However a true phase transition corresponding to long range order with singularities in specific heat (and in $d\sigma/dT$) will occur at a lower temperature, perhaps as low as $\frac{1}{3}$ to $\frac{1}{4}$ of T_P^{MF} depending on the interchain interactions. An example of experimental results interpreted in this way is shown in Figure 4. The metal-semiconductor (Peierls) transition temperature of TCP is considerably sharpened by application of hydrostatic pressure. According to the above argument this is because the difference between T_P^{MF} and T_P^{3D} is reduced as pressure is applied and the interchain coupling is increased.

A special feature of the Peierls semiconductor state, as distinct from usual semiconductors, is that the energy gap is tied to the Fermi level (Fig. So if the electrons are given a drift velocity by application of an electric field the energy gap will "follow" the electron distribution. This leads to the possibility of an enhanced conductivity arising from a collective motion of the electrons and the lattice - Fröhlich conductivity. This conductivity is usually treated as motion of a charge density wave (CDW). Namely the electron density is non-uniform in the Peierls state:

$$\rho(x) = \rho_0 + \frac{\rho_0 \Delta}{\hbar v_F k_F} \cos(2k_F x + \phi) \quad \text{- - - -} \quad (5$$

where 2Δ is the mean field energy gap, $2\Delta = 3.5 k_B T_P^{MF}$

of the phase of the CDW is not fixed to the underlying lattice - as happens when $2\pi/2k_F$ is not an integral multiple of the lattice spacing, then the CDW can be made to "slide" by

application of an electric field. That is to say (7)
its phase ϕ varies with time. Uniform motion,
corresponding to $\dot{\phi}$ = const throughout the crystal,
gives an extra electrical current density

$$j_{cdw} = \rho_0 e v_s \quad \ldots\ldots \quad (6)$$

where v_s, the drift velocity of the CDW is
given by $v_s = \frac{\dot{\phi}}{2k_F}$, and ρ_0 is the total electron density

In real materials the CDW is pinned
by defects and sometimes by interaction with
the lattice or with CDWs on neighbouring
chains. The extra CDW conductivity is only
observed above a certain threshold field
E_T. Some experimental results which provided
the first evidence for CDW conductivity above
E_T are given in Figures 6a to 6e. They
were taken on single crystals of $NbSe_3$ (Refs. 5)
$NbSe_3$ is slightly unusual in that there are three
inequivalent Nb chains, one of which does not
undergo a Peierls transition, hence $NbSe_3$ remains
a good conductor down to $T = 0$. The other two
chains undergo Peierls distortions giving large
increases in resistivity (Figure 6b). Note that these
anomalies are not observed at microwave frequencies
(9 GHz). This is a consequence of the unusual
frequency dependence of CDW conductivity associated (8)
with the peculiar dynamics of charge
density waves (for a recent review see reference
5) Typical current-field and derivative (dV/dI)
curves are shown in Figure 6c. The threshold field
is nearly 6 mV/cm. The enhancement of the
conductivity is typically 2 to 10 times
larger than the (ohmic) value observed below
threshold. In all materials studied until
now (including spin density waves to be
discussed in Lecture 4) the extra CDW
conductivity observed with DC techniques has
similar magnitude and temperature dependence
to the 'normal' electron conductivity measured
below E_T.(7) Initially this was a problem because
the maximum current associated with the Fröhlich
mechanism (corresponding to equation (6) with $v_s \approx \frac{\Delta}{\epsilon_F} v_F$,
is much larger than the normal conductivity.
(The ratio should be at least $\Delta \exp(\Delta/kT)/e E_T \ell$
where ℓ is the electron mean free path).

However as explained in ref. 6 for example,
it is now thought that the CDW does
not propagate rigidly with constant and uniform
values of ϕ. Instead it is distorted and

propagates past different pinning centres. On a local scale this changes the electron density in a non-uniform way and causes a flow of normal electrons. Thus there is a dissipation of energy (or a CDW 'viscosity') which is proportional to the ohmic resistivity $1/\sigma(T)$.

Another interesting property of CDW crystals is the presence of narrow band noise above the threshold field. As shown in Figure 6d a spectrum analysis of the noise voltage shows well defined peaks in the kHz and MHz frequency range. The fundamental frequency (f_0) increases linearly with the excess current carried by the CDW. (Figure 6e). It is quite precisely given by the relation

$$v_s = \frac{2\pi}{2k_F} f_0 \quad \ldots\ldots \quad (7)$$

combined with equation (6) for j_{CDW}.

There is some preliminary evidence for such narrow band noise in low dimensional organic conductors but there is also room for much more experimental work.

