Condensed matter physics in the 21st century: The legacy of Jacques Friedel

The Peierls instability and charge density wave in one-dimensional electronic conductors

Instabilité de Peierls et onde de densité de charge dans les conducteurs électroniques à une dimension

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ABSTRACT

We review salient structural and electronic features associated with the concomitant Peierls–charge density wave (CDW) instabilities observed in most one-dimensional (1D) inorganic and organic electronic conductors. First of all, the genesis of these concepts is placed in an historical perspective. We then present basic experimental facts supporting the general description of these 1D electron–phonon coupled systems developed in the 1970s. In this framework we shall consider in particular the role of 1D fluctuations on both lattice and electronic degrees of freedom, and of the inter-chain Coulomb coupling between CDWs in stabilizing in 3D the Peierls transition at finite temperature. We also clarify, in relation with experimental findings, the various conditions of adiabaticity of the electron–phonon coupling. Finally we illustrate by recent structural measurements the pioneering work of Jacques Friedel on CDW elasticity and plasticity and CDW pinning to defects through the appearance of Friedel oscillations.

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RÉSUMÉ

Nous passons en revue les principaux aspects structuraux et électroniques de l’instabilité Peierls–onde de densité de charge (ODC) observée dans la plupart des conducteurs inorganiques et organiques à une dimension (1D). Nous commençons par remplacer la genèse de ces concepts dans une perspective historique. Puis nous présentons les faits expérimentaux à la base de la description générale de ces systèmes 1D couplés électron–phonon développée à partir des années 1970. Dans ce cadre, nous considérons en particulier l’effet des fluctuations 1D sur les degrés de liberté structuraux et électroniques et le rôle du couplage coulombien inter-chaine dans le mécanisme de stabilisation 3D de la transition de Peierls à température finie. Nous clarifions aussi, en relation avec les données expérimentales, les différentes conditions d’adiabaticité du couplage électron–phonon. Finalement, nous illustrons avec des mesures structurales récentes les travaux

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1. Historical perspective

The framework used nowadays to describe the metal–insulator (M–I) transition occurring in 1D conductors by the setting of a \(2k_F\) periodic lattice distortion (PLD) was established by Peierls [1] and Fröhlich [2] in the mid-1950s \((k_F\) is the Fermi wave vector of the 1D electron gas, which amounts in reciprocal chain unit, \(d^*\), to one quarter of the charge \(\rho\) per site). However, as pointed out by Friedel [3], the physics underlying these works had already emerged in the beginning of the 1930s when Jones [4] showed that superstructures can be stabilized in normal metals and alloys when the Fermi sphere touches a maximum number of Brillouin zone boundaries issued from the superstructure reciprocal lattice periodicities. More precisely, Peierls calculated in 1930 [5] the energy spectrum of a free electron gas submitted to an external sinusoidal potential. He found that the effect of a periodic potential of wave number \(q\) is to open an energy gap \((2\Delta)\) in the band structure at wave vectors \(\pm q/2\). For a 1D electronic structure, there is a full gap opening at the Fermi level for \(\pm k_F\) if the potential wave number amounts to \(q = 2k_F\) (see Fig. 1). In addition if, as considered by Peierls and Fröhlich in the 1950s, the potential is set by a \(2k_F\) PLD, the lattice modulation trims an insulating ground state. However, Peierls first demonstrated that the gap opening is stable whatever the magnitude of the \(2k_F\) PLD and, for this reason, the metal–insulator (M–I) transition that results is now called a Peierls transition (the argument of Peierls was given for an half-filled band where, with \(\rho = 1\), \(2k_F = d^*/2\) is commensurate, but the result can be easily generalized whatever \(\rho\)). Independently of Peierls' work, Fröhlich [2] then Kuiper [6] developed the thermodynamics of the M–I transition due to the setting of a \(2k_F\) PLD. Interestingly, their (mean-field) theory gave at \(T = 0\) K a (half) energy gap \(\Delta_{MF}\), which exponentially depends on the inverse of the dimensionless electron–phonon coupling constant \(\lambda\) (expression (2.53) in Ref. [2]):

\[
\Delta_{MF} \sim E_F e^{-1/\lambda}
\]

In addition, \(\Delta_{MF}\) was found to be proportional to the (mean-field) critical temperature of the M–I transition, \(T_{MF}^p\) (expression (3.1) in Ref. [6]):

\[
\Delta_{MF} = 1.75k_B T_{MF}^p
\]

\(\lambda\) and \(T_{MF}^p\) will be more precisely defined by relations (22) and (23) below in section 2.3. Relations (1) and (2) are similar to expressions obtained later in 1957 for the superconducting gap and critical temperature in the BCS theory of superconductivity (in the BCS theory, the Debye phonon energy replaces the Fermi energy, \(E_F\), in expression (1)). However the analogy between the Peierls–Fröhlich and BCS theories was only noticed a few years later [7], but not really commented in the literature at that time. Then the pioneering works of Peierls, Fröhlich and Kuiper were forgotten and the thermodynamics of the Peierls transition was re-derived (using a more transparent formalism) independently several times during the 1970s [8,9] when the study of the M–I phase transition became a major subject of research.

