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COMPARATIVE STUDY OF THE CDW SYSTEMS

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Abstract The physics of conducting trichalcogenides ($NbSe_3$) and organic metals (TTF-TCNQ) is considered from the point of view of 1d many body theories. It is argued that the former belong to the Peierls and the latter to the strongly correlated CDW limit.

Our aim is to investigate the applicability of the existing 1d theoretical results[1,2] to the real materials which exhibit the strongly anisotropic quasi 1d conductivity. At the preceding conference our attention was focused on the superconductivity and thereby on the corresponding $(TMTSF)_2$ X materials. In particular the role of Umklapp term g_3 in suppresing the $2k_F$ CDW in favor of the $2k_F$ SDW was mentioned there but the main role in promoting the superconducting instead of the density (SDW, CDW) correlations was attributed to the efficiency of screening of the forward Coulomb scattering, i.e. to the smallness of the corresponding coupling constant g_2 with respect to the backward scattering g_1.

Here we choose to consider the opposite situation in which g_2 is large enough[3] to produce the strong CDW instability. The corresponding class of materials is presumably well represented by the widely studied organic crystal TTF-TCNQ[4].

The CDW instability is in general accompanied by the lattice deformation due to the coupling of electrons to the lattice. In fact it is well known that even in absence of Coulomb forces the coupled 1d electron-phonon system undergoes the Peierls instability. In order to clarify the differences and the similarities between this well

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known case and the more intricate situation with strong Coulomb forces we shall also consider conducting trichalcogenides which fall presumably quite close to the Peierls limit. The extended version of the arguments presented here, except for some most recent conclusions, can be found in two recent review papers[5].

The fact that conducting trichalcogenides fall in the Peierls limit follows on considering their high temperature behavior[6]. The Kohn anomaly is present in $NbSe_3$ already at room temperature but the $2k_F$ phonon softening triggers the lattice instability only at 144K and 59K. Such a slow behavior can be reasonably well fitted by the log T law, which is the high T counterpart of the T=0 Peierls theory. In contrast to that the phonon softening in TTF-TCNQ at 80K is less than 10% of the unrenormalized phonon frequency but the instability occurs already at 54K, followed by two others at 49K and 38K. The singularity involved in these transitions is apparently much stronger than the Peierls log T law. Similar difference between $NbSe_3$ and TTF-TCNQ is found on the pressure scale. TTF-TCNQ is much more sensitive to the pressure than $NbSe_3$ although the two have the comparable elasticities.

Beside these differences the two materials have an important property in common. They undergo the lattice instability at temperatures comparable to the respective phonon frequencies ω_D of the acoustic phonons. Since the mean-field (MF) transition temperature T^o which sets one of the relevant energy scales is higher than the true transition temperature the inequality

$$2\pi\, T^o > \omega_D \tag{1}$$

is well satisfied in both cases. This inequality allows us to neglect all virtual processes involving acoustic phonons (and in particular the Cooper pairing). The lattice field becomes classic when the virtual processes are neglected bacause in those processes the lattice acts primarly through its zero-point motion. In other words

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the electron-electron interaction mediated by acoustic phonons is strongly retarded. The acoustic phonons can thus excite only the real electron-hole pairs, which interact more or less intensively through the Coulomb forces. As a result the phonon self-energy Π is proportional to the CDW bubble χ^{CDW}, which includes the Coulomb renormalizations,[3] as shown for example in Fig 1a

$$\omega_D^{-2}\,\Pi = \lambda\,\chi^{CDW} \qquad (2)$$

Here λ denotes the electron-acoustic phonon coupling constant. Eq. (2) is a direct consequence of the inequality (1) and is thus valid for both TTF-TCNQ and $NbSe_3$. The MF transition temperature T^o is defined by $\omega_D^{-2}\,\Pi \approx 1$. The differences occur in respect to whether the Coulomb correlations are important or not at T^o. This is determined by the ratio of λ to the Coulomb coupling constants $g_{1,2}$. For $\lambda > g_{1,2}$ $\chi^{CDW} \sim \log \varepsilon_F/T$ for $T \gtrsim T^o$, i.e. the Peierls theory is valid whereas in the opposite case the parquet approximation[3] gives $\chi^{CDW} \sim (\varepsilon_F/T)^{2g_2 - g_1}$ close to T^o, i.e. the system develops the stronger, power law singularity. This corresponds respectively to $NbSe_3$ and TTF-TCNQ. Such difference between the two materials can be understood on noting that in the tight-binding theory $\lambda \sim W$, where W is the band-width, whereas $g_{1,2} \sim W^{-1}$ through the density of states $n_F \sim W^{-1}$. Hence the narrow band TTF-TCNQ is expected to have $g_{1,2} > \lambda$ in contrast to $NbSe_3$ where $\lambda > g_{1,2}$.

