CHARGE FLUCTUATIONS AND SUPERCONDUCTIVITY IN LAYERED MOLECULAR CRYSTALS

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OUTLINE

- In layered molecular crystals D_2X with the θ and β'' arrangement of the donor molecules D one observes a subtle competition between metallic, superconducting, insulating, and charge ordered phases.
- The simplest strongly correlated electron model that can describe this competition is an extended Hubbard model at quarter filling on the square lattice.
- Using slave-boson theory we show that near the quantum critical point for charge ordering superconductivity occurs with d_{xy} symmetry and is mediated by charge fluctuations.
- This is in contrast to the κ-(BEDT-TTF)$_2$X family, for which theoretical calculations give superconductivity mediated by spin fluctuations and with $d_{x^2-y^2}$ symmetry.

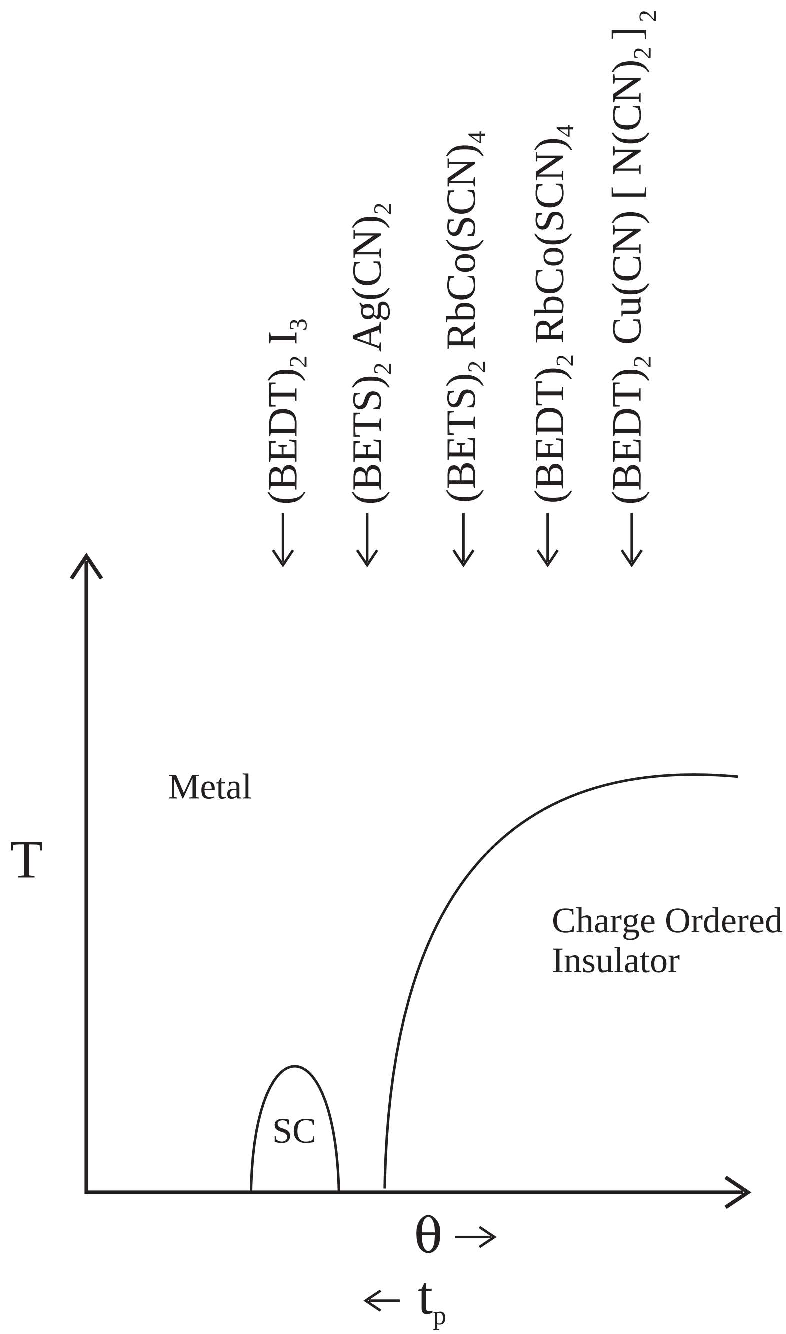
STRUCTURE OF LAYERED MOLECULAR CRYSTALS, D_2X

- X is an anion (e.g., $X=CsZn(SCN)_4$) which captures an electron from each pair of donor molecules (e.g., D=BEDT-TTF):

$$[D^{+0.5}]_2X^{-1}$$

- Alternating conducting layers of donor molecules and insulating layers of anions.
- Layered crystal structure leads to quasi-two-dimensional electronic properties.
- Greek letter (e.g., θ, κ, β") denotes different packing patterns for the donor molecules.

SCHEMATIC PHASE DIAGRAM OF θ-D_2X



Proximity to a charge ordering quantum critical point?