In addition, Fröhlich showed that because of the electron–phonon coupling, the PLD induces a \(2k_F\) periodic charge density wave (CDW) modulation of the electronic density whose charge can couple with an external electric field, \(E\). In this framework, the main purpose of Fröhlich's work [2] was to provide an explanation for the zero-resistance state of superconductors by showing, using a 1D model, that the (incommensurate) \(2k_F\) CDW could collectively slide under the action of \(E\) and thus behaves as a superfluid. In this respect, Fröhlich was the first to introduce in 1954 the concept of CDW as the counterpart of the PLD and to notice that the two modulations should stabilize each other. Later, Overhauser proposed [10] the formation of pure electronic CDWs in a simple metal. However, Friedel provided physical arguments [3] suggesting that it is unlikely that an electronic CDW could be stabilized in the absence of a PLD.

The \(2k_F\) PLD/CDW instability driving the Peierls transition was first observed in 1973 in the framework of an X-ray diffuse scattering investigation of the 1D conductor \(K_2Pt(CN)_3Br_3\cdot3H_2O\) (KCP) [11]. Note that at the same time, electron diffraction studies provided evidence of a PLD/CDW modulation in layered metallic transition-metal di-chalcogenides \(MX_2\). However, if the Peierls mechanism provides a clear explanation of most of the M–I transition observed in 1D conductors, the microscopic origin of the PLD/CDW instability of \(MX_2\) compounds is still debated. Then in the following years, the \(2k_F\) PLD/CDW Peierls transition was observed in charge-transfer organic salts such as TTF–TCNQ (TTF, TCNQ and the other organic molecules quoted in the text are defined in the chemical index at the end of the paper), in the blue bronze \(K_{0.3}MoO_3\) and in the transition-metal tri-chalcogenide NbSe$_3$ (see section 2). Finally, the Fröhlich type of collective sliding of a \(2k_F\) CDW under the action of large enough external electric fields was observed in the Peierls ground state of NbSe$_3$ [12] and \(K_{0.3}MoO_3\) [13].

It is also interesting to remark that before the work of Peierls, Fröhlich and Kuiper, Slater proposed in 1951 [14] that the staggered exchange potential due to anti-ferromagnetic (AF) order could similarly drive a M–I transition in a half-filled \((\rho = 1)\) 1D electronic system because the magnetic periodicity of wave number \(d^*/2\) amounts to twice the Fermi wave vector of the 1D band, \(2k_F\). Then it was shown later that more general \(2k_F\) Fermi surface (FS) nesting processes could
stabilize either a spiral [15] or an oscillating [16] 2k_F spin density wave (SDW). Although SDWs stabilized by the FS nesting mechanism are known since more than half a century in 3D metals such as Cr [17], the type of M–I transition predicted by Slater was only observed in the 1980s in the Bechgaard salt (TMTSF)_2PF_6 [18]. However, recent diffraction experiments provide evidence that the insulating ground state of (TMTSF)_2PF_6 is in fact a mixture of 2k_F SDW and 2k_F CDW modulations [19]. Such a composite 2k_F modulated state was previously considered by Overhauser [20].

The organic salt TTF–TCNQ not only undergoes a 2k_F PLD/CDW Peierls instability (on the TCNQ stack), but also an additional instability (on the TTF stack) at twice the 2k_F wave vector [21]. Since the 4k_F wave vector amounts to ρ d^* units, the associated PLD can be viewed as the lattice fingerprint of a Wigner charge localization (or 4k_F CDW) achieving a charge periodicity of 1/ρ in chain direction [22,23]. In the limit of infinite intra-site repulsion U, the 4k_F instability is analogous to the 2k_F Peierls instability in a 1D spin-less electron gas. Note that the spin-less denomination is due to the fact that when U is infinite, a site is most occupied by one fermion whose spin degree of freedom is thus irrelevant. Note that if k_F (in d^* units) remains defined for the 1D free electron gas by ρ /4, one has k_{SL} = 2k_F. Thus, in the presence of electron–phonon coupling, the 1D pseudo-fermion gas should develop a Peierls instability at the 2k_{SL} = 4k_F critical wave vector.