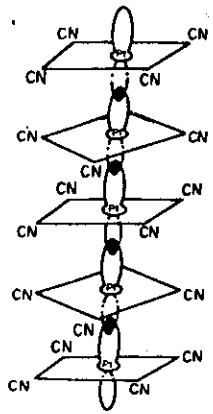
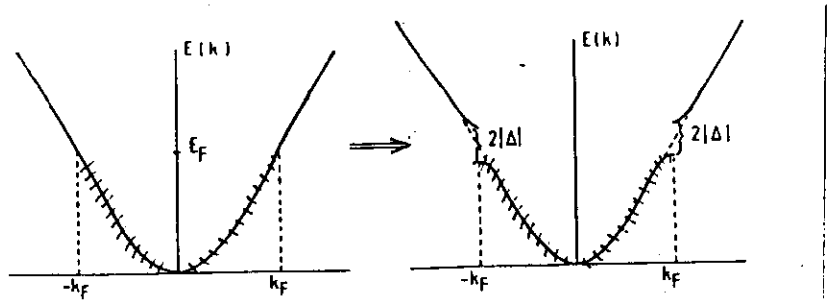
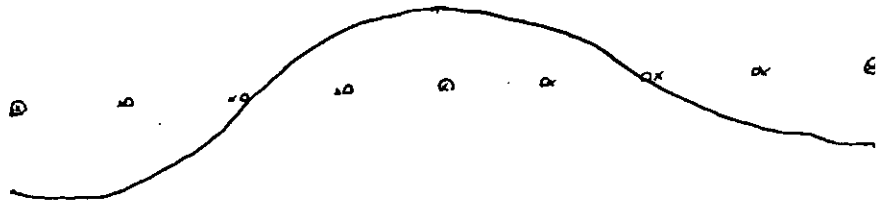


FIG. 27. — *Unit cell of $K_2Pt(CN)_4Br_{0.30}.3H_2O$ (KCP) projected along the c and b axes* (reproduced with permission of [115]).

Figure 1

Figure 2 PEIERLS DISTORTION AND CDW





× undistorted lattice — electron density

o distorted lattice

Fig. 20

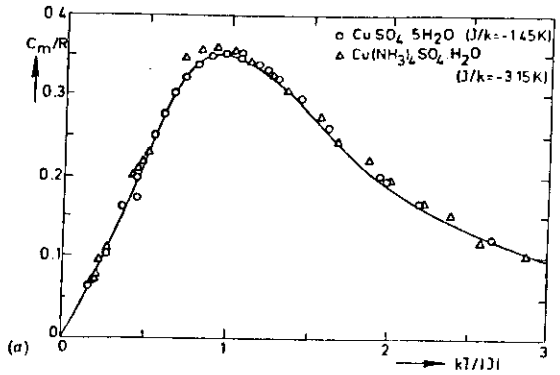
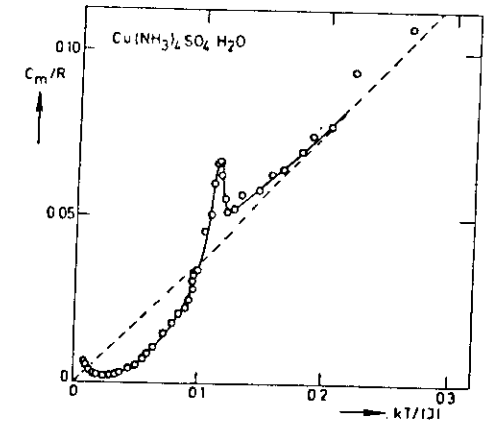


Figure 3a



Specific heats of two examples of the antiferromagnetic, $S=\frac{1}{2}$, Heisenberg chain (for the references, see the text). (*a*) Fit of the data to the theoretical curve of Bonner and Fisher (1964) (J/k is the only adjustable parameter). (*b*) The low-temperature region, in which in the case of $Cu(NH_3)_4SO_4 \cdot H_2O$ the transition to long-range 3-d ordering has been observed. The dashed curve is the theoretical specific heat, which is linearly dependent on temperature at the lowest temperatures. The increase in C_m observed below $kT/|J| \simeq 0{\cdot}03$ is due to the hyperfine contribution.