Quasi-one-dimensional vanadium bronzes

Yamauchi, Ueda, and Mori, submitted to *Nature.*

The common features of these 11 superconductors are

- quarter filling
- proximity to an insulating phase
- proximity to charge ordering

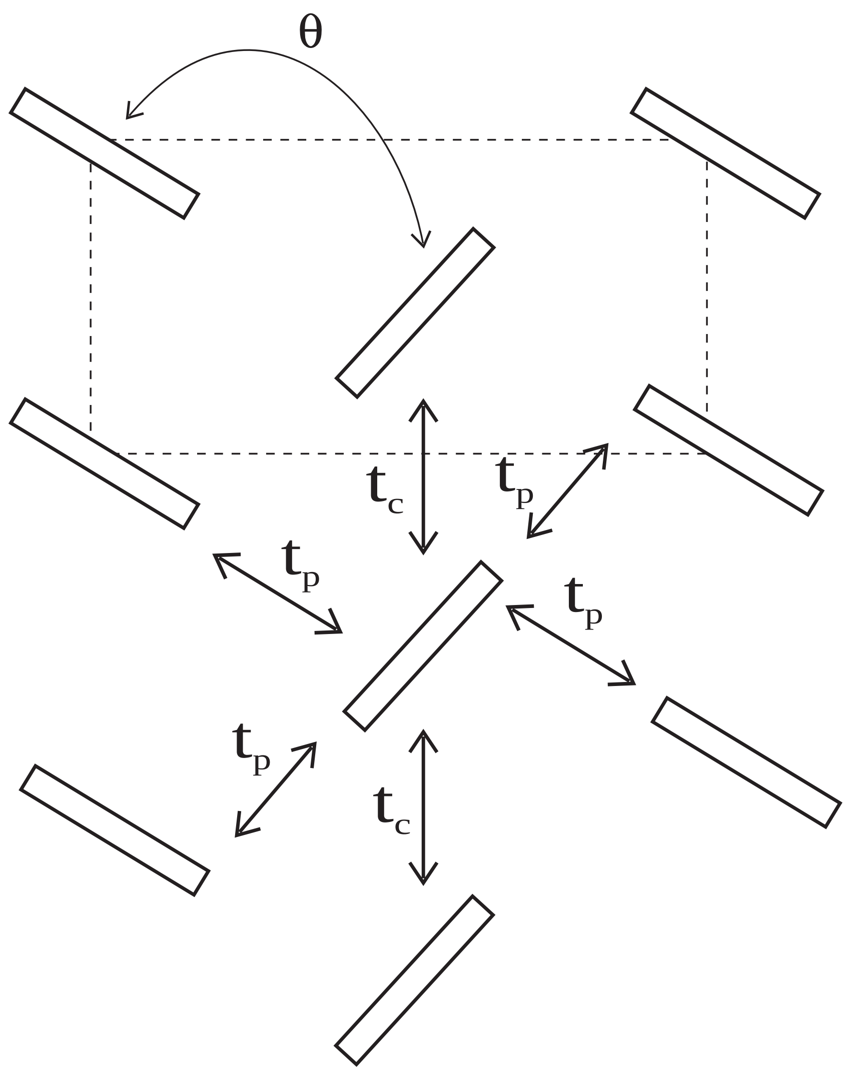
5 of the 11 have the unusual property that the resistivity increases with decreasing temperature before becoming superconducting at T_c.

The evidence for charge ordering (i.e., half of the donor molecules have a charge of more than +0.5e and half less than +0.5e) comes from from Raman scattering, X-ray diffraction and NMR.

MAGNETIC SUSCEPTIBILITY IN THE INSULATING PHASE

Temperature dependence of magnetic susceptibility

TIGHT-BINDING MODEL FOR θ-D_2X



Charge of $+0.5e$ corresponds to a quarter-filled band.

Generally $t_c \ll t_p$.

All materials should be metals!

Need to include effects of interactions.

EXTENDED HUBBARD MODEL

This is the simplest strongly correlated electron model that can potentially account for the competition between metallic, charge ordered and superconducting phases, at quarter-filling on a square lattice. The Hamiltonian is

$$H = t \sum_{<ij>,\sigma} (c^\dagger_{i\sigma} c_{j\sigma} + c^\dagger_{j\sigma} c_{i\sigma})$$

$$+U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_{<ij>} n_i n_j - \mu \sum_{i\sigma} n_{i\sigma}$$

t is the hopping amplitude between neighbouring sites.

U is the on-site Coulomb repulsion.