In fact it is possible to estimate $g_{1,2}$ with better accuracy. The idea is to relate $g_{1,2}$ to the high frequency non-critical properties and to use such $g_{1,2}$ in the evaluation of the low frequency critical behaviors. In particular the RPA screened g_2 can be related to the plasma edge ω_p of the material as

$$g_2 \approx n_F \left[U + \frac{e^2}{d_{\parallel}} \left(\log \frac{\varepsilon_F}{\omega_p} + 1 \right) \right] \qquad (3)$$

The characteristic Coulomb matrix element $\frac{e^2}{d_{\parallel}}$ between the first neighbors can also be expressed through the plasma frequency as

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$$n_F \frac{e^2}{d_{\parallel}} \simeq \frac{\omega_p^2}{\varepsilon_F^2} \frac{d_{\perp}^2}{d_{\parallel}^2} \tag{4}$$

leaving unknown only the Hubbard U ($d_{\perp}$ is interchain distance). We can note that all long-range terms in Eg.(3) are positive[8], i.e. the average interaction through plasmons is repulsive.

The Hubbard U can be estimated from the high-temperature magnetic susceptibility evaluated in the parquet approximation[9]

$$\chi(T) = \chi_p \frac{1+g_1(T)}{1 - g_1}$$

where
$$g_1(T) = \frac{g_1}{1+g_1 \log \frac{\varepsilon_F}{T}} \tag{5}$$

and
$$g_1 \simeq n_F U$$

provided that we neglect the terms of the order of $\frac{e^2}{d_{\parallel}}$ with respect to U (or unity with respect to $\log \frac{\varepsilon_F}{T}$ in Eq.(3)). Comparing Eqs.(3-5) with the optic and magnetic data for $NbSe_3$ and TTF-TCNQ we can conclude that $g_{1,2}$ is indeed considerably larger in the former case.

This type of analysis can be continued a step further in TTF-TCNQ on considering each chain separately. Recently it proved possible to separate experimentally the contributions of TTF and TCNQ chains to the magnetic susceptibility[10]. It turned out that the dominant, temperature dependent contribution comes from TCNQ, whereas the TTF susceptibility is Pauli like. In contrast to that the $4k_F$ anomaly occurs on the TTF chains[7]. This can be reconciled with the usual theory in the following way. The $4k_F$-CDW singularity is given by[2]

$$\chi_{4k_F}^{CDW} \sim \left(\frac{\varepsilon_F}{T}\right)^{8\, g_2 - 4g_1 - 2} \tag{6}$$

Further we realize that through overall screening g_2 of Eq.(3) is the common property of both chains, $g_2^{TCNQ} \simeq g_2^{TTF}$, whereas $g_1 \simeq n_F U$ is

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the local property, and from magnetic susceptibility of Eq.(5). $g_1^{TCNQ} > g_1^{TTF}$. By Eq.(6) this is in qualitative agreement with the $4k_F$ behavior of TTF-TCNQ ($4k_F$ on TTF).

The idea that $U^{TCNQ} > U^{TTF}$ is not contradicted by other relevant facts. It has been shown recently[11] that TMTSF, a parent of TTF, is quite polarizable, which leads in the usual way to the reduction of the effective U. In addition, the crystalographic structure[12] of TTF-TCNQ consisting of charged sheets of TTF and TCNQ requires the existence of (van der Waals-like) dispersive forces between chains, stronger within one than the other family. Accurate calculations[13] show that the coupling of long wave-length metallic polarizabilities can not provide for the required cohesive energy, contrary to earlier expectations[5] based on perturbative arguments. The remaing mechanism is the vdW coupling of the TTF molecular polarizabilities, suggesting that those are large and different for TTF and TCNQ.

This remark completes the discussion of the density-density correlations χ^{CDW} i.e. of Π of Eq.(2). From the lattice point of view this theory is harmonic, because linear in λ i.e. quadratic in the linear electron-phonon coupling. Π is thus proportional to the harmonic deformation energy. Harmonic theory is however insufficient for $T < T^o$, the temperature range to which we turn now. In this temperature range anharmonic terms as well as interchain couplings have to be included too. This is shown in Figs. 1b and 1c. Fig.1b denotes the Coulomb interchain coupling bilinear in displacements of neighboring chains. Fig. 1c is the usual, electron-induced anharmonic term. Altogether the terms 1a-1c represent the usual Landau expansion of the free energy density in terms of the $2k_F$ displacements and the Fourier components in their neighbourhood, $\psi = |\psi| e^{i\phi}$. Table I gives the values of the Landau coefficients for the Peierls and the correlated CDW limit.

