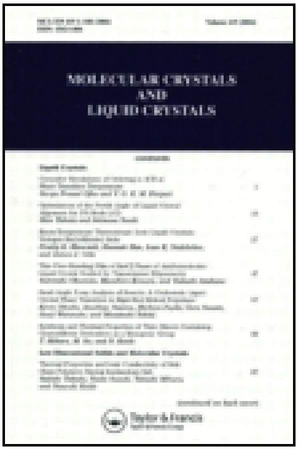

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 17 Oct 2011.

To cite this article: C. Bourbonnais & L. G. Caron (1985): Lattice Stability and Magnetic Properties of Quasi-1D Materials: Theory and application to $(TMTTF)_2$ x Compounds, Molecular Crystals and Liquid Crystals, 119:1, 287-292

To link to this article: http://dx.doi.org/10.1080/00268948508075172

Mol. Cryst. Liq. Cryst. 1985, Vol. 119, pp. 287-292
0026-8941/85/1194-0287/$15.00/0

LATTICE STABILITY AND MAGNETIC PROPERTIES OF QUASI-1D MATERIALS : THEORY AND APPLICATION TO $(TMTTF)_2X$ COMPOUNDS.

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Abstract We investigate the properties of a one-dimensional (1D) half-filled-band electron gas with both electron-electron and electron-phonon interactions. We estimate the variation of 1D $2K_f$ dimerization pseudo-gap Δ as a function of umklapp scattering strength g_{3H} or the correlation gap Δ_H. The effect of pressure on the phase diagram is analyzed in connection with the available data on $(TMTTF)_2X$ ($X=PF_6$, AsF_6, Br....) compounds.

I- INTRODUCTION

The recognition of the role played by umklapp scattering processes in the properties of quasi-1D conductors has led to sizeable progress in the understanding of the various phase transformations taking place in the $(TMTSF)_2X$ and $(TMTTF)_2X$ series of compounds[1,2,3]. Following Barisic and Brazovskii[1], an important contribution to the processes comes from the anion potential that produces a $4K_f$ dimerization gap $\Delta(4K_f)$ in the middle of the conduction band of the organic stack. This is quite relevant to the sulfur series of compounds $(TMTTF)_2X$ ($X=PF_6$, AsF6, Br....) with centro-symmetrical anions, where an activated behavior of the conductivity is clearly observed[4]. In this scheme, the effect of pressure acts to reduce $\Delta(4K_f)$ which in turn, reduces the correlation gap[2] Δ_H responsible for the activated conductivity. Another important source of umklapp scattering that can be quite sensitive to pressure[3] comes from the electron-phonon interaction. This second mechanism is quite relevant to the phase diagram of organic materials. In this work, we will be mainly interested in the properties of a 1D model which incorporates both electron-electron and electron-phonon interactions. We use its predictions in the phase diagram analysis of the sulfur series. It is the one-dimensional nature of the model which retains our attention. This is so because of the 1D origin[2] of the correlation gap Δ_H which tell us that the 1D properties of the electron-phonon system should prevail until the solid is close to a real low temperature phase transition[6] ($T_c \sim 10....20K$). This has been clearly confirmed for the $(TMTTF)_2PF_6$ compound which presents 1D $2K_f$ diffuse scattering over a large temperature range[7] ($15K < T < 60K$).

II- THE ELECTRON-PHONON MODEL AND ITS RENORMALIZIBILITY

We start our analysis with the Peierls extended Hubbard model of a 1D electron-phonon system. This system has recently received considerable attention[5,8] since it appears to be the best candidate for realistic applications to real quasi-1D materials[1]. For our purposes, it is more convenient to write the corresponding model Hamiltonian for a half-filled band in a "g-ology" form:

$$\begin{aligned} H=&\sum_q \omega_q (d_q^+ d_q + \tfrac{1}{2}) + \sum_{K\alpha}{}' \{V_f (K-K_f) a_{K\alpha}^+ a_{K\alpha} + V_f(-K-K_f) b_{K\alpha}^+ b_{K\alpha}\} \\ &+ N_s^{-1} \sum_{\alpha\beta} (\sum_{K_1 K_2 p}{}' g_{1H} + \sum_{K_1 K_2 p}{}'' g_{1ph})\ a_{K_1\alpha}^+ b_{K_2\beta}^+ a_{K_2+2K_f+p\beta} b_{K_1-2K_f-p\alpha} + \\ &N_s^{-1} \sum_{\alpha\beta} \sum_{K_1 K_2 p}{}' g_{2H} a_{K_1\alpha}^+ b_{K_2\beta}^+ b_{K_2+p\beta} a_{K_1-p\alpha} + N_s^{-1}/2 \sum_{\alpha\beta} (\sum_{K_1 K_2 p}{}' g_{3H} + \sum_{K_1 K_2 p}{}'' g_{3ph}) \\ &[a_{K_1\alpha}^+ a_{K_2\alpha}^+ b_{K_2-2K_f+p\beta} b_{K_1+2K_f-p-4K_f} + h.c], \end{aligned} \tag{1}$$

where the acoustic phonon frequency is $\omega_q = 2(\kappa/M)^{\frac{1}{2}} \mathrm{Sin}\frac{qa}{2}$. d_q (d_q^+) annihilates (creates) a phonon of wave number q. Here a is the lattice constant and N_s in the number of sites. The second term is the linearized energy spectrum of electrons with $a_{K\alpha}$ $(b_{K\alpha})$ as the electron annihilation operator of wave number $K>0$ $(K<0)$ measured from the Fermi level K_f $(-K_f)$. Because of the retarded nature of the electron-phonon interaction, the double-prime summation in (1) indicates that the phonon-induced electron-electron backward and umklapp scattering terms $g_{1pb} = -4\lambda^2/\kappa$ and $g_{3ph} = g_{1ph}$ are cut-off at $2K_f$ phonon energy $\omega(2K_f)$[5]. λ is the electron-phonon coupling and κ is the elastic constant between nearest-neighbor sites. One note that in the present model the electron-acoustic phonon contribution to the forward scatteting term g_{2ph} is neglibible[5]. For the extended Hubbard interaction, the backward, forward and umklapp scattering processes are respectively given by $g_{1H} = U-2V$ $g_{2H} = U+2V$ and $g_{3H} = g_{1H}$, where U and V are the intrasite and intersite electron-electron interactions, both with a higher energy cut-off of the order of the Fermi energy $E_f = V_f K_f > \omega(2K_f)$. This cut-off energy restricts the range of the primed summation in (1). Clearly, this formulation reflects the two cut-off nature of the electron-phonon system[9,5]. In the energy range $]\omega(2K_f), E_f]$, the electron-phonon interaction couple only electron-hole correlations and can lead to a possible 2Kf phonon softening[1,5,9]. It does not contribute significantly to the pairing correlations (Cooper channel) because the energy involved in the virtual phonon exchange is less than $\omega(2K_f)$[1,5,9].

The $2K_f$ phonon softening is directly connected with the renormalization of g_{1ph} and g_{3ph} to g'_{1ph} and g'_{3ph} due to the electron gas correlations. This is straightforward and leads to[5]:

$$g'_{1(3)ph}=g_{1(3)ph}/[1+(g_{1ph}+g_{3ph})N(T)], \qquad (2)$$

where N(T) is the $2K_f$ charge density response at temperature T (or frequency ω). The softening temperature occurs when $1+(g_{1ph}+g_{3ph})N(T_{mf})=0$, namely at the mean-field transition temperature T_{mf}. In 1D, this coincides with the occurence of a mean-field dimerization pseudo-gap $\Delta \sim T_{mf}$. It is important to note that such a condition for the $2K_f$ phonon soft mode is only valid when $2\pi T_{mf}>\omega(2K_f)$, otherwise for $2\pi T_{mf}<\omega(2K_f)$, virtual phonon exchange processes become relevant and renormalization group (RG) arguments tell us that the system has scaled to a non-adiabatic quantum regime[5,9] with no possibility of dimerization ($\Delta=0$). In the present model, the electron-phonon interaction comes from a modulation of the 1D transfer integral and for $g_{1H}=g_{3H}>0$, it is the $2K_f$ charge response between the sites that will be the strongest[5] and also the only relevant correlation function for the $2K_f$ phonon softening[5]. Moreover, in the presence of electron-electron interactions, N is no longer logarithmic which means that the expression for Δ has a non-BCS form[5].