The 4k_F Wigner charge localization induces a spin–charge decoupling. Thus below the 4k_F PLD/CDW transition, the spins S = 1/2, generally coupled in an AF manner, remain available for an additional magnetic instability towards either S = 1/2 AF or S = 0 spin–Peierls (SP) ground states. In the latter case, in the presence of strong enough magneto-elastic coupling, the pairing of neighboring S = 1/2 into a singlet is achieved via a dimerization of the 4k_F 1D superstructure. This spin–lattice coupled instability, which is analogous to the electron–lattice coupled Peierls instability in a half-filled band, is called SP instability. More precisely, if spins 1/2 are coupled by transverse (XY) AF exchange interaction, the mechanism of the SP transition is formally equivalent to the mechanism of the Peierls transition in a half-filled band of spin-less fermions [24]. In the case of AF exchange Heisenberg coupling, the theory of the SP transition is more elaborate because the longitudinal exchange component introduces attractive interaction between the 1D pseudo-fermions [25]. In the SP ground state, the singlet spin pairing is stabilized by the dimerization of the 4k_F super-structure of localized S = 1/2. The superstructure of double periodicity that results implies the 2k_F critical wave number as for the Peierls transition. This means, when Coulomb repulsions progressively increase, that one passes continuously from the 2k_F Peierls instability to the SP instability. SP ground states have been detected both in organic (TTF–CubDIT, MEM–(TCNQ)_2 and Fabre (TMTTF)_2PF_6 salts) and inorganic (V_1–Cr_xO_2, CuGeO_3) magnetic chain compounds.

2. The Peierls instability

1D organic and inorganic conductors generally crystallize in anisotropic structure made of relatively well decoupled stacks of molecules (see Fig. 13a below) or atomic clusters (see Fig. 14 below). Due to the segregated chain structure and the anisotropic overlap of p_x (d) orbitals in organic (inorganic) compounds, there is a weak inter-chain transfer integral t_L. If t_L is negligible, the 1D band structure of dispersion ε(k) is filled from −k_F to +k_F and the FS is composed of two points at ±k_F in the chain’s direction (Fig. 1). The longitudinal wave vector 2k_F perfectly nests the 1D FS. Below we shall consider the situation where the transverse warping of the FS, due to t_L, is less than the thermal broadening of the FS above the 3D Peierls critical temperature T_p. Thus precisely for t_L < πk_BT_p, the one-electron Hamiltonian contains only 1D interactions:

\[ H_{1D} = \sum_i \varepsilon(i) n_i + \sum_i t(i)(c_i^\dagger c_{i+1} + \text{h.c.}) \]  

In this Hamiltonian, ε(i) and t(i) are respectively the energy of site i and the near-neighbor i + 1 intra-chain transfer integral.

The simplest excitation, of energy \( h\omega_k(q) = \varepsilon(k + q) - \varepsilon(k) \), of the electronic structure create an hole in k together with an electron in k + q (see Fig. 1). It consists of the formation of an electron–hole pair of wave vector q. The energy \( h\omega_k(q) \) is involved in the denominator of the electron–hole polarizability of the free electron gas (also called Lindhard response function), which is expressed by [18]:

\[ \chi(q, \omega, T) = \frac{2}{\hbar} \sum_k \frac{\varepsilon(k + q) - \varepsilon(k)}{\varepsilon(k + q) - \varepsilon(k) - \hbar \omega + i\hbar \eta} \]
In expression (4), \( f(\varepsilon(k)) \) is the Fermi–Dirac function, \( L \) is the chain length and \( \eta \to 0^+ \) is a small quantity due to adiabatic continuity in the response process. For the FS nesting wave vector \( q = 2k_f \) and a 1D linearized electron dispersion, expression (A.3) of the Appendix gives the analytical expression of \( \chi(2k_f, \omega, T) \). The static (\( \omega = 0 \)) electron–hole response function diverges in temperature as:

\[
\chi(2k_f, \omega = 0, T) = N(E_F) \ln \left( \frac{2\gamma \epsilon_c}{\pi k_B T} \right)
\]

In (5), \( \epsilon_c \) is a cut-off energy of the order of the Fermi energy \( E_F \) and \( 2\gamma / \pi \approx 1.13 \). The logarithmic thermal divergence of expression (5) for \( q = 2k_f \) drives the Peierls instability.