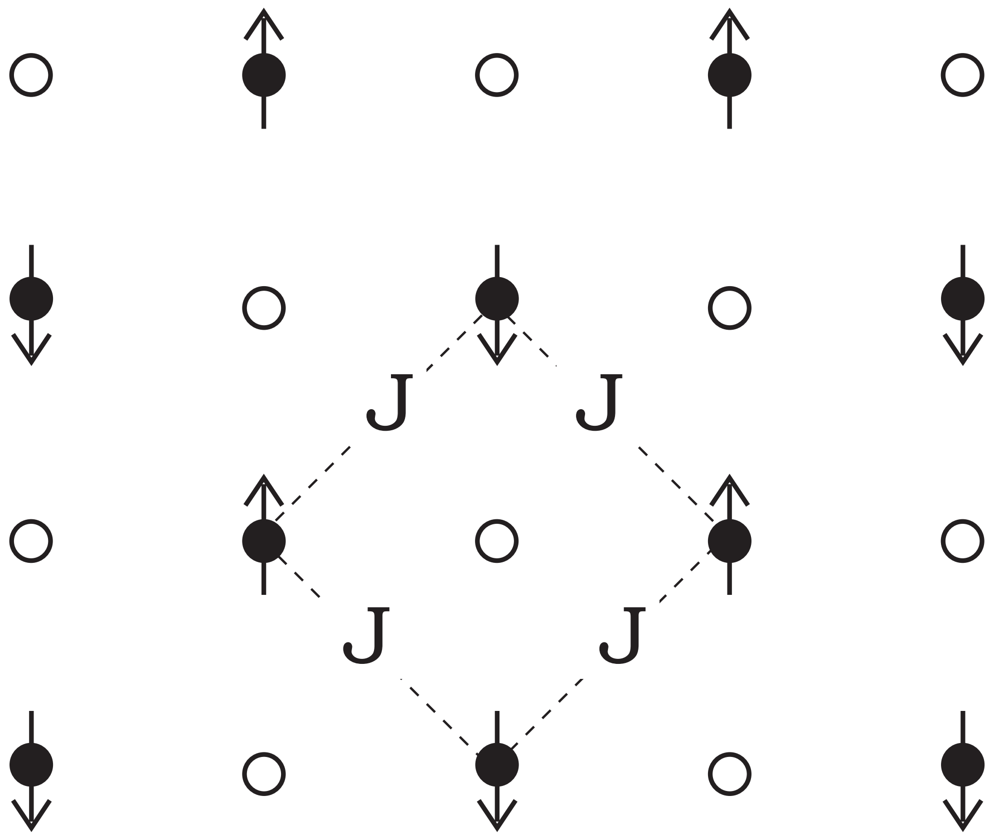
V is the nearest-neighbours Coulomb repulsion.

CHARGE ORDERED PHASE

$$U \gg V \gg t$$

Quantum chemistry calculations predict $U \gg V, t$ so that doubly-occupied sites are precluded.

In the limit $V \gg t$, we have a checker board charge-ordered insulator.



• Antiferromagnetic interaction J is due to fourth order processes.

ANTIFERROMAGNETIC INTERACTION

Ring-exchange spin process

Spin degrees of freedom are described by an antiferromagnetic Heisenberg Hamiltonian:

$$H = J \sum_{\langle \mathbf{ij} \rangle} \mathbf{S_i} \cdot \mathbf{S_j}$$

with $J = 4t^4/9V^3$ along the diagonals of the original square lattice.

METALLIC PHASE

$V/t \to 0$ limit

- The Hubbard model ($V = 0$) with $U \to \infty$, and at quarter-filling is expected to be metallic.

- Is there a quantum phase transition between the metallic and insulating charge ordered phases at a finite V/t?

- If so, can superconductivity occur close to the quantum phase transition?

SLAVE-BOSON THEORY

Barnes (1976), Read and Newns (1983) Coleman (1984).

- Applicable to models with $U \to \infty$:
- Extensively applied to the Kondo, Anderson, and $t - J$ models.
- The SU(2) symmetry associated with the electron spin is extended to SU(N). The large N limit is then considered.
- Mean-field theory gives a good description of the Kondo effect for $T < T_K$.
- $1/N$ corrections may be computed.

Kotliar and Ruckenstein (1986) generalised this to finite U:

- predicts Mott metal-insulator transition in the Hubbard model at half-filling.
- mean-field theory is equivalent to the Gutzwiller approximation

SLAVE-BOSON REPRESENTATION

Replace the electron operators by

$$c_{i\sigma}^{\dagger} = f_{i\sigma}^{\dagger} b_i$$

$f_{i\sigma}^{\dagger}$ is a neutral fermion that carries spin σ
b_i is a charged spinless boson.
This preserves the fermion anti-commutation relations when doubly occupied sites are precluded and the bosons satisfy the constraint

$$f_{i\sigma}^{\dagger} f_{i\sigma} + b_i^{+} b_i = N/2.$$

Projected Hilbert space

$$b_i|\Omega\rangle = f_{i\uparrow}|\Omega\rangle = f_{i\downarrow}|\Omega\rangle = 0$$

$$f_{i\uparrow}^{\dagger}|\Omega\rangle = |i\uparrow\rangle, f_{i\downarrow}^{\dagger}|\Omega\rangle = |i\downarrow\rangle$$

$$b_i^{\dagger}|\Omega\rangle = |i0\rangle$$

SLAVE-BOSON THEORY: $N \to \infty$
Renormalized Fermi Liquid

σ is allowed to vary from $1, .., N$.