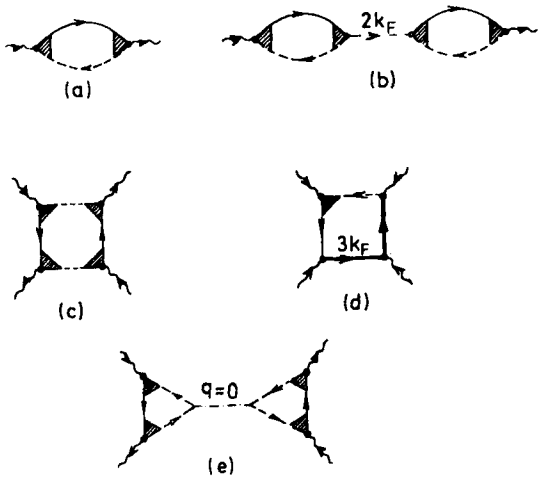

FIGURE 1 —— k_F electron, - - - $-k_F$ hole, ═══ $3k_F$ electron ~~~ $2k_F$ displacement, ● linear electron-phonon coupling, -·-·- Coulomb interaction, backward interchain $g_1^{\perp}$ In 1b and unscreened forward in 1e. Shaded triangles are Coulomb renormalizations of $2k_F$ electron-phonon vertices.

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Peierls limit	Correlated CDW limit
$\chi^{CDW} \approx \log \frac{\varepsilon_F}{T}$	$\chi_{CDW} \approx \frac{1}{2g_2-g_1}(\frac{\varepsilon_F}{T})^{2g_2-g_1}$
$T_p^o \approx \varepsilon_F\, e^{-1/\lambda}$	$\frac{T_L^o}{\varepsilon_F} \approx (\frac{\lambda}{2g_2-g_1})^{\frac{1}{2g_2-g_1}}$
$\xi_o \approx \frac{v_F}{T_p^o}$	$\xi_o \approx \frac{v_F}{T_L^o}$
$\xi_{o\perp} \approx d_\perp \frac{\sqrt{g_1^\perp}}{\lambda}$	$\xi_{o\perp} \approx d_\perp \sqrt{\frac{g_1^\perp}{\lambda}}$
$\omega_c \approx \frac{T_p^o}{\sqrt{\lambda}}$	$\omega_c \approx T_L^o$
$\Delta_p^2 \approx \lambda \frac{C}{n_F} \lvert\psi\rvert^2$	$\Delta_L^2 \approx \frac{C}{n_F} \lvert\psi\rvert^2$
$\Delta_p^o \sim T_p^o$	$\Delta_L^o \sim T_L^o$

TABLE I

We note that for a given λ the Coulomb correlations increase T_p^o to T_L^o, and decrease ξ_o and $\xi_{o\perp}$. If instead of space scales the time scale is considered the frequency ω_c of the breakdown of the adiabatic approximation is determined. Combining the results of Table I for ω_c with the assumption (1) it follows that this condition not only makes the phonon field classic but also the electron response to it adiabatic.

In all expressions of Table I we have set $T=T^o$, except in $\varepsilon=(T-T^o)/T^o$ and neglected the terms beyond those quartic in displacements. This truncation procedure together with the suitable choice of the constant of proportionality between the $2k_F$ displacement $|\psi^o|$ at $T=0$ and electron gap Δ^o leads to nearly the exact result for Δ^o, expressed through the law of corresponding states $\Delta^o \approx T^o$. However the low temperature dependence $\Delta(T) \propto \sqrt{\varepsilon}$ obtained in this way is not quite correct. This is not so important because the error concerns the amplitude $|\psi| \sim \Delta(T)$ of the order parameter, whereas the low temperature behaviors are determined by the motion of the phase ϕ, the treatment of which is essentially exact in this way. The question of the motion of ϕ brings us to the terms of Fig. 1d and 1e. However before going to these terms let us note that the described truncation procedure "sums" the problem to all orders in λ and only to the first order in $g_1^\perp$ of Fig. 1b. Such approach is valid only provided that $\lambda > g_1^\perp$ (but $\lambda \lesssim g_{1,2}$).