The Peierls gap \( 2\Delta \) (Fig. 1) that opens at the Fermi level due to the \( 2k_f \) electron–hole instability is stabilized by the formation of a \( 2k_f \) PLD. In most of the cases, the PLD consists of a modulation of the bond distances. This forms a \( 2k_f \) bond order wave (BOW). The modulation of bond distances leads to a concomitant \( 2k_f \) modulation of the charge density or CDW as illustrated in Fig. 2. The CDW corresponds to a macroscopic condensate of \( 2k_f \) electron–hole pairs involved in the \( h\rho_k(q = 2k_f) \) excitation process; each of them is expressed as a function of creation \( (c_k^+ \delta \rho) \) and annihilation \( (c_k \delta \rho) \) electron operators (see Fig. 1). Thus the amplitude of the CDW modulation is given by the \( k \) average of all the \( h\rho_k(q = 2k_f) \) excitation processes:

\[
\rho_{2k_f} = \langle c_k^+ \delta \rho \rangle_k
\]

and its spatial dependence is expressed by:

\[
\delta \rho(x) = \rho_{2k_f} \cos(2k_f x + \varphi)
\]

The amplitude of the CDW \( \rho_{2k_f} \) is proportional to the Peierls gap:

\[
\rho_{2k_f} \propto \frac{N(E_F)}{\lambda} \Delta
\]

The PLD is achieved by the coupling of the Hamiltonian (3) to phonons. Fig. 2 shows that the BOW that modulates the inter-site distance, \( u(x) \), is in quadrature with the charge modulation (CDW) where \( \delta \rho(x) \propto -\partial u(x)/\partial x \). The modulation of the charge on the site \( i \) formed by a molecule or an atomic cluster, \( \rho + \delta \rho(x_i) \), should be accompanied by an intramolecular/cluster bond deformation in phase with the CDW: \( d(x_i) \propto \partial \delta \rho(x_i) \) (see Fig. 2). Both \( u(x) \) or \( d(x) \), which are in quadrature, stand for the PLD introduced in section 1. The BOW \( u(x) \) is basically achieved by electron–phonon coupling with acoustic phonons that, via a change of the inter-site distances, modulate the transfer integral \( t(i) \) in expression (3). The site deformation \( d(x_i) \) is achieved by electron–phonon coupling with internal (optical) phonons that, via a change of the intra-molecular/cluster distances, modulate the site energy \( \varepsilon(i) \) in expression (3). For a free-electron system, the Peierls gap \( \Delta \) is proportional to the amplitude of the PLD. Rigorously, one should introduce two Peierls gaps linearly related via the “bond” and “site” electron–phonon coupling constants, “g”, to each component \( u(x) \) and \( d(x) \) of the PLD. In this case, the total Peierls gap is the sum in quadrature of the “bond” and “site” Peierls gaps.

2.1. Structural fluctuations

The Peierls instability is announced by the development below \( T_{1D} \) of \( 2k_f \) PLD fluctuations accompanied by a fluctuating CDW condensate of electron–hole pairs (expression (6a)). The PLD/CDW fluctuations are correlated in chain direction on \( \xi(T) \), \( \xi(T) \) increases upon cooling below \( T_{1D} \) (Fig. 5 below). Diffraction by 1D PLD fluctuations gives rise to diffuse sheets centered at the \( \pm 2k_f \) wave vector in reciprocal space (Fig. 3). The detection of such diffuse sheets, through the formation of \( \pm 2k_f \) diffuse lines on X-ray patterns, provided the first observation of the Peierls instability in KCP [11]. Since this pioneering work, X-ray diffuse scattering methods have been widely used to detect PLD fluctuations (mostly by their BOW component) pre-transitional at the Peierls transition in many families of inorganic and organic 1D conductor. For example, Fig. 4 presents X-ray patterns exhibiting this \( 2k_f \) diffuse scattering at room temperature (RT) in \( \text{K}_{0.3}\text{MoO}_3 \) (left part) and \( \text{NbSe}_2 \) (right part).

In the absence of fluctuation, the isolated Peierls chain should undergo a phase transition at the mean-field critical temperature \( T_{p}^{MF} \) defined by expression (23) below. However, 1D thermal fluctuations prevent the establishment of a long-range PLD/CDW order at finite temperature. The observation of a 3D Peierls transition at finite temperature, \( T_F \), which is generally...
Fig. 3. Diffraction (in reciprocal space – left side) by the 2kF PLD, represented in direct space on the right side, in the 1D fluctuation regime (below T_{1D}), in the inter-chain short range coupling regime (between T_{CD} and T_{P}) and in the 3D Peierls ground state (below T_{P}).

