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HIGH TEMPERATURE STRUCTURAL INSTABILITY IN QUASI-ONE--DIMENSIONAL CONDUCTORS

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Abstract: The most important steps on the way from the simple tight-binding band approximation to the simple fluctuation theory for high-temperature quasi-one-dimensional conductors are discussed. The tight-binding formulation is reviewed with particular emphasis on the strong anisotropic effects. This formulation is then set into the context of the many-body theory. It appears that at sufficiently high temperatures the parquet degeneracy of the many-body theory might break. The ensuing simplification leads to a single-order parameter phase transition theory which is reviewed and completed in respect of the problem of quasi-one-dimensional conductors.

1. Introduction

This paper deals with the recently discovered quasi-one-dimensional conductors KCP ($K_2Pt(CN)_4\ Br_{0.3} \cdot 3H_2O$) and TTF — TCNQ, but touches also some more general problems. The common feature of the mentioned conductors is that they show[1,2] a structural instability at rather high temperatures $k_B T_c \sim \sim \hbar\,\omega_0(\vec{\varkappa})$, where $\omega_0(\vec{\varkappa})$ is the bare frequency of the phonon $\vec{\varkappa}$, the softening of which is related to the instability.

The first purpose of the present paper is to set the approximate theory which was developed in a series of papers[3-5], into a more general context of the many body theory. The thinking behind the rather drastic simplifications of Refs.[3-5] is exposed in Sections 2 and 3. Our further aim here is to present our previous results, scattered in literature, in an unified text, in order to emphasize their logical interdependence. This is done in Sections 3 and 4. The Section 4 contains some previously unpublished calculations added here for the sake of completeness.

2. Tight-binding background

Both KCP and TTF-TCNQ are built of parallel linear chains. The chains are quite well separated, and so the electrons propagate over a long distance along a conducting chain before hopping on to a neighbouring chain. In a perfect conductor this hopping from chain to chain will be coherent and can be described by the well-known tight-binding band approximation. The propagation along the chains also occurs by hopping. The corresponding hopping frequency is smaller than that of the circular movement of electrons around the nucleus on a given site, i. e. the tight-binding very probably applies also to the intrachain propagation.

The general theory of the electron-phonon interaction in the tight-binding approximation has been described in our previous works[3]. It was shown that if the electron spectrum is described by tight-binding, then the bare phonon spectrum should be regarded roughly as including all the renormalizations unrelated to the electron propagation. The extra renormalization due to the band formation can be added through an appropriate bare (rigid-ion) electron-phonon coupling by taking also into account the Coulomb interaction of the displaced charge density waves (CDW). Simultaneously with the bare phonon frequencies $\omega_0(\vec{q})$, which vanish in the long-wave-length limit, the bare electron-phonon matrix element also vanishes in this limit. This illustrates the fact that in the tight-binding limit the *bare* electron-phonon coupling is *short-ranged.*

The fact that the bare coupling is short-ranged, or more precisely, that its anisotropy is roughly the same as that of the electronic band, is important in order to understand the very existence of quasi-one-dimensional materials. If the electron band is quasi-one-dimensional, such will also be the bare electron-phonon matrix element. E. g. band

$$\varepsilon(\vec{k}) = 2J\{\cos k_{\|} d_{\|} + \eta\,[\cos(k_{\perp} d_{\perp})_1 + \cos(k_{\perp} d_{\perp})_2]\} \tag{1}$$

corresponds to the bare matrix element for the polarization $\vec{\varepsilon}^{\,\lambda}_{\vec{q}}$

$$I^{\lambda}_{\vec{k},\vec{k}+\vec{q}} = 2iq_0 J\left\{\frac{\vec{d}_{\|}}{d_{\|}}\vec{\varepsilon}^{\,\lambda}_{\vec{q}}\,[\sin k_{\|} d_{\|} - \sin(k_{\|}+q_{\|})\,d_{\|}] + \right.$$

$$\left. + \eta'\left(\frac{\vec{d}_{\perp}}{d_{\perp}}\right)_{1,2}\vec{\varepsilon}^{\,\lambda}_{\vec{q}}\,[\sin k_{\perp} d_{\perp} - \sin(k_{\perp}+q_{\perp})\,d_{\perp}]_{1,2}\right\}, \tag{2}$$

where q_0 and η' are the appropriate coefficients. Equs. (1,2) with $\eta, \eta' \ll 1$ correspond to KCP, while the geometry of TTF-TCNQ is more complicated; but even so the tight-binding formulation remains tractable. Here we shall ignore the geometrical problems currently under consideration by A. Bjeliš and the author and keep in mind only Equs. (1) and (2). Since the small overlap ηJ is more sensitive to the change in intersite distance than the large, one, J, η' is probably larger than η, but this difference can safely be ignored in qualitative considerations.

To Equs. (1,2) we have to add the Fourier transform of the bare Coulomb matrix element

$$U(\vec{q}) = V_0 + \frac{e^2}{d_{\|}} \{\alpha (q_{\|},0) + [\alpha (q_{\|}, d_{\perp},0) \cos q_{\perp} d_{\perp}]_{1,2}\}. \tag{3}$$

This matrix element is associated with the CDW occurring on the lattice sites of the crystal, i. e. we neglect here the presumably small displacements of ions accompanying the CDW. In Equ. (3), V_0 is the on-site Coulomb interaction, while

$$\alpha (q_{\|},0) = - \log [2 (1 - \cos q_{\|} d_{\|})] \tag{4}$$

is the intrachain Madelung constant, and

$$\alpha (q_{\|}, d_{\perp}, 0) \sim \frac{e^{-q_{\|} d_{\perp}}}{\sqrt{q_{\|} d_{\perp}}} \tag{5}$$

is the interchain Coulomb coupling. Expressions (3—5) are valid, provided that $q_{\|} d_{\perp} \gtrsim 1$ (with a simple modification[4] in Equ. (5) for $q_{\|} \approx \pi/d_{\|}$).