Taking the mean-field value of the boson fields:

$$b = \langle b_i \rangle, \lambda = \langle \lambda_i \rangle$$

we get a renormalized Fermi liquid (i.e., metallic) phase with dispersion

$$\epsilon_{\mathbf{k}} = \frac{-tb^2}{N} T_{\mathbf{k}} + \lambda - \mu + 4V \frac{n}{N}$$

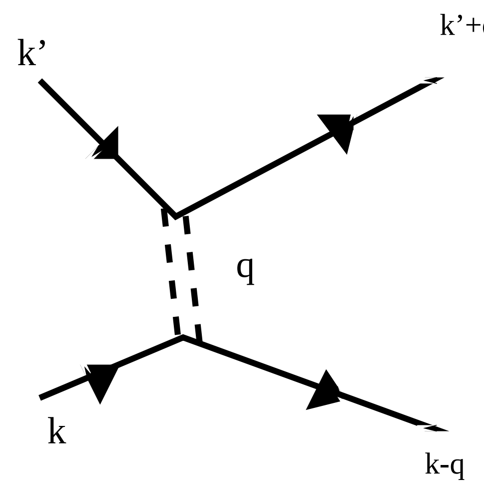
where $T_k = 2(\cos(k_x) + \cos(k_y))$
$b^2 = N/2 - n$
n is the band filling.
At a quarter filling $(N = 2, n = 1/2)$ the correlations reduce the band width by a factor of two.

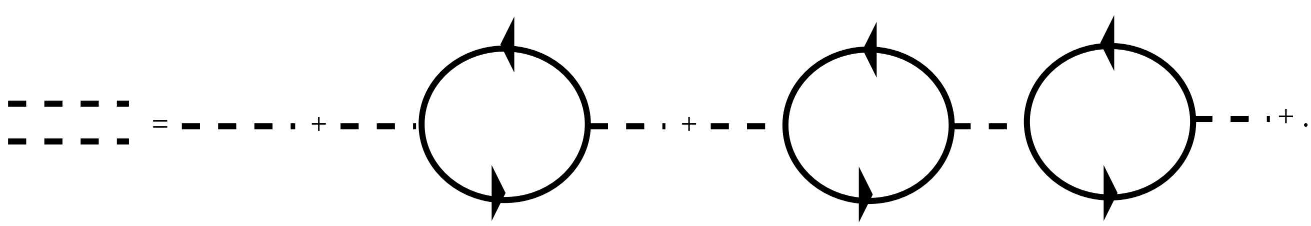
SLAVE-BOSON THEORY: $1/N$ CORRECTIONS

Fluctuations of the Fermi liquid

Using a path integral formulation, and taking into account fluctuation of boson fields we arrive at an effective fermion-boson problem

$$H = H^f + H^b + H^{f-b}$$





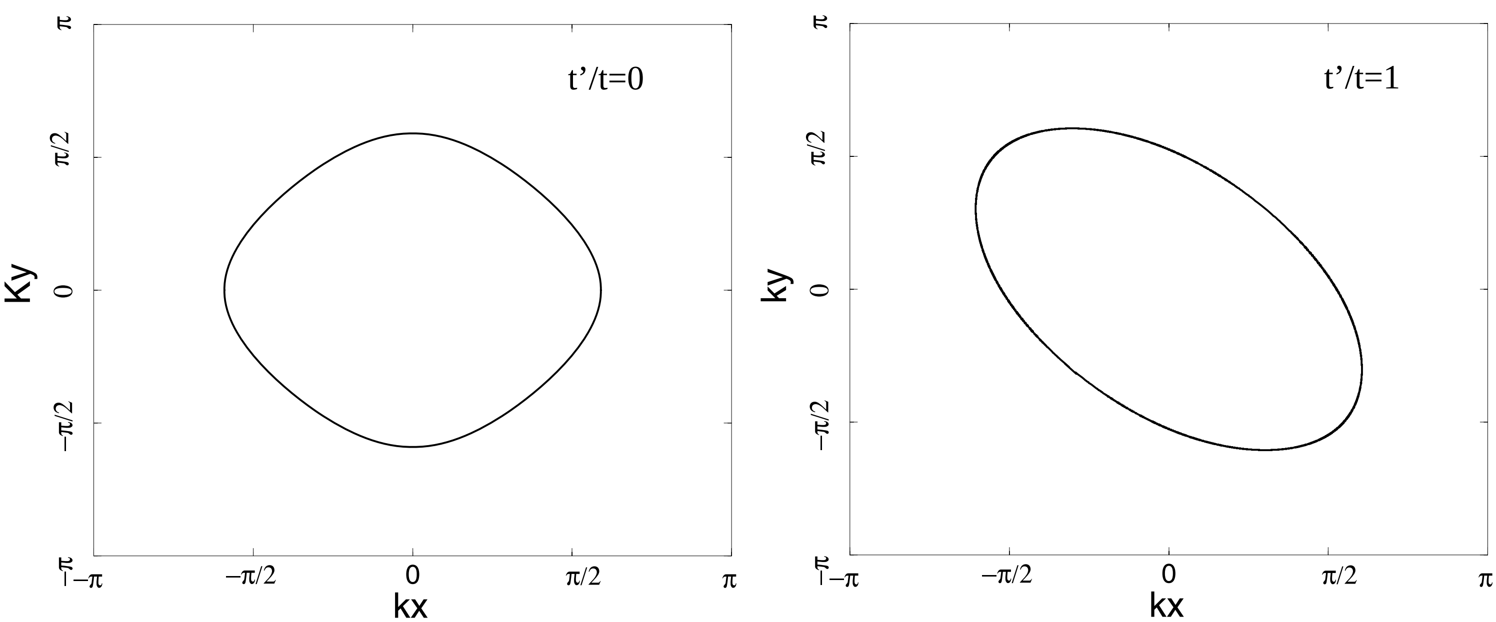
Bosons arise from the electron-electron interaction, resummation includes all diagrams to order $1/N$.