Fig. 4. X-ray patterns from K0.3MoO3 (left) and NbSe3 (right) at RT showing different sets of 2kF diffuse scattering (adapted respectively from Refs. [26] and [27]). Note that the 2kF diffuse segments (black arrows) of K0.3MoO3 perpendicular to the chain direction b are located in broad diffuse lines (white arrows) perpendicular to the a + 2c direction and whose origin is commented in the text. In NbSe3 black-and-white arrows show two sets of diffuse lines perpendicular to the chain direction b, which respectively correspond to 2kF fluctuations on type-I and type-III chains defined in Fig. 14b.

Table 1
Bare phonon frequency (Ω_{2k_F}), and nature of the critical phonon mode, mean field (T_{MF}) and Peierls (T_{P}) transition temperatures, Fermi (v_F) and electron–hole pair coherence length (ξ_{eh}) dimensionless product Ω_{2k_F}v_{eh} (see section 2.3) and type of the Kohn anomaly observed in several families of 1D conductors. T_{MF} is calculated from the Peierls gap using the “BCS” relationship [2]. ξ_{eh} corresponds also to the temperature T_{1D} at which the 2kF PLD begins to be detected. ξ_{eh} is obtained either from the curvature of the Kohn anomaly (a) or from the high-temperature value of the CDW correlation length ξ_{||} (b).

<table>
<thead>
<tr>
<th>1D conductor</th>
<th>Ω_{2k_F} (meV)</th>
<th>T_{MF}/T_{P} (K)</th>
<th>v_F (10^5 m/s)</th>
<th>v_{eh}</th>
<th>ξ_{eh} (Å)</th>
<th>Ω_{2k_F}v_{eh}</th>
<th>Kohn anomaly</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_{2}Pt(CN)<em>{6}Br</em>{13}·3H_{2}O</td>
<td>7 (LA)</td>
<td>650/100</td>
<td>0.10</td>
<td>0.94</td>
<td>Large (50?)^2</td>
<td>0.04</td>
<td>Giant</td>
<td>[33]</td>
</tr>
<tr>
<td>K_{0.3}MoO_{3}</td>
<td>7 (mode mixture)</td>
<td>500/180</td>
<td>5.5/1.7</td>
<td>0.94</td>
<td>(55)</td>
<td>0.04</td>
<td>Phonon softening at T_P</td>
<td>[34]</td>
</tr>
<tr>
<td>TTF–TCNQ (2kF)</td>
<td>5 (TA)</td>
<td>150/54</td>
<td>1.8</td>
<td>0.94</td>
<td>0.17</td>
<td>Incomplete phonon softening at T_{P}</td>
<td>[35]</td>
<td></td>
</tr>
<tr>
<td>TTF–TCNQ (4kF)</td>
<td>8.5 (LA)</td>
<td>600/49</td>
<td>0.9</td>
<td>0.94</td>
<td>0.17</td>
<td>Incomplete phonon softening at T_{P}</td>
<td>[36]</td>
<td></td>
</tr>
<tr>
<td>NbSe_{2} (2k_{III})</td>
<td>8 (TA/LA)</td>
<td>700/145</td>
<td>2.4</td>
<td>0.94</td>
<td>0.17</td>
<td>No Kohn anomaly</td>
<td>[37]</td>
<td></td>
</tr>
<tr>
<td>BaVS_{3}</td>
<td>5.8 (?)</td>
<td>170/70</td>
<td>4.9</td>
<td>0.94</td>
<td>0.17</td>
<td>Incomplete phonon softening at T_{P}</td>
<td>[38]</td>
<td></td>
</tr>
</tbody>
</table>

A sizeable fraction of T_{MF} (see Table 1), is due to the presence of the inter-chain coupling. The inter-chain coupling manifests below a cross-over temperature T_{CD}, generally close to T_{P}, by correlating near-neighbor 1D CDW fluctuations on a transverse length ξ_{⊥}. As illustrated in Fig. 3, the anisotropy of these different fluctuations regimes can be clearly distinguished through X-ray diffuse scattering measurements. In the weak electron–phonon coupling limit (λ < 1), 1D fluctuations begin to be detected around T_{MF} when ξ_{||} amounts to the 2kF PLD wave length.
There are three principal mechanisms of inter-chain coupling:

- the Coulomb coupling between CDW, which will be considered in section 3;
- the transverse coupling of the warped FS due to \( t_\perp \). This mechanism is relevant in the temperature range \( T < T^* = t_\perp / k_B \pi \) where the thermal broadening of the FS is smaller than \( t_\perp \). In that case, the transverse component of the FS nesting wave vector fixes the inter-chain CDW periodicity in the Peierls ground state. Such a mechanism plays a role in the SDW transition of \((\text{TMST})_2\text{PF}_6\), where \( T_D = 12 \, \text{K} < T^* \sim 100 \, \text{K} \). However, in most of the CDW compounds considered in Table 1 where \( T_D > T^* \), the transverse FS nesting process is not relevant;
- the anisotropic dispersion \( \hbar \Delta \) of the bare phonon branch bearing the \( 2k_F \) Kohn anomaly for transverse wave vectors \( q_\perp \).