It may be of use to make here a short physical digression. The quantity $\alpha(q_{\|}, d_{\perp}, 0)$ has a simple physical interpretation. It is proportional[4] to a potential created at the distance $d_{\perp}$ from a chain carrying a CDW with the wavelength $2\pi/q_{\|}$. At distances $d_{\perp}$ larger than the CDW wavelength, many periods contribute to the potential. Since the overall charge of the CDW is zero, the resulting potential is (exponentially) small. However, the range of α, $q_{\|}^{-1}$, is always larger than the range of the overlap integrals J, given by q_0^{-1} of Equ. (2), which is an atomic distance.

Returning to our formulation, we realize that the problem is completely defined if the frequencies $\omega_0(\vec{q})$, the anharmonic interactions of bare phonons, and the higher-order electron-phonon couplings are known. The frequencies $\omega_0(\vec{q})$ are also expected to be very anisotropic because, as mentioned above, they roughly correspond to the forces in a neutral insulator. The inclusion of electron-phonon couplings beyond the linear term (2) presents a considerable problem[3], and so we should only mention that for most purposes all these terms may be combined into a phenomenological anharmonic coupling.

3. *Many-body formulation*

General. The many-body theory for the problem defined above has been worked out diagrammatically[6,7] by neglecting both the anharmonic couplings of bare phonons and the electron-phonon couplings beyond the linear term (e.

g. Equ. (2)). The omission of these terms leads to an important formal simplification, i. e. the whole theory can be formulated[6)] in terms of an effective electron--electron coupling

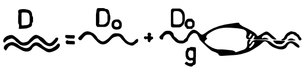
$$\gamma(\vec{k}, \vec{k}', \vec{q}, \omega) = U(\vec{q}) - g_{\vec{k}, \vec{q}}\, g_{\vec{k}', -\vec{q}}\, D_0(\vec{q}, \omega), \tag{6}$$

where

$$g_{\vec{k}\,\vec{q}} = \left(\frac{\hbar}{2NM\,\omega_0(\vec{q})}\right)^{\frac{1}{2}} I_{\vec{k}, \vec{k}+\vec{q}}. \tag{7}$$

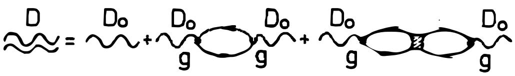
Here D_0 is the bare phonon Green function while $I_{\vec{k}, \vec{k}+\vec{q}}$ is given by Equ. (2). As usual, the phonon mediated electron-electron interaction is retarded in time.

Following Ref.[6)] we express the renormalized phonon Green function D



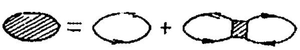
(8)

in terms of effective electron-electron interaction



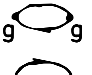
(9)

The shaded square represents the renormalized vertex involved in the usual Bethe--Salpeter equation


(10)

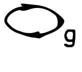
shown here rather schematically for a two-particle two-points correlation function. The renormalized vertex in Equs. (9,10) represents the sum of the usual »electron--electron« diagrams, with the elementary interaction (6).

At a finite temperature the elementary bubbles[3)] in Equs. (9, 10)

$\Pi^{\circ}(\underline{q}, \omega) =$ 

(11)

$P^{\circ}(\underline{q}, \omega) =$  (12)

$Q^{\circ}(\underline{q}, \omega) =$ 

(13)

are regular for any q, ω. Therefore, exempting the trivial singularities in D_0, any divergence in the correlation functions (9, 10) must come from the singularity of the renormalized vertex itself.

Space effects. The singularity of the vertex will not always be reflected in the same way in a susceptibility to the staggered stress (9) or the electric field (10). This is due to the k-structure (band structure) of quantity $g_{\vec{k}\vec{q}}$ as given by Equs. (7) and (2). This $\vec{k}$ dependence causes the quantity Q° $(\vec{q}, \omega)$ to vanish for certain highly symmetric (simply commensurate) deformations and/or for a half filled band. (A detailed discussion of Q° is given in Ref[3]). In order to illustrate the possible consequence of the disappearance of Q°, with P° and Π° finite, we split the vertex into the part which starts and/or finishes with a phonon line (e. g. diagrams a, c of Fig. 1) and the part containing all other diagrams (e. g. diagrams 1b, d). The first part will be multiplied by a small quantity Q° in Equ. (10) but not in Equ. (9). Thus, if the part starting with a phonon line contains a strong singularity, this singularity will be strongly reflected only in the phonon correlation function. This is the case in which a small charge density wave (CDW) accompanies a large lattice deformation. One can also easily imagine the opposite situation where the leading divergence occurs in that part of the vertex which starts with the Coulomb line. Then, again because of the possibly small Q°, or else, because of the small g, the deformation will be small with respect to the appropriately normalized CDW.

As a rule, the complication with Q° may be ignored[3] when dealing with incommensurate deformations and partially filled bands. Then the $\vec{k}$ structure of $g_{\vec{k}\vec{q}}$ may be roughly neglected everywhere, especially in the dangerous quanitity Q°. Π°, P° and Q° become roughly proportional[4]. Now, there is no difference in discussing Equs. (9) and (10). Deformations and CDWs are simply proportional. The temperature at which the vertex diverges is the common transition temperature for structural (Peierls) and dielectric (CDW) instability. However, it is important to distinguish between the phonon and the Coulomb mechanism of instability, according to which one of the two possibly attractive terms, (7) or (4,5), dominates the vertex (6). Not only will the ratio of the deformation and CDW be different in these two limits, but even the whole aspect of the many-body theory may change. The latter point is further discussed in the next sub-section.