INSTABILITY TO CHARGE ORDERING

• The charge susceptibility diverges at $\mathbf{q} = (\pi, \pi)$ at $V/t = (V/t)_c = 0.69$: quantum phase transition from a metal to checkerboard charge ordering.

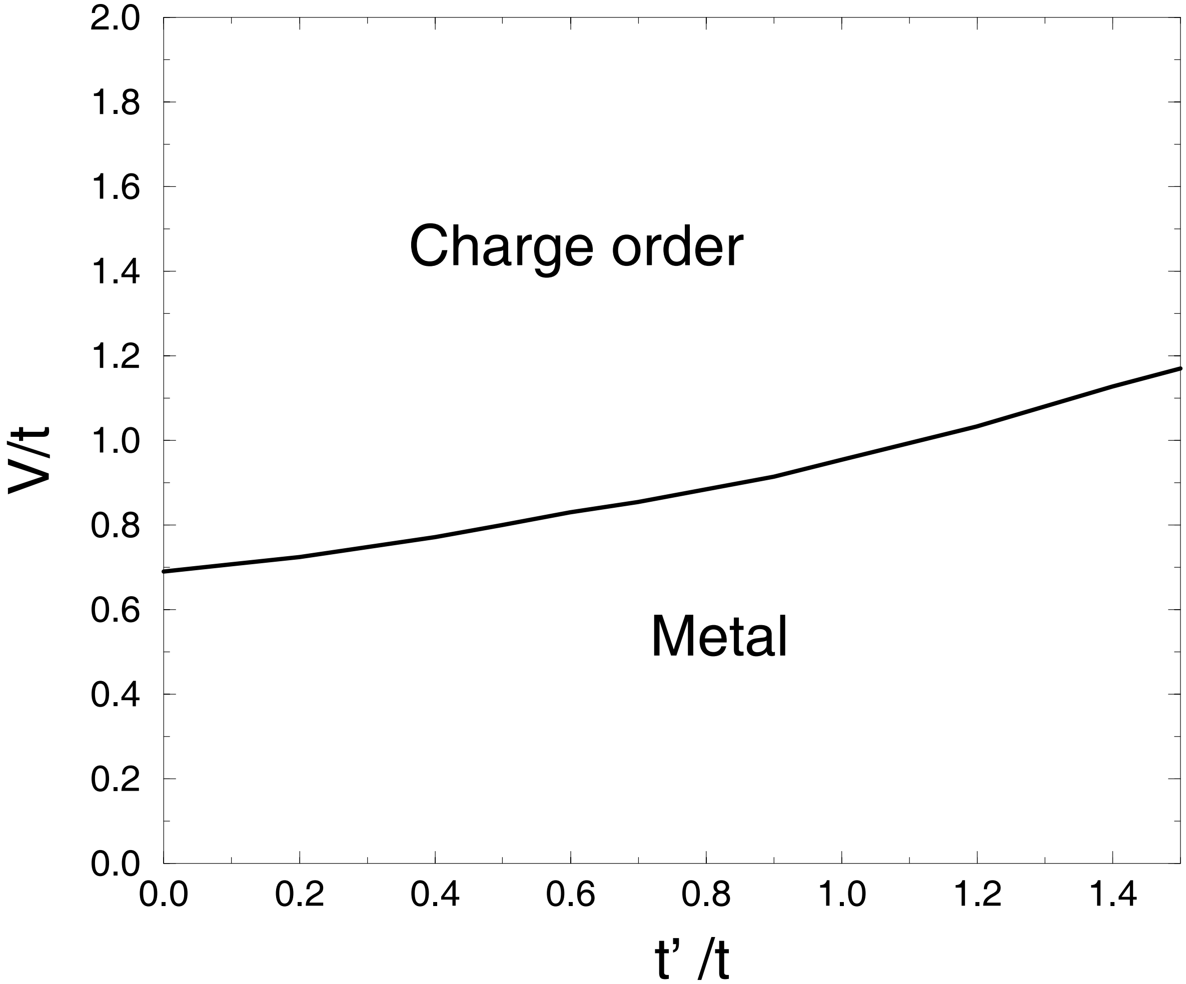
• Charge ordering is NOT due to nesting of the Fermi surface as it is quarter-filled.