III- CHARACTERISTICS OF THE HALF-FILLED BAND ELECTRON-LATTICE SYSTEM

RG and perturbation theories clearly show that the off-site $2K_f$ charge response N increase with $g_{1H}=g_{3H}>0$ from its free electron gas value[10]. This should prevail as long as the system is in a weak coupling regime or equivalently when the correlation gap Δ_H is irrelevant ($T>\Delta_H$)[5]. Obviously, from Eq.(2) an increase of g_{3H} means a growth of the dimerization pseudo-gap Δ. According to the exact result of Lieb and Wu[12], Δ_H also increases with g_{3H}. However, at $\Delta \simeq \Delta_H$, N will reach a maximum as a function of g_{3H} and finally decrease for $\Delta_H>\Delta$ due to a gradual freezing of the charge degrees of freedom. This is confirmed by the exact form of N in the limit of $U/t>>1$ ($\Delta_H \sim U$) namely[11], $N(T)\sim(\frac{t}{U})^2 T^{-1}$. In this way, it has been predicted[5] that Δ first increases with g_{3H}(or U)>0, reaches a maximum at $\Delta \simeq \Delta_H$ and decreases for $\Delta_H>\Delta$, this is shown in figure 1. When Δ_H is relevant ($\Delta_H>\Delta$), the phonon softening occurs in the presence of strong antiferromagnetic correlations and therefore Δ acquires a spin-Peierls character. This contrasts with the Peierls situation where Δ_H is not relevant ($\Delta<\Delta_H$) to N (see figure 1). Another interesting feature of the model is the existence of a critical electron-phonon coupling $g^c_{1ph}=g^c_{3ph}$ or λ_c for which a non-zero dimerization gap can occur. It is a $2\pi T_{mf}=\omega(2K_f)$. When $\lambda<\lambda_c$, $2\pi T_{mf}<\omega(2K_f)$ and the system becomes non-adiabatic. It can only develop antiferromagnetic ($2K_f$) spin density-wave (SDW) correlations. On the other hand, when $\lambda>\lambda_c$, $2\pi T_{mf}>\omega(2K_f)$ and the system can be dimerized in Peierls fashion if $\Delta_H<<\omega(2K_f)$ or spin-Peierls fashion whenever $\Delta_H>>\omega(2K_f)$ (see figure 1.b). These two important features of the electron-phonon system are at the center of our analysis for the $(TMTTF)_2X$ properties.

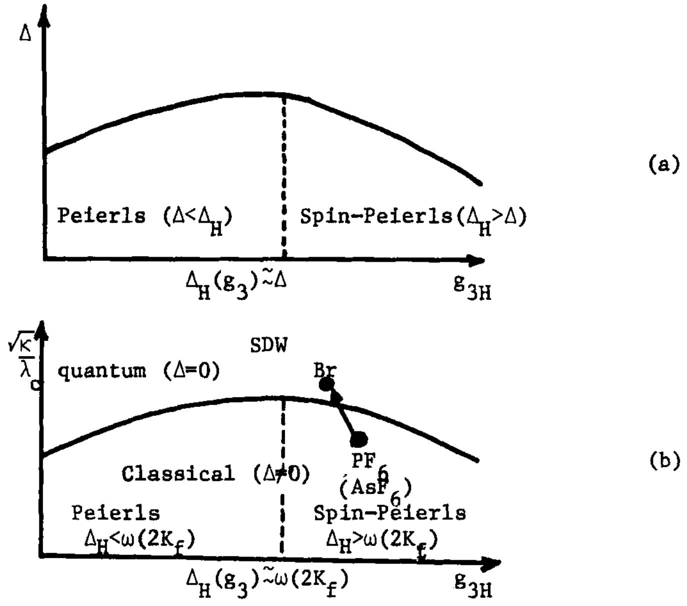

FIGURE 1 Characteristics of the half-filled band electron-phonon system : The dimerization gap Δ as a function of g_{3H} (a) and quantum (SDW) to classical ($\Delta\neq0$) crossover as a function of λ_c and g_{3H} (b).