Retardation effects. If the phonon contribution dominates the bare vertex (6), the retardation effects associated with heavy ions can play an important role in the many-body theory. In order to develop this point in greater detail let us, for reasons of clarity, ignore the Coulomb contribution to the bare vertex (6). Some simple vertex corrections are shown in Fig. 1. These particular diagrams are chosen because in the one-dimensional case ($\eta = \eta' = 0$) they all yield the same*) $g^6 \log^2 T$ contribution to the vertex, provided that the retardation effects are neglected. Such a degenerate situation is usually named parquet.

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*) Note however that the two logarithmic contributions are incompatible with the momentum $2k_F$ on all wavy lines of Fig. 1c. This can be remedied by exchanging say, the lower ends of the electron lines in the Cooper bubble, but then the spins in the bubble can not be different.

The retardation effects in the parquet become important[6] for temperatures $k_B T > \hbar\omega_0\,(\vec{q})$. All Matsubara frequencies ($\hbar\omega_n = 2\,n\,k_B T$) except one ($n = 0$) in D_0's will then exceed $\omega_0\,(\vec{q})$. All vertex diagrams can then be conveniently divided into two classes. Let the first class incorporate the diagrams which contain integrations over the phonon frequency (e. g. diagrams 1b, c, d). Diagrams such as 1a will then belong to the second class. Due to the energy conservation in the electron-phonon vertex, each phonon line in Fig. 1a carries only and the same frequency, i. e. the external frequency of the entering electron-hole pair. In a phase transition we are interested in the static response $\omega_n = 0$. For this external frequency the retardation effects are entirely absent from (1a). In contradistinction, the retardation effects are expected to reduce the contribution of the diagrams belonging to the first class, through summation over the presumably predominantly small D_0 functions. The retardation effects on diagrams of the type (1b, d) involved in the Eliashberg equations have been studied in considerable detail by a number of authors[3,8,9]. As pointed out in Ref.[3], phonons with frequencies $\hbar\,\omega^{RPA}\,(\vec{q}) < < k_B T$ are not very active in superconductivity, even if the external frequency in Eliashberg equations vanishes. The stronger condition $k_B T > \hbar\,\omega_0\,(\vec{q}) > \hbar\,\omega^{RPA}(\vec{q})$ is probably sufficient to ensure that all diagrams of the first class (1c etc.) are negligible with respect to those of the second class, provided that η is not too large. In fact, η primarily reduces[9] the diagrams of the Migdal (RPA) channel (Fig. 1a).

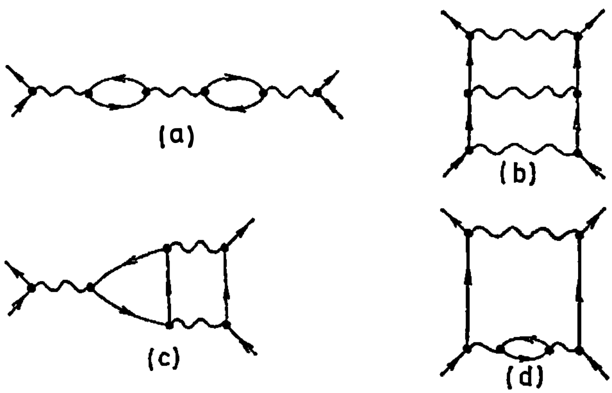

Fig. 1. Four (low order) parquet diagrams, degenerate at low temperatures.

To sumarize:

- within the phonon mechanism the parquet degeneracy of Fig. 1 breaks for $k_B T > \hbar\,\omega_0$ if η is small, and
- only the RPA vertex corrections remain.

This conclusion differs somewhat from certain other calculations where the RPA singularity in D was obtained by neglecting (in particular) these corrections. Since this question is of physical importance, we are devoting the next sub--section to a detailed derivation of the RPA result.

RPA theory. The usual quantity used in phonon theories is the phonon self-energy defined here by Equ. (8). This exact phonon selfenergy can easily be expressed in terms of the electron-electron vertex by eliminating the Green function D between Equs. (8) and (9). Introducing further the RPA and $g_{\vec{k}\vec{q}} \simeq g_{\vec{q}}$ simplifications, we find immediately that

$$\Pi_{\mathrm{RPA}} = \frac{-g^2 P^{\circ} (1 + \Gamma_0 P^{\circ})}{1 - g^2 D_0 (1 - \Gamma_0 P^{\circ})}, \tag{14}$$

where Γ_0 represents the RPA vertex, obtained by the summation of all diagrams of type 1a,

$$\Gamma_0 = \frac{-g^2 D_0}{1 - g^2 D_0 P^{\circ}}. \tag{15}$$

Inserting Equ. (15) into Equ. (14), we obtain

$$\Pi_{\mathrm{RPA}} = -g^2 P^0 = \Pi^0. \tag{16}$$

Equ. (14) has the same algebraic structure as has the exact equation for Π, except that in RPA the matrices are replaced by numbers. From this it is clear that Equ. (16) for Π could have been obtained alternatively by saying that both the bare vertex in the denominator and the renormalized vertex in the nominator of Equ. (14) are small due to the smallness of D_0 for $k_B T > \hbar \omega_0 (\vec{q})$. (The Coulomb contribution is already omitted here). But to remain consistent, we have to regard the external lines D_0 in Equs. (8) or (9) as also being small, i. e. to arrive to $D \simeq D_0$, far from the untrivial singularity in D.

It was therefore important to show above that Equ. (16) holds not only when Γ is small, but also when it is large and given by Equ. (15). Γ_0 is large when

$$1 \approx g^2 D_0 P^{\circ}. \tag{17}$$

Of course, condition (17) coincides with the equation which gives the singularity in D and is obtained by combining Equs. (16) and (8). This coincidence agrees with our general statement (the end of sub-section *General*) that the nontrivial singularity in D can arise only from the singularity in Γ.