FERMI SURFACE



INSTABILITY TO CHARGE ORDERING

Phase diagram for anisotropic lattice



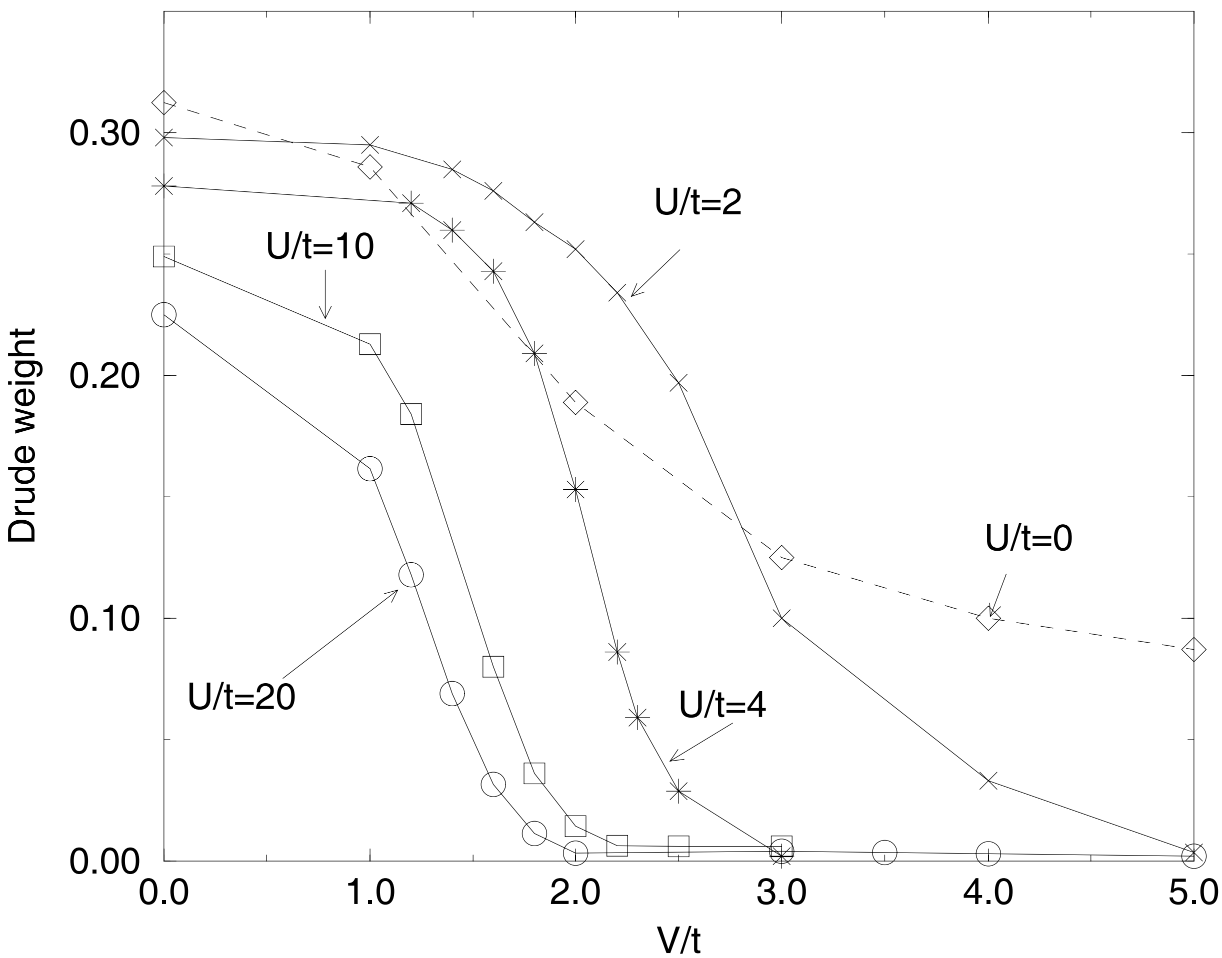
• V/t or t'/t can drive the system through the transition.

METAL-INSULATOR TRANSITION

Exact diagonalisation of 4×4 lattice

J. Merino and M. Calandra

Drude weight versus V/t



INSTABILITY TO SUPERCONDUCTIVITY

Symmetry of the Cooper pairs

$$\Delta_{s^*}(\mathbf{k}) = \cos(k_x) + \cos(k_y)$$

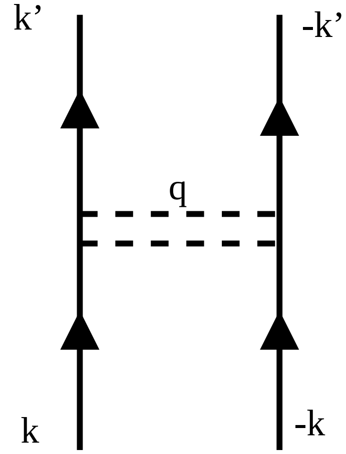
$$\Delta_{d_{x^2-y^2}}(\mathbf{k}) = \cos(k_x) - \cos(k_y)$$