IV- APPLICATION TO $(TMTTF)_2X$ COMPOUNDS

One common feature of the $(TMTTF)_2X$ compounds with centro-symmetric anions ($X=PF_6, AsF_6$, Br.....) is the existence of an activated behavior for the conductivity that takes place at moderate temperatures ($T_H\sim100K(Br)...200K(PF_6)$)[4]. This has been interpreted by the presence of a 1D correlation gap Δ_H due to the relevance of electron-electron umklapp processes (g_{3H}) in these compounds[2]. According to the theory, this is the signature of strong antiferromagnetic SDW correlations[12] at $T<T_H$. The observed antiferromagnetic

ground state of (TMTTF)$_2$Br at ambiant pressure clearly supported this view[13]. Under the same conditions of pressure, however, there is strong evidence for a non-magnetic state for the PF$_6$ and the AsF$_6$ compounds. This has been attested by the low temperature isotropy of the magnetic susceptibility[14] and the NMR data[15]. Moreover, the X-ray data[7] on a PF$_6$(AsF$_6$) have shown the existence of important 1D $2K_f$ lattice fluctuations below 60K(40K) or so. It has been conjectured from this that the transition at 15K(11K) is of the spin-Peierls type[2,4,7]. This is highly consistent with the results of section III which predict a spin-Peierls transition whenever g_{3H} g_{3ph} and Δ_H are relevant. The Debye frequency in organic compounds is around 200 ....250K[16] and from the X-ray data[7], this leads to $2\pi T_{mf} \sim \omega(2K_f)$. Therefore according to the results of section III, the (TMTTF)$_2$PF$_6$(AsF$_6$) compound at ambiant pressure ($\Delta \neq 0$) would be situated just below the quantum classical border line (see fig.1b). This is quite interesting, especially if one looks at the conductivity[4] and NMR data under pressure[15]. The activated behavior of the conductivity appears to be shifted to lower temperature under pressure, indicating a decrease of g_{3H}. In fact, from the work of Barisic and Brazovskii[1], the relevance of g_{3H} at $T<\Delta(4K_f)$ is linked to the stack dimerization which can be reduced under pressure[2] thereby decreasing Δ_H. When the electron-phonon interaction is added, this reasoning can be easily extended to accomodate a decrease of g_{3H} with pressure. Indeed, pressure increases the unrenormalized phonon frequencies $\omega(2K_f)$ thereby decreasing both g_{1H} and $g_{3H}(\sim 1/\omega^2(2K_f))^3$. It follows from Eq.2 that we have a significant drop of T_{mf} and the condition $2\pi T_{mf} > \omega(2K_f)$ for a $2K_f$ dimerization might no longer be satisfied. One should expect from figure 1.b a crossover to a non-adiabatic regime for the phonons under sufficient pressure thus making room to SDW correlations ($\Delta_H \neq 0$). This result agrees quite well with the recent NMR experiments of Creuzet et al[15] which clearly demonstrate the existence of a magnetic ground state for the PF$_6$ compound under 13Kbar of pressure.

In summary, we have analyzed the microscopic conditions under which an electron-phonon model can develop a $2K_f$ soft mode. When the band is half-filled or when umklapp processes are relevant, it is the off-site electron gas charge fluctuations that play the dominant role for an acoustic $2K_f$ phonon softening. This can occur in spite of strong site to site spin correlations of an antiferromagnetic character. In such a case $\Delta > \Delta_H$ and the lattice soft mode is of the spin-Peierls type and of the Peierls type otherwise. The ambiant pressure dimerized ground states of (TMTTF)$_2$PF$_6$ and (TMTTF)$_2$AsF$_6$ would belong to the spin-Peierls type. We have shown that for the PF$_6$ compound an appreciable decrease of g_{3ph}, g_{3H} and g_{1ph} under pressure can be at the origin of a SDW magnetic phase at 13Kbar. The latter appears to be quite similar to the SDW phase of Br compound at ambiant pressure[13,15].

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