Equ. (17) may have one or more (complex) solutions $\omega (\vec{q}, T)$ for a given $\vec{q}$ and T (working now with a retarded $D (\vec{q}, \omega)$. The requirement $\omega (\vec{q}, T) = 0$ gives $T = T (\vec{q})$, while the largest of these temperatures $T (\vec{\varkappa}) = T_{\mathrm{MF}}$ plays the role of the (mean-field) transition temperature. In more physical terms, $D^{-1} (\vec{q}, 0)$ calculated within RPA is proportional to the harmonic deformation energy[3]. This energy is minimal at $\vec{q} = \vec{\varkappa}$. The value of the minimum is proportional to

$T - T_{MF}$, while the expansion of this energy in terms of $\vec{q} - \vec{\varkappa}$ determines[4] the longitudinal and transverse correlation length, $\xi_{0||}$ and $\xi_{0\perp}$, respectively.

The limit $\eta = \eta' = 0$ in Equ. (17) has been thoroughly studied in Refs.[10,4]. Let us denote the characteristic frequency of Π_{RPA} by ω_c. For $T \ll T_F$ (Fermi temperature) $\hbar\,\omega_c \sim \lambda_{\vec{q}}^{-1/2}\, k_B T$, where $\lambda_{\vec{q}} = -\, n_F g^2/\omega_0\,(\vec{q})$. $\omega_c \gg \omega_0$ means practically $k_B T \gg \hbar\,\omega_0$ since usually $\lambda_{\vec{q}} \sim 1$. In the latter inequality we recognize a condition for the applicability of the RPA theory. On other hand, $\omega_c > \omega_0$ ensures that Equ. (17) has only one (adiabatic) solution. In the opposite limit $\omega_c < \omega_0$, Equ. (17) has two solutions. Close enough to T_{MF}, which is given by

$$T_{MF} \approx 2.28\; T_F\, e^{-1/\lambda_{\vec{\varkappa}}} \tag{18}$$

irrespective of the value of ω_c/ω_0, the two solutions occur rather close to the real ω-axis. The first solution corresponds to $\omega \approx \omega_0$. In the vicinity of this frequency, Π_{RPA} is small, i. e. $D \approx D_0$ (despite the fact that Γ_0 is large). Thus, this solution corresponds essentially to the trivial D_0 pole in Equ. (9). But since $\omega_c < \omega_0$, $\Pi_{RPA}\,(\omega)$ varies rapidly on the scale fixed by ω_0 becoming large for $\omega = 0$. This time the large Γ_0 corresponds to a large renormalization Π_{RPA} and to the instability at $T = T_{MF}$. The two solutions give rise to a three peak structure of the neutron scattering cross--section. But $\omega_c \ll \omega_0$ also means $k_B T_{MF} < \hbar\,\omega_0$, the limit in which the RPA results are incomplete. This might be one of the reasons why the fit[1] of the neutron cross-section obtained on KCP by the RPA results is not too successful.

The requirement $T_{MF} \ll T_F$ was omitted in Refs.[3,11] with Nb_3 Sn-like compounds in mind, but keeping $\eta = \eta' = 0$.

In Refs.[9,12] $k_B T_{MF}$ is again taken as being much smaller than T_F but $\eta \neq 0$, while $\eta' = 0$. The most unstable mode occurs at $\vec{\varkappa} = [2k_F, \pi/d_\perp, \pi/d_\perp]$, where k_F is the Fermi wave vector of the corresponding $\eta = 0$ band. Such $\vec{\varkappa}$ corresponds to the best nesting of the Fermi surfaces. T_{MF} is still given roughly by Equ. (18). The $\eta \neq 0$ model[9,12] leads to interchain correlations. The longitudinal and transverse correlation lengths are

$$\xi_{0||} \simeq \frac{\hbar\, v_F}{k_B\, T} \tag{19}$$

$$\xi_{0\perp} \approx \eta\, k_F\, d_\perp\, \xi_{0||}\,, \tag{20}$$

respectively. Not surprisingly, the length and time scale are related here, $\xi_{0||} \sim \sim v_F/(\lambda^{1/2}\,\omega_c)$.

The interchain distance (10Å) and the character of the d-functions forming the band in KCP lead to a very small η. Thus, although the most unstable mode is actually observed for the $\vec{\varkappa}$ found above, the measured avalues[1] of $\xi_{0\perp}$ are too large to be reconciled with Equ. (20). For KCP one must go back to the Coulomb mechanism of interchain coupling, Equ. (5).

The situation in TTF-TCNQ and similar materials is less clear, because of the considerable geometrical complications. It is not clear at present whether our model[4] is sufficient or not to describe the empirical findings[2] in these con ductors.

The Coulomb coupling (3) is always present and is probably important[4] in both types of materials mentioned above. Extending simply the foregoing discussion to the combined vertex (6), we shall find that the Coulomb coupling has to be combined with a phonon term in the RPA channel; in other parquet diagrams the phonon contribution may presumably be neglected for $k_B T \gg \hbar\,\omega_0(\vec{q})$. Then, if the phonon coupling in the RPA channel is larger than the Coulomb term, the lowest order Coulomb correction of the purely phonon RPA result is again given by the RPA diagrams. This suggests that we can work with the RPA channel not only up to the zeroth order in Coulomb coupling but also up to the first order. Obviously, the quantitative elaboration of this idea requires a more detailed investigation of the retardation effects in the parquet.