$$\Delta_{d_{xy}}(\mathbf{k}) = \sin(k_x)\sin(k_y)$$

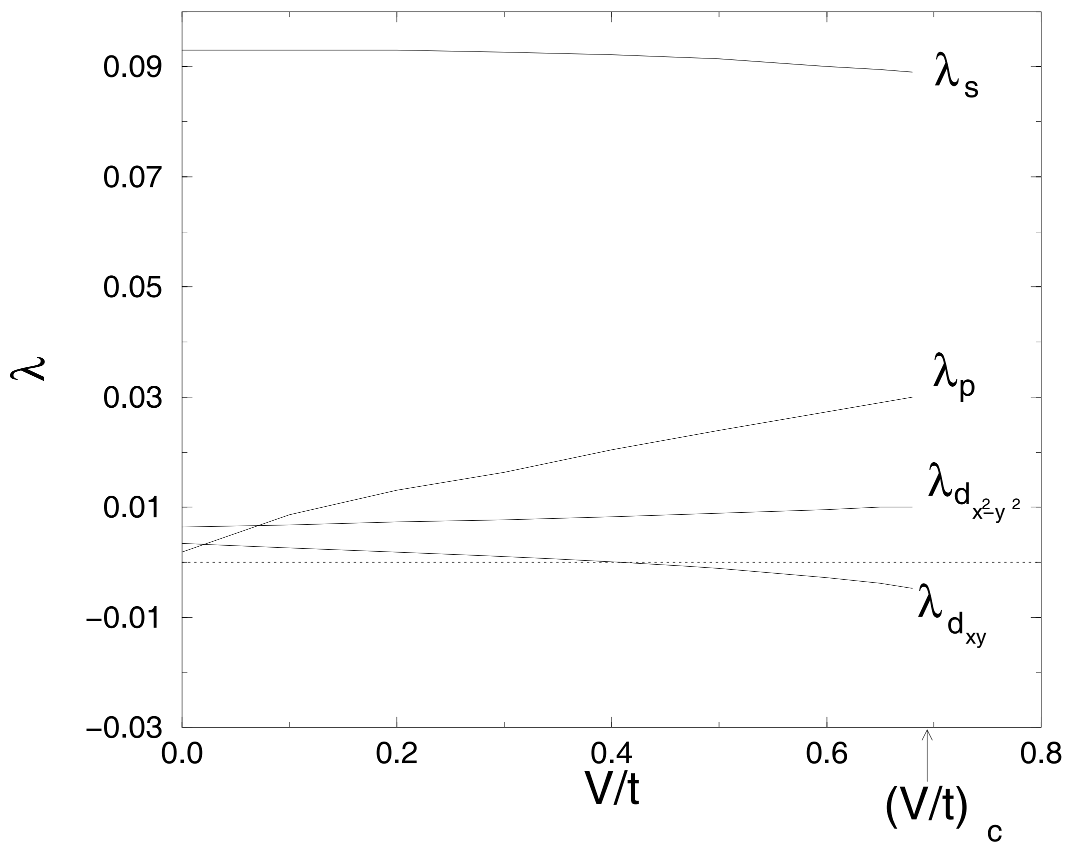
INSTABILITY TO SUPERCONDUCTIVITY

Attraction in the d_{xy} channel

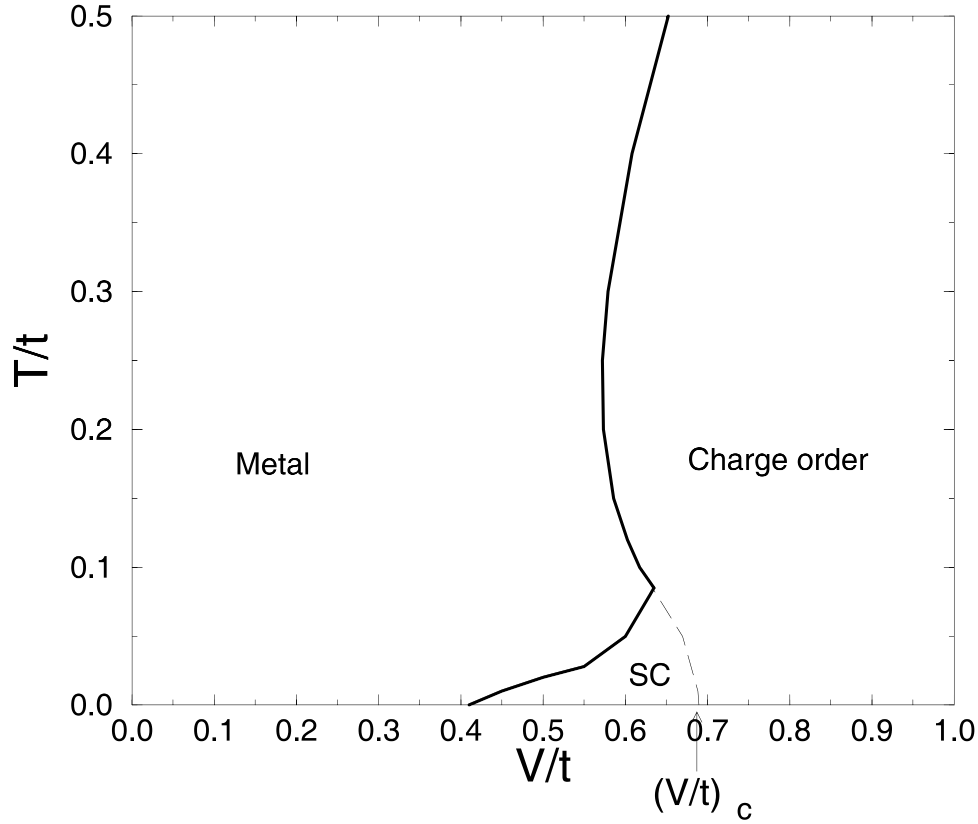
Particle-particle scattering channel



Different Cooper pairing channels



FINITE TEMPERATURE PHASE DIAGRAM



- Re-entrant behaviour of the charge-ordering transition may explain the anomalous behaviour of resistivity close to T_c.
- Changing the Fermi surface significantly $(0 \leq t'/t \leq 1)$, does NOT destroy d_{xy} pairing. Hence results relevant to β" materials.