In that case the minimum of phonon frequency along \( q_\perp \) should stabilize the inter-chain PLD periodicity in the Peierls ground state. This effect should be relevant in \( K_3\text{MoO}_3 \) where the Kohn anomaly develops in a pre-existing valley of soft phonons due to ferroelectric-like fluctuations along the Mo\( \text{O}_2 \) segment direction shown by red arrows in Fig. 14a (these low frequency phonon modes manifest by the broad X-ray diffuse scattering shown by white arrows in Fig. 4a).

Dynamics of PLD fluctuations is controlled by the bare frequency of the phonon mode \( \Omega_{2k_F} \) which, when coupled with the electron degrees of freedom of Hamiltonian (3), drives the structural instability of the Peierls transition through the logarithmic divergence of the electron–hole response function \( \chi(2k_F, \omega = 0, T) \) – see expression (5). \( \Omega_{2k_F} \) given in Table 1 is estimated from either the frequency of the critical phonon mode extrapolated at \( 2k_F \) from frequencies taken outside the dip of the Kohn anomaly (in the adiabatic regime) or from the \( 2k_F \) phonon frequency when the Kohn anomaly is not really developed above \( T_{\text{MF}} \) or not formed at all (in the anti-adiabatic regime) – see section 2.3. The nature of the regime of PLD/CDW fluctuations depends on the relative value of the bare phonon energy \( \hbar \Omega_{2k_F} \) with respect to the mean-field Peierls gap \( \Delta_{\text{MF}} \) given by (1) [28].

In the classical (adiabatic) regime, when \( \hbar \Omega_{2k_F} < \Delta_{\text{MF}} \), electron–hole pairs are induced by the “quasi-static” \( 2k_F \) short ranged potential originating from the PLD. When below \( T_{\text{MF}} \) the PLD correlates on \( \xi \) a local Peierls condensate is formed. The increase of \( \xi(T) \) upon cooling leads to the progressive development of a pseudo-gap in the one-electron density of states around the Fermi level (see section 2.2). In this case, the pseudo-gap reduces the number of carriers available for charge transport, but also the number of states contributing to the Pauli spin susceptibility. In short, the pseudo-gap achieves a progressive freezing of both charge and spin degrees of freedom.

In the quantum (anti-adiabatic) regime, when \( \hbar \Omega_{2k_F} > \Delta_{\text{MF}} \), electronic interactions mediated by high-frequency \( 2k_F \) phonons become non-retarded and attractive. Quantum fluctuations significantly reduce the \( T = \text{OK PLD} \) and Peierls gap 2\( \Delta \) [28]. However, the Peierls instability remains present whatever the value of the electron–phonon coupling [29], showing the generality of the Peierls’ result. Note that quantum fluctuations have more drastic effect on the Peierls instability in a spin-less electron gas [28,29] and by consequence on the SP instability. In this case, which will be considered in section 2.2, quantum fluctuations can completely destroy the SP gap.

The classical-quantum crossover of the Peierls chain occurs for \( \hbar \Omega_{2k_F} \sim \Delta_{\text{MF}} \). Experimental Peierls systems are located in the classical/adiabatic regime where, with a soft lattice dynamics, one has \( \hbar \Omega_{2k_F} \ll k_B T_{\text{MF}} \) (see Table 1). Note that the non-observation of a Peierls ground state in the C nanotubes, which are hard materials with \( \hbar \Omega_{2k_F} \sim 0.15 \, \text{eV} \gg T_{\text{MF}} \sim 15 \, \text{K} \) [30], could be due to the wipe out of \( \Delta \) by quantum fluctuations. The classical-quantum crossover can be well studied in SP systems (see Fig. 7 below).

For an incommensurate \( 2k_F \) modulation, the structural order parameter \( u(x) \), in quadrature with \( \delta \rho(x) \) expressed by (6b) is given by:

\[
u(x) = u_0 \sin(2k_F x + \varphi) \quad (8)
\]

At finite temperature, the Peierls long-range order of 1D systems is destroyed by thermal fluctuations. These fluctuations are those of the phase \( \varphi \) of the order parameter at low temperature and of its amplitude \( u_0 \) at high temperature (see Fig. 5). Due to fluctuations, there is only a short-range order on the correlation length \( \xi(T) \) on which the 1D order parameter develops. Below we shall label this short-range order parameter by the complex quantity \( \tilde{u}(x) \). In the adiabatic limit previously defined, the thermodynamics of the 1D fluctuating Peierls chain can be well approximated from the exact solution [31] of the Landau–Ginzburg free-energy functional:

\[
F[u] = \int dx [a |\tilde{u}(x)|^2 + b |\tilde{u}(x)|^4 + c |\partial \tilde{u}(x)/\partial x|^2]
\]

with \( a = a' (T - T_{\text{MF}}^P)/T_{\text{MF}}^P \), \( b \) and \( c \) can be calculated by the microscopic theory of the Peierls transition [18]. Note that the use of a 1D functional assumes that lattice fluctuations associated with the critical phonon mode coupled with fluctuating electron–hole pairs are 1D. This 1D fluctuation regime is assessed by the observation by X-ray diffuse scattering between \( T_{\text{co}} \) and \( T_{\text{ID}} \approx T_{\text{MF}}^P \) of 2\( k_F \) diffuse sheets (see Fig. 3).

The thermodynamics of the chain only depends on the extent of the reduced critical region \( \Delta t_{1D} \) defined from the parameters of the functional (9) by:

\[
\Delta t_{1D} = \left(\frac{b k_B T_{\text{MF}}^P}{J_{\text{ID}}} \right)^{2/3} / \left(\frac{a' c^{1/3}}{a' c^{1/3}} \right)
\]
2.2. The pseudo-gap

Fig. 5 shows that the intra-chain correlation length $\xi_l$ of 1D fluctuations of a classical system diverges at 0 K. At this temperature, a true 1D Peierls gap opens at $\sim 2\Delta_{MF}$ (quantum fluctuations are weak in the adiabatic limit). At $T$ finite when $\xi_l$ is finite, the Peierls gap transforms into a pseudo-gap in the density of states whose magnitude and energy dependence is fixed by the length $\xi_l(T)$ on which the local Peierls order is established [39]. Upon cooling from $\sim T_{MF}$, the increase in $\xi_l(T)$ leads to a progressive vanishing of the density of states at the Fermi level, $N(E_F)$. Such a vanishing, which involves also the spin degrees of freedom in a free electron gas, can be probed by the decrease of the Pauli spin susceptibility $\chi_P$. This effect was nicely followed by an earlier investigation of KCP using $^{195}$Pt Knight shift measurements [40].

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The expression \( \Delta_{SP} = \frac{\hbar}{2} \Omega_{SP} \) gives the energy gap \( \Delta_{SP} \) of the single-particle state for spin 1/2 in the Heisenberg spin chain. This expression is a consequence of the zero-point quantum fluctuations, which are significant at low temperatures. The energy gap \( \Delta_{SP} \) is proportional to the mean-field critical frequency \( \Omega_{SP} \) of the spin chain. This proportionality constant is \( \frac{\hbar}{2} \).

In the adiabatic limit, the effective exchange coupling is \( J_{eff} = \frac{\hbar}{2} \Omega_{SP} \), and the pseudo-gap energy \( \Delta_{SP} \) is proportional to the mean-field critical frequency \( \Omega_{SP} \). This is in agreement with the experimental data for the spin-glass transition temperature \( T_{SG} \) and the mean-field critical frequency \( \Omega_{SP} \).

In the anti-adiabatic limit, the effective exchange coupling is \( J_{eff} = \frac{\hbar}{2} \Omega_{SP} \), and the pseudo-gap energy \( \Delta_{SP} \) is proportional to the mean-field critical frequency \( \Omega_{SP} \). This is in agreement with the experimental data for the spin-glass transition temperature \( T_{SG} \) and the mean-field critical frequency \( \Omega_{SP} \).

These results suggest that the pseudo-gap energy \( \Delta_{SP} \) is proportional to the mean-field critical frequency \( \Omega_{SP} \), and the pseudo-gap energy \( \Delta_{SP} \) is proportional to the mean-field critical frequency \( \Omega_{SP} \). This is in agreement with the experimental data for the spin-glass transition temperature \( T_{SG} \) and the mean-field critical frequency \( \Omega_{SP} \).
excitation. Thus the spin susceptibility of MEM–(TCNQ)$_2$ follows the thermal dependence of the uniform $S = 1/2$ AF chain until the SP transition (right-hand side of Fig. 8). Well inside the quantum phase, the high-frequency critical phonon mode renormalizes the near-neighbor exchange interaction $J$ and adds next near-neighbor exchange components [47] as observed in CuGeO$_3$.

2.3. The Kohn anomaly

While Peierls transitions occur in the classical regime defined by $\hbar \Omega_{2k_F} < \Delta_{MF}$, the various compounds quoted in Table 1 exhibit quite different pre-transitional critical lattice dynamics. This requires the need to define a second adiabatic condition for the formation of a Kohn anomaly. To account for different critical dynamics, we derive in the Appendix the mean-field (RPA) phonon dynamics for a free electron gas weakly coupled with the lattice ($\lambda < 1$).

To introduce the notations let us re-derive the critical phonon dynamics in the adiabatic limit for a weak electron–phonon coupling. One considers, as illustrated in Fig. 9a, an harmonic chain of atoms of mass $M$ linked by the spring constant $K_q$ and coupled with the 1D electron gas by the electron–phonon coupling potential $V_{ep}(q)$.

When one ignores the coupling with the electron gas, the $q$ Fourier component $u_q$ of the atomic displacements follows the harmonic oscillator equation:

$$\ddot{u}_q + K_q u_q = 0$$

The mode $q$ corresponds to atomic oscillations with the bare phonon frequency:

$$\Omega_q = \sqrt{\frac{K_q}{M}}$$

Due to the electron–phonon coupling, the atomic displacements submit the electron gas at an “external” potential $V_{ep}(q)$. For a PLD of small amplitude $u_0$ (typically $u_0 \sim 0.025–0.06$ Å for most Peierls systems), the Peierls chain can be treated in the weak electron–phonon coupling limit. In this case $V_{ep}(q)$ can be taken proportional to $u_q$:

$$V_{ep}(q) = g u_q$$

In (15) $g$ is the electron–phonon coupling constant that we shall take for simplicity to be independent of $q$. The conduction electrons respond to this external potential by modulating their density. For small $V_{ep}(q)$ in the framework of the linear response theory, the $q$ Fourier component of the charge modulation $\rho_q$ is given by:

$$\rho_q = \chi(q, T) V_{ep}(q)$$

where we use, for $\Omega_q$ much smaller than the characteristic frequencies of the dynamics of the electron–hole pairs, the static limit $\omega = 0$ of the electron–hole response function.

The Hamiltonian of coupling between the charge modulation and the electron–phonon potential can be expressed by:

$$H_{ep} = \sum_q \rho_{-q} V_{ep}(q)$$

This Hamiltonian gives rise to a “force” $F_q$:

$$F_q = \frac{\partial H_{ep}}{\partial u_{-q}}$$
which must be added to the elastic force $K_q u_q$ in the equation of movement (13). The harmonic oscillator equation thus becomes:

$$\ddot{u}_q + \Omega_q^2 \left[ 1 - \frac{2g^2}{K_q} \chi(q, T) \right] u_q = 0$$

(19)

In (19) the electron–electron, electron–hole long-range process obtains from the equation of motion.

The third member of expression (21) involves the mean-field Peierls transition temperature:

$$T_p^{MF} = \frac{2Y\varepsilon_c}{\pi} e^{-1/\lambda}$$

(23)

$T_p^{MF}$ is the temperature at which the frequency of the Kohn anomaly given by expression (21) in the RPA approximation vanishes. $T_p^{MF}$ is, in absence of thermal fluctuations, the critical temperature of the Peierls transition calculated in the 1950s (see expressions (1) and (2)).

When $\Omega_q$ is not negligible with respect to characteristic frequencies of the dynamics of the electron–hole pairs, the $\omega$-dependence of the electron–hole response function must be kept. The equation of movement (19) becomes an explicit equation in $\omega$. In that case, the calculation of the dynamics of the Peierls transition is more elaborated. It is performed in the Appendix using a simplified analytical expression of the electron–hole response function. This calculation allows us to clarify the condition of adiabaticity for the dynamics of the Peierls transition and for the formation of a Kohn anomaly. This condition that controls the nature of the critical phonon dynamics of the Peierls transition relies on a comparison between the frequency of fluctuation of the amplitude of the order parameter, $\omega_A = \sqrt{\lambda} \Omega_{2k_F}$ entering in expression (21) and the lifetime $\tau_{eh}$ of the electron–hole pairs at $T_p^{MF}$, which will be considered below.

The lifetime of the