If in the presence of a small Coulomb term the RPA procedure is accepted, the corresponding results are obtained by simply replacing $g^2 D_0$ with $g^2 D_0 - U$ in Equs. (15) and (17) (the RPA theory in which g keeps its k dependence is described in Ref.[3]). Taking $\eta = \eta' = 0$ and considering again the limit $T_{MF} \ll T_F$, with

$$T_{MF} \approx 2.28\, T_F \exp\left[1/n_F\left(\frac{g^2}{\omega_0} + U(\vec{\varkappa})\right)\right] \tag{21}$$

we recover the most unstable mode $\vec{\varkappa}$ at $\vec{\varkappa} = [2k_F, \pi/d_\perp, \pi/d_\perp]$. $q_\perp = \pi/d_\perp$ makes the best use of the attractive coupling (5). Expanding again in terms of $(\vec{q} - \vec{\varkappa})$, we also also recover Equ. (18), but Equ. (19) is replaced by

$$\xi^2_{0\perp}/d^2_\perp \approx \frac{2n_F\, e^2}{d_{||}}\, a\,(q_{||}, d_\perp, 0)\log^2\frac{2T_F}{T} \tag{22}$$

with a from Equ. (5).

Equ. (22) seems to fit reasonably well the experimental findings[1] in KCP. Also, the Coulomb model is currently being extended to include the geometrical complications encountered in TTF-TCNQ. Although the preliminary results[4] seem to agree with the phase sliding ($\varkappa_\perp = \varkappa_\perp(T)$) observed[2] in TTF-TCNQ, the respective work has not yet produced any firm conclusions.

Obviously, the mechanism which gives the larger interchain correlation, i. e. the one which within the simple model defined by Equs. (1—5) produces the larger $\xi_{0\perp}$ between Equs. (20) and (22), is the one which should be retained physically as the cause of the interchain correlations. However, we wish to warn once more against using the too large (negative) α's of Equs. (4) and/or (5) in the RPA theory. It is true that Equs. (20, 21) remain well defined[12] in the limit $|U(\vec{q})| \gg |g^2/\omega_0|$, and have a simple physical meaning of the CDW instability in Equ. (10) with nothing much happening to the Peierls Equ. (9). However, the strong Coulomb mechanism requires full many-body treatment, beyond RPA, as discussed in Refs,[6,7,14,15]. It should also be kept in mind that some of our basic approximations, especially the omission [3] of the electron-phonon coupling through Coulomb forces in Equ. (3), may become questionable*) in the strong Coulomb--weak hopping limit.

Transitory remarks. The RPA or even the parquet approximation are mean--field theories in the sense that even in the one-dimensional system they lead to phase transition at finite temperature T_{MF}. Of course, the physical systems under consideration are not one-dimensional and the phase transition is allowed to occur at some finite T_c. However, T_c may be considerably lower than T_{MF}. If $k_B T_c$ is still larger than $\hbar\,\omega_0$, the arguments which led us to retain the RPA diagrams remain valid close to $T_c < T_{FM}$. The shift from T_{MF} to T_c may be attributed to the terms mentioned in Section 2 as giving rise to an effective anharmonic coupling. These terms are omitted in the discussion of this Section. Also, the diagrams beyond RPA may contribute[16] to the effective anharmonic coupling, but this point too would require a careful consideration regarding the retardation effects.

This line of thinking brings us to a rather simple Ginzburg-Landau-like model in which an effective anharmonic coupling of deformations is added to the harmonic deformation energy D^{-1}_{RPA}. In a one-dimensional conductor such a single--order parameter model would lead to $T_c = 0$. But in the range $k_B T < \hbar\,\omega_0$, the results of the model are not applicable to the one-dimensional conductor. In this range of temperatures the situation is parquet like[6,14,15], i. e. it involves two- (or more) order parameters at the same time. For the quasi-one-dimensional conductors, however, the model may apply to the whole range of temperatures if it leads to $k_B T_c > \hbar\,\omega_0$. Below the three-dimensional transition at T_c the situation may continue to be non-parquet like, down to low temperatures.

In the following section we shall investigate the Ginzburg-Landau (GL) single-order parameter model. Althought this model, applies to low-dimensional conductors with the reservations made above, it is relevant for other, simpler low--dimensional systems. One important approximation (mean-field treatment of interchain coupling), which is usually used without justification in this[17,18] or more complicated models, is shown to lead to correct results, at least within the Ginzburg-Landau model.

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* This point arose during a discussion with G. Grüner.

4. *Ginzburg-Landau theory*

General considerations. The starting point of this Section is the spatially anisotropic G-L functional

$$f(r) = a' \left[\frac{T - T_{MF}}{T_{MF}} |\psi|^2 + \xi_{0\|}^2 \sum_{i=1}^{d'} \left| \frac{\partial \psi}{\partial x_i} \right|^2 + \xi_{0\perp}^2 \sum_{i=d'+1}^{d} \left| \frac{\partial \psi}{\partial x_i} \right|^2 \right] + b |\psi|^4. \quad (23)$$

Here ψ is the n-component order parameter, and we assume

$$\frac{\xi_{0\perp}^2}{\xi_{0\|}^2} = a_{GL} \ll 1. \quad (24)$$

We keep here the one-dimensional notations (18—22) but do not specify d and d' for the moment.

The G-L functional (23) has to be combined with appropriate cut-off wave-lengths. These wave-lengths need not be the same in d' longitudinal and $\Delta = d-d'$ transverse directions. Let us denote them with $Q_{\|}^{-1}$ and $Q_{\perp}^{-1}$, respectively. The cut-offs describe that portion of the Brillouin zone to which harmonic part of the expansion (23) applies. As will be shown below and as argued previously[5,12,19] the question of cut-offs is quite important and thus requires some discussion.

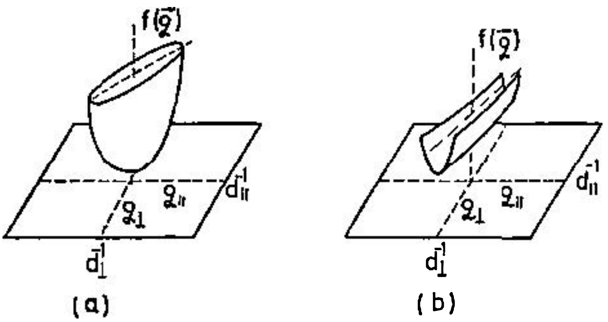

Fig. 2. Two opposite limits for the behaviour of the Fourier transform $f(\vec{q})$ of the harmonic free energy given by Equ. (23). The Fourier componet ψ $(\vec{q})$ of ψ $(\vec{r})$ is kept independent of $\vec{q}$ in the figure.

If both $\xi_{0\|}^{-1}$ and $\xi_{0\perp}^{-1}$ are smaller than the corresponding Brillouin zone dimensions, it is natural to truncate the harmonic part of Equ. (23) at the same energy in all directions (Fig. 2a).

This leads to

$$\frac{a_{GL}\, Q_{\perp}^2}{Q_{\|}^2} = 1. \quad (25)$$

We shall note that the limit of small a_{GL} can be achieved in the regime (25) only by taking $Q_{||}$ small ($\xi_{0||}$ large) since $Q_\perp$ cannot exceed the Brillouin zone dimension. When a_{GL} of Equ. (24) is decreased by decreasing $\xi_{0\perp}$, with $\xi_{0||}$ remaining fixed, $Q_\perp$ reaches its maximal value determined by the Brillouin zone and then stays constant (Fig. 2b); Equ. (25) breaks. In conclusion, the limit of small $\xi_{0\perp}$ is physically associated with a_{GL}-independent cuf-offs $Q_{||}$ and $Q_\perp$ and the limit of large $\xi_{0||}$, $\xi_{0\perp}$ with Equ. (25). Let us start by considering the former.

Crossover limit. This is the situation in which the system (23) exhibits a crossover behavior. Above a certain crossover temperature $T^*(a_{GL})$, it behaves according to the d'-dimensional critical indices; below it, the critical behavior is essentially d-dimensional (for d and d' see Equ. (23)). When a_{GL} tends towards zero, both $T^*(a_{GL})$ and the critical temperature $T_c(a_{GL})$ tend continuously towards the critical temperature of the d'dimensional system. For brevity, we shall deal here only with situations in which the dimensionality d' is so low that there is no phase transition at finite temperature associated with this dimension. That is to say that we are considering here the crossover from the unshaded into the shaded region of the n, d' diagram of Fig. 3. But instead of extending our homogeneity argument[5] to this whole region, we will pay particular attention to the $n \to \infty$ limit, where the otherwise lacking constants of proportionality can be calculated in detail.

It seems therefore advisable to try and clarify the analogy between the familiar free Bose gas[5] and the $n \to \infty$ G-L system. We shall do it by calculating $T_c(a_{GL})$ for the latter case. In the limit $n \to \infty$ the anharmonic term in Equ. (23) can be treated in the Hartree approximation. The transition temperature is then determined by

$$a' \frac{T_{MF} - T_c}{T_{MF}} = n\, \Sigma_c. \tag{26}$$

Neglecting the contribution to the self-energy Σ_c coming from wave vectors beyond the cut-offs $Q_{||}$, $Q_\perp$, we obtain

$$\Sigma_c \approx \frac{b\, k_B\, T_c}{(2\pi)^d\, a'\, \xi_{0||}^2} \int^{Q\perp} d^\Delta\, k_\Delta \int^{Q_{||}} d^{d'} k_{d'}\, \frac{1}{k_{d'}^2 + a_{GL}\, k_\Delta^2}. \tag{27}$$

Here $\Delta = d - d'$, and $k_{d'}$ and k_Δ are the wave vectors in d' and Δ dimensions, respectively. We notice the analogy between Equ. (27) and the equation (5) determining the transition temperature of the free anisotropic Bose gas: with $a_{GL} \to 0$, Σ_c tends towards the constant a'/n which here plays a role which is analogous to the total number of free bosons in the boson equation. For $T_c \ll T_{MF}$, Equ. (27) can conveniently be rewritten as

$$\frac{a'}{n} = \frac{b\, S_{d'}\, S_\Delta}{(2\pi)^d\, a'\, \xi_{0||}^2}\, k_B\, T_C\, a_{GL}^{\frac{d'-2}{2}} \int_0^{Q_\perp} k_\Delta^{d-3}\, \mathrm{d}k_\Delta \int_0^{Q_{||}/k_\Delta a_{GL}^{1/2}} \frac{x^{d'-1}\, \mathrm{d}x}{1 + x^2} \tag{28}$$

with

$$S_p = 2\pi^{p/2}\,\Gamma(p/2).$$

In the last integration the upper limit is large for any finite $k_\Delta \leq Q_\perp$, provided that

$$\frac{Q_{\parallel}^2}{Q_\perp^2\, a_{GL}} \gg 1, \tag{29}$$

i. e. that Equ. (25) is not fulfilled. In other words, the infrared cut-off $Q_{\parallel}$ disappears from Equ. (28) if the increase of $Q_\perp^2$ with decreasing $\xi_{0\perp}^2$ is slower than a_{GL}^{-1}. This is particularly the case for small $\xi_{0\perp}$ when $Q_\perp$, as mentioned before, is roughly independent of a_{GL}. The integrations (28) are easily carried out when the upper limit in the second integral is set equal to infinity (a_{GL} small). The result is convergent, provided that $d > 2$ and $2 > d' > 0$. In analogy with the result[5] for the Bose gas we find that

$$k_B T_C = \frac{4a'\,\xi_{0\parallel}^2}{n\, b\, Q_\perp^{d-2}}\; \frac{(2\pi)^{d-1}(d-2)\sin\frac{\pi d'}{2}}{S_{d'}\, S_\Delta}\; a_{GL}^{\frac{2-d'}{2}}. \tag{30}$$

Equ. (30) coincides in fact with a more general expression

$$T^* \sim T_C \sim \xi_{0\parallel}^2\, a_{GL}^{\frac{2-d}{2}}, \tag{31}$$

which K. Uzelac and the author propose, extending the $d' = 1$ homogeneity argument[15] to the shaded region of Fig. 3. The latter argument is more general because it is independent of n, assumed large in Equ. (30). Since for T^* and T_c the exact cross-over exponents, i. e.

$$\psi = \psi = \frac{2}{2-d'} \tag{32}$$

are independent of n, Equs. (30) and (31) coincide in this respect in the case of an arbitrary n. The same cross-over exponent was obtained previously[17, 18] for $d' = 1$, $n = 2$ applying the mean-field approximation to the interchain coupling $\xi_{0\perp}^2$ in Equ. (23). We can see here that in the Ginzburg-Landau model this approximation leads to the exact result (32).

Equ. (30) gives the prefactor lacking in Equ. (31), provided that only the lowest-order anharmonic coupling b is retained. Of course, the dependence on n in Equ. (30) should not be taken too seriously if n is of the order of one. For $d' = 1$, $n > 1$, Equ. (30) reduces to

$$\frac{T_c}{T_b^\perp} = \frac{3\,(2\pi)^{d-1}(d-2)}{n\, S_{d-1}}\, \xi_{0\perp}\, Q_\perp \tag{33}$$

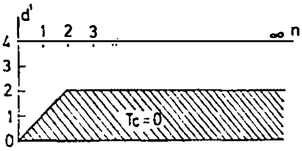

Fig. 3. Parts of the d', n plane for which the $\xi_{0\perp} = 0$ model of Equ. (23) has respectively finite or zero transition temperature. The $d' = n$ line has not been firmly established.

which defines the characteristic temperature scale

$$k_B T_b^{\perp} = \frac{4}{3} \frac{a'^2 \xi_{0\parallel}}{b Q_{\perp}^{d-1}}. \tag{34}$$

The same temperature $T_b^{\perp}$ also occurs for $d' = 1$, $n = 1$ when[5,19]

$$\frac{T_c}{T_b^{\perp}} \sim |\log \xi_{0\perp} Q_{\perp}|^{-1}. \tag{35}$$

We shall note that $T_b^{\perp}$ has nothing in common with T_{MF}, which becomes an unimportant parameter for $T_c \ll T_b^{\perp}$.

Symmetric limit. This is the limit in which Equ. (25) applies. Let us start again by considering the simple $n \to \infty$ equation. With Σ_c defined by Equ. (26), and introducing a new variable

$$q_{\Delta} = \sqrt{a_{GL}}\, k_{\Delta} \tag{36}$$

into Equ. (27) and taking into account Equ. (25), we shall find that

$$\Sigma_c \approx \frac{b\, k_B\, T_c}{a'\, \xi_{0\parallel}^2\, Q_{\parallel}^{2-d}} \frac{S_d}{d-2} a_{GL}^{-\frac{\Delta}{2}}, \tag{37}$$

provided that $d > 2$. It should be noted that with $Q_{\parallel} \sim 1/\xi_{0\parallel}$ (small), Σ_c is roughly independent of $\xi_{0\parallel}$. In fact we should always ensure that the retained contribution to Σ_c is really dominant. Equs. (26) and (37) can easily be solved for T_c

$$T_c \approx \frac{T_{MF}}{1 + \frac{T_{MF}}{T_b^{\parallel}} a_{GL}^{-\frac{\Delta}{2}}} \tag{38}$$

where

$$k_B T_b^{\parallel} = \frac{a'\, \xi_{0\parallel}^2}{n\, b\, Q_{\parallel}^{d-2}} \frac{(2\pi)^d (d-2)}{S_d}. \tag{39}$$

As pointed out before, Equ. (38) is roughly independent of $\xi_{0\parallel}$ (large).

An equation similar to Equ. (38) is found in the linearized renormalization group theory[21]. In order to show that, we shall follow the prescription of Ref.[19] and symmetrize the expression (23) with cut-offs (25), and change the variables (36) in the direct space. Thus introducing

$$x'_{\Delta} = \sqrt{a_{GL}}\, x_{\Delta} \tag{40}$$

we have

$$F[\psi] = \int_{\Omega} \mathrm{d}^d \vec{r} f(\vec{r}) = \int_{\Omega'} \mathrm{d}^d \vec{r}' f'(\vec{r}'). \tag{41}$$

Here[19]

$$\vec{r}' = \{x_1 \ldots x_{d'}, x'_{d'+1} \ldots x'_{\Delta} \ldots x'_d\}, \quad f'(\vec{r}') = a_{GL}^{\frac{\Delta}{2}} f(\vec{r}), \quad \Omega' = a_{GL}^{\frac{\Delta}{2}} \Omega. \tag{42}$$

The new function $f'(\vec{r}')$ has a symmetric gradient term $\left| \frac{\partial \psi(\vec{r}')}{\partial \vec{r}'} \right|^2$ and is associated, by Equ. (25), with the same cut-off $Q_{||}$ in all directions.

Applying now the usual $\varepsilon = 4\text{-}d$ expansion procedure to the determination of the critical surface (line) in the parameter space defined by Equ. (42), we find

$$T_c = \frac{T_c^*}{1 + w \frac{b\, k_B\, T_{MF}}{\xi_{0||}^2\, a'^2\, Q_{||}^{2-d}}\, a_{GL}^{-\frac{\Delta}{2}}} . \tag{43}$$

Here

$$w \sim \frac{(n+2)\left(1 + \frac{n+2}{2n+16}\,\varepsilon\right)}{2 + \left(1 - \frac{n+2}{n+8}\right)\varepsilon}, \tag{44}$$

and T_c^* depend on the recurrence step used in the renormalization procedure[21]. Equ. (43) is valid for n arbitrary, $4 > d \geqslant 2$, and with $T_{MF} \approx T_c^*$. Equ. (38) is valid for large n, $4 > d > 2$ and T_{MF} arbitrary. For large n and $T_c^* \approx T_{MF}$, Equs. (28) and (48) coincide (and determine the lacking, n-independent factor in w of Equ. (44)). It is interesting that the constant $T_b^{||}$ of Equ. (39) approximates the corresponding quantity of Equ. (43) rather faithfully over the whole range of n.

As argued previously[19], the symmetrizable system (23) and (25) obeys the d-dimensional critical laws. Only the scales are changed according to relations (40) and (42). The critical range is increased and the fluctuation effects are enhanced. In particular, the fluctuation specific heat is increased. Both temperature dependent correlation lengths $\xi_{||}(T)$ and $\xi_{\perp}(T)$ follow the same temperature law because they are deduced from the correlation length $\xi_{||}(T)$ by the inverse transformation (40). Their ratio is therefore independent of temperature,

$$\frac{\xi_{\perp}^2(T)}{\xi_{||}^2(T)} = \frac{\xi_{0\perp}^2}{\xi_{0||}^2} = a_{GL}, \tag{45}$$

in contrast to the cross-over case where this ratio is strongly temperature dependent.

Conclusion. In this Section we have seen that according to the choice of cut-offs the large anisotropy ($a_{GL} \ll 1$) may correspond to two qualitatively different situations, the cross-over or the symmetric limit. In both limits the shift of the transition temperature from its mean-field value may be considerable, depending on the parameters. The clear-cut difference between the two limits occurs in the critical behaviour itself.

At sufficiently high temperatures KCP falls into the cross-over limit. $\xi_{0\perp}$, measured[11], or calculated from Equ. (22), is considerably smaller than $d_{\perp}$. However, $\xi_{0\perp}$ itself is (non-critically) temperature dependent and at T_c is estimated to be of of the order of $d_{\perp}$. However, the temperature dependence given by Equ. (22) (and also by Equs. (19, 20)) should not be taken too seriously for $T < T_{MF}$. This equation neglects (at least) the electron-self-energy effects[13,22,23] (the Peierls pseudogap). Still, it appears probable that close to T_c, KCP falls somewhere between the two extreme limits considered here.

The symmetric limit corresponds very probably to the BCS superconductivity in the conducting polymer[24] $(SN)_x$. It seems that there the ratio of the longitudinal and transverse correlation lengths is temperature independent, as in Equ. (45).

The situation in TTF-TCNQ is potentially much richer than that in KCP. Transverse correlations in this material are probably considerably stronger in one than in the other of the two transverse directions. This can lead to a complicated 3—2—1 dimensional cross-over for $n = 2$. Empirically[2], however, the fluctuation tails do not seem to be as large in this material as they are in KCP. It might well be that the structural transition in TTF-TCNQ falls into the symmetric limit, with only the fluctuations enhanced. It would be interesting therefore to have more data about the temperature behaviour of all three, or at least of two correlation lengths.

5. *Final remarks*

In this paper we have tried to describe the most important steps on the way from the simple tight-binding approximation to the simple fluctuation model for quasi-one-dimensional conductors. A major crossing on this way is certainly traversed in earlier sub-sections, where are given the arguments in favour of the single-order parameter phase transition theory for high-temperature quasi-one-dimensional conductors.

In order to emphasize the main line of reasoning, many details were deliberately left out and some problems neglected. Such are, for example, the electron-self-energy effects which merit at least to be mentioned here. The lowest-order self-energy correction gives rise to the Peierls pseudogap above T_c[13,22,23]. The Peierls pseudogap is present in the electron spectrum even when the phonon retardation effects are included[23]. The role of the Peierls pseudogap in parquet corrections or even in the Eliashberg-BCS equation has not yet been carefully investigated. Related with it is the problem of the role played by the long-range

($q_{\|} \approx 0$) part of the interaction[6]. This question has been discussed in detail, for example in Ref[7], using the unretarded long-range forces. In this connection it should be noted that the quasi-one dimensional equation (3) obtained here for $q_{\|}\, d_{\perp} \gg 1$ becomes strongly three-dimensional in the »long range« limit $q_{\|}\, d_{\perp} \ll 1$. In the ensuing many-body theory[7], the decisive ratio seems to be $e^2/\hbar v_F$ or equivalently $\frac{e^2/d_{\perp}}{k_B T_{MF}}$ versus $\frac{\xi_{0\|}}{d_{\perp}}$. $e^2 \ll \hbar\, v_F$ was shown[7] to correspond to the one-dimensional-like »infrared catastrophe« situation; the other limit has not been examined in detail. Although $\xi_{0\|}/d_{\perp}$ is large in KCP and probably also in TTF-TCNQ, it is still very likely that $\frac{e^2}{d_{\perp}}/k_B\, T_{MF}$ is even larger in these materials. It might be therefore reasonably expected that the $q_{\|} \approx 0$ part of the forces does not play a very important role in the theory of these materials.

Obviously, many of the ideas presented or mentioned here are qualitative and require a more careful examination. Therefore the present paper should not be misunderstood as an attempt to supply a final answer to the question of basic physics in KCP and TTF-TCNQ; it only indicates a possibly fruitful line of research and gives some results along this line.

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STRUKTURNA NESTABILNOST LANČASTIH VODIČA PRI VISOKIM TEMPERATURAMA

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Sadržaj

Izložen je put od jednostavne aproksimacije čvrste veze u računu vrpci do jednostavne teorije fluktuacija za lančaste vodiče pri visokoj temperaturi. Opisana je aproksimacija čvrste veze s posebnim naglaskom na jakoj anizotropiji koja slijedi za lančaste vodiče. Ta je formulacija zatim unesena u teoriju mnoštva čestica.

Predloženo je mišljenje da pri dovoljno visokim temperaturama nestaje »parket« degeneracija te teorije. To pojednostavnjenje vodi teoriji faznog prijelaza s jednim parametrom uređenja, koja je opisana i upotpunjena s obzirom na problem lančastih vodiča.

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