Let us now turn our attention to the term of Fig.1e, which is usually not considered. The meaning of this term is best understood on noting that each triangle in this figure represents the slow component $\delta\rho^{(2)}$ of the CDW induced to the second order of the perturbation theory by the departure of the displacemant pattern from the $2k_F$ wave. $\delta\rho^{(2)}$ thus contrasts with the linear response $\delta\rho^{(1)}$ which contains only the fast components of the charge density around $2k_F$. The analytic expression for $\delta\rho^{(2)}$ in the Peierls limit is [14]

$$\delta\rho^{(2)} \approx \frac{1}{2\pi i} \frac{\lambda C}{2n_F (T_p^o)^2} (\psi^* \frac{\partial\psi}{\partial y} - \psi \frac{\partial\psi}{\partial y}) \approx \frac{\varepsilon}{2\pi} \frac{\partial\phi}{\partial y} \qquad (7)$$

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where C is the elastic constant.
The last equality is obtained on taking the amplitude $|\psi|$ uniform and fixed. Fig. 1e thus represents the Coulomb energy associated with long-wave $\partial\rho^{(2)}$. It is important to note that Fig. 1e we are using the unscreened Coulomb interaction. The reason is that below T^o the (pseudo) gap $\Delta(T)$ opens in the electron spectrum inhibiting the screening. (In fact in $NbSe_3$, unlike in TaS_3 some electron and hole pockets do remain, leaving some metallic screening but with long screening length).

Using the rhs of Eq.(7) in Fig. 1e and associating this energy with usual terms which define the phason frequencies we find these latter as

$$\omega_{ph}^2 \approx v_{ph}^2 q_{\parallel}^2 + \omega_L^2 \frac{q_{\parallel}^2}{q_{\parallel}^2+q_{\perp}^2} \qquad (8)$$

Here we have omitted the $\xi_{0\perp}$ coupling (i.e. Fig.1b) in order to stress the analogy between the phasons (8) and the well known plasmon spectrum of the quasi 1d materials. The unscreened Coulomb singularity of Fig.1e occurs in the second term of Eq.(8). ω_{ph} has therefore two $\omega \approx 0$ limits. For $q_\perp > q_\parallel$ $\omega_{ph} \approx \omega_T = 0$, whereas for $q_\parallel > q_\perp$ $\omega_{ph} = \omega_L \approx (\lambda\varepsilon)^{\frac{1}{2}}\omega_D$. The first limit is associated with the uniform ($q_\perp > q_\parallel$) sliding of electrons along the chain, i.e. with the Fröhlich conductivity and with the large dielectric constant. In contrast ω_L describes the longitudinal Coulomb waves coupled to the lattice and is associated with the zero of the dielectric constant. ω_L was well observed in the reflectivity measurements on KCP and is expected to show up in TaS_3. The electron-hole pockets in $NbSe_3$ may on the other hand lead to the reduction of ω_L by screening the singularity (8) but only at extremly large wavelengths.

Let us finally discuss the Umklapp term 1d. This term is relatively small compared to the direct anharmonic term 1c, for two reasons. First, it involves the highly excited electron states. Second it has only one $2k_F$ vertex, enhanced by Coulomb interactions. As a result it is approximately $(\frac{T^o}{\varepsilon_F})^{2+3g_2-3g_1/2}$ times smaller than the direct term. This means that by increasing T^o from T_p^o to T_L^o at constant λ the Coulomb interaction enhance somewhat the Umklapp. Here and else we neglect the effects of the lack of screening in g_2, which are probably of the order of Δ/ω_p.

Let us finally put all the terms of Fig.1 togather, except 1b and consider for brevity the Peierls limit. In absence of Coulomb forces 1e the Umklapp term although small leads through sine-Gordon equation to soliton excitations of the commeusurate phase or to the formation of soliton lattices in the incommeusurate phase. Eq.(7) shows however that these solitons are charged. In fact they carry non-elementary, ε e/2 charges, being the generalization of the longitudinal modes ω_L. The Coulomb energy of Fig.1e has therefore to be taken into account. For a 1d soliton of the width ξ_s this

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energy is[14]

$$U_s \approx \frac{e^2}{\xi_s} \log \frac{\xi_s}{d_{\parallel}} \qquad (9)$$

Unlike the short range Hubbard force, the long range Coulomb interaction can suppress soliton due to the singularity (9). Indeed for $n_F U_s > d_{\parallel}|\epsilon| / \xi_s$ the appearence of solitons is energetically unfavorable and the commensurate phase turns abruptly into the incommensurate phase built from only one $2k_F$ harmonic. This conclusion concerning the somewhat idealized 1d situation completes our brief discussion of Coulomb effects, leaving the investigation of more realistic 3d models for the forthcoming paper.

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