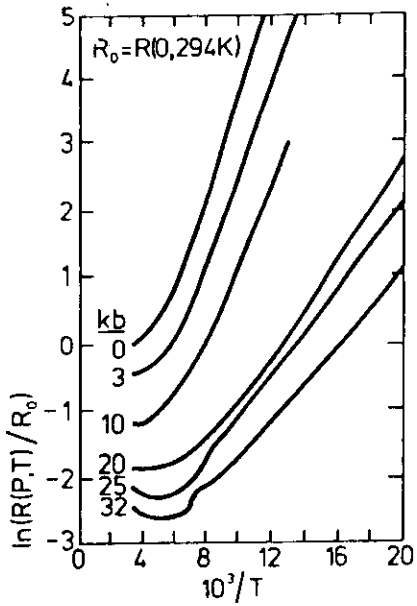


Figure 4

Figure 5a Fröhlich conductivity

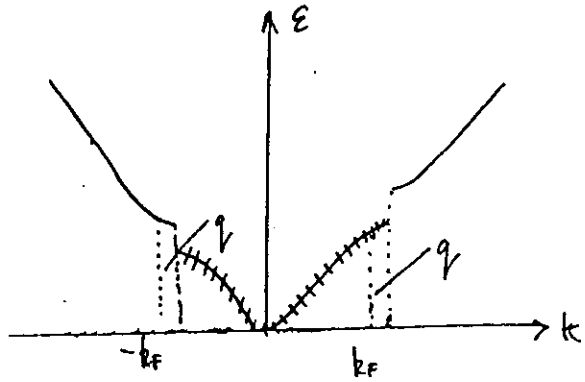


Figure 5b

Soft phonons

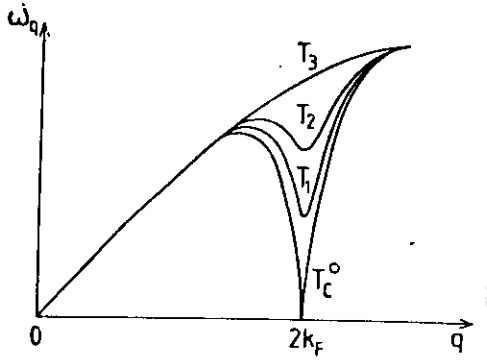
phonons

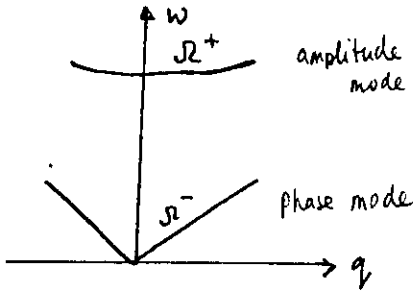
$T \gtrsim T_c$

phase and amplitude modes of CDW

CDW

$T < T_c$





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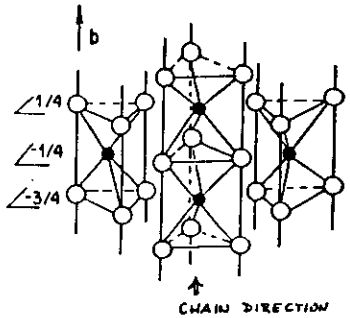
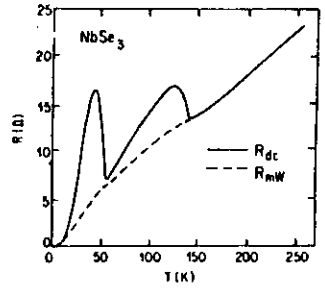
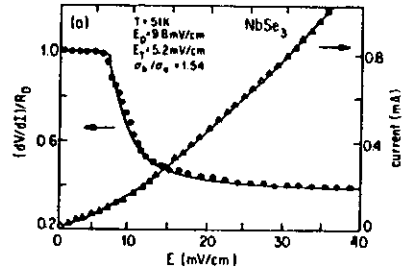


Figure 6a

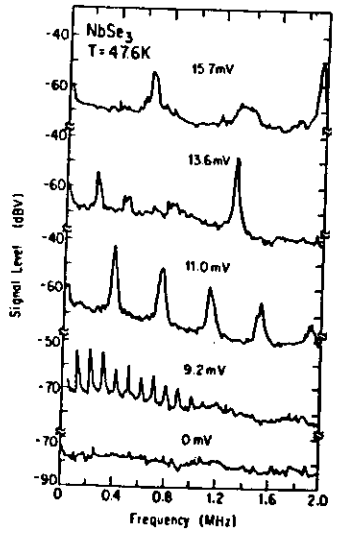
Some CDW properties of $NbSe_3$



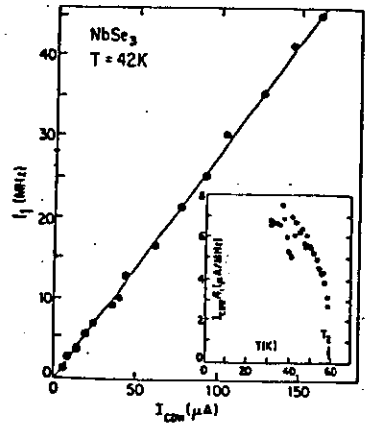
6(b)



6(c)



6(d)



6(e)

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(2) A. Bjelis in "Low Dimensional Conductors and Superconductors" D. Jérome and L. Caron Editors NATO ASI Series, Plenum (1987) P. 409

(3) A. Miedema and L. de Jongh "Experiments on simple magnetic model systems" Advances in Physics (1974)

(4) P.A. Lee, T.M. Rice and P.W. Anderson Solid State Commun. 14, 703 (1974)

(5) G. Grüner and P. Monceau in "Charge Density Waves in Solids" Edited by L.P. Gor'kov and G. Grüner Elsevier Science Publishers B.V. 1989.

(6) R.M. Fleming in "Low Dimensional Conductors and Superconductors" Loc. cit. P. 433

(7) One possible exception to this statement is the blue bronze $K_{0.3}MoO_3$ for which $j_{CDW} >> j_{normal}$ at 4.2 K. G. Mihaly and P. Beauchêne Solid State Commun. 63, 911 (987)