PREDICTIONS

- Metallic θ-salts such as θ-$(BETS)_2Ag(CN)_2$, θ-$(BETS)_4Cu_2(Cl)_6$, and θ-$(BO)_2Cl(H_2O)_3$ should become superconducting under pressure.

- Unconventional pairing with d_{xy} symmetry. Polarisation dependent Raman scattering can distinguish d_{xy} from $d_{x^2-y^2}$ and s-wave.

- Above T_c the spin fluctuations should be much less than in the κ-$(BEDT\text{-}TTF)_2X$ materials. This can be detected in nuclear magnetic resonance. For example, the Korringa ratio will not be enhanced.

CONCLUSIONS

- In layered molecular crystals D_2X with the θ and β'' arrangement of the donor molecules D one observes a subtle competition between metallic, superconducting, insulating, and charge ordered phases.
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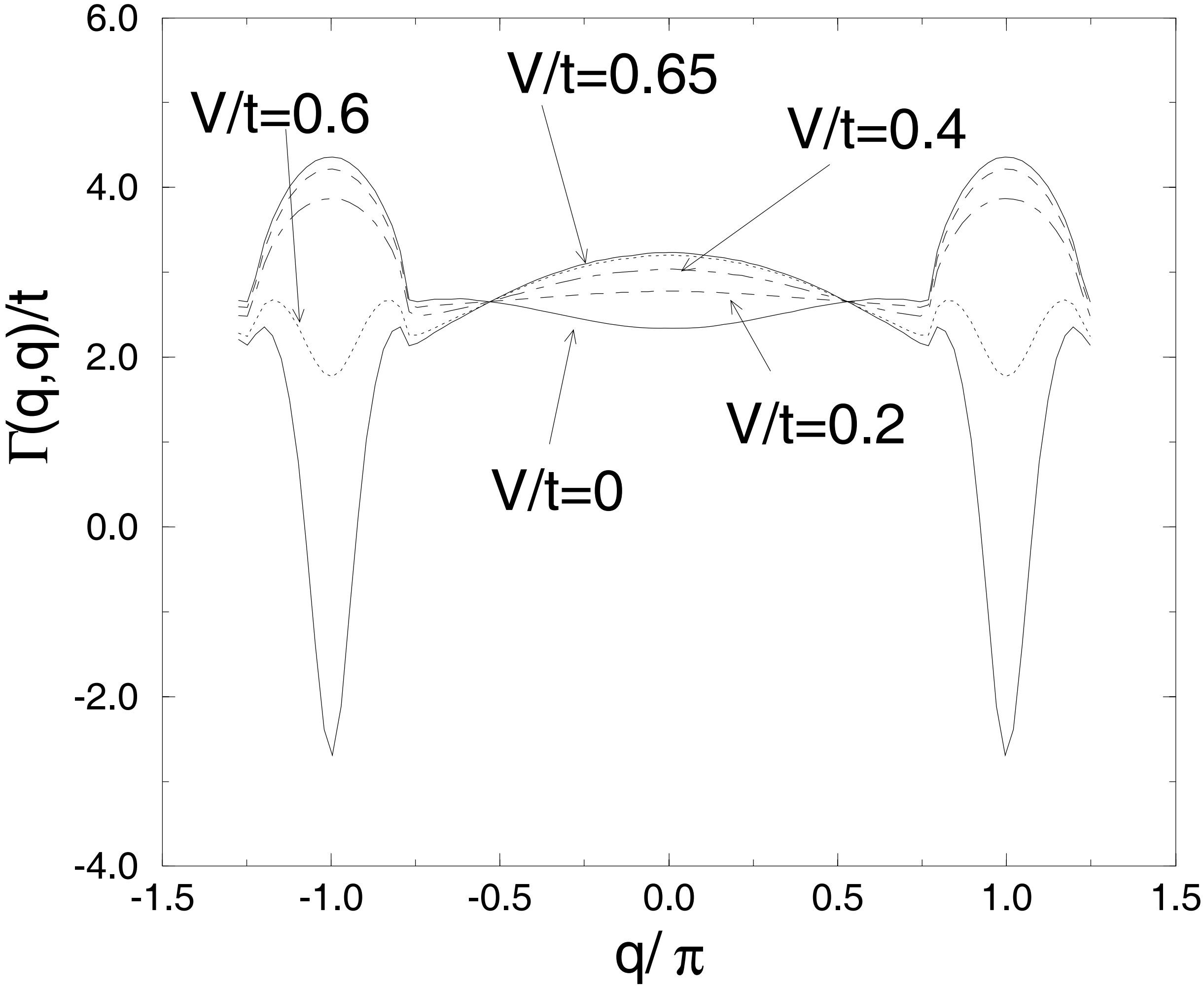
V/t=0.65
V/t=0.6
V/t=0.4
V/t=0.2
V/t=0
Γ(q,q)/t
q/ π
6.0
4.0
2.0
0.0
-2.0
-4.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5

Structure of β''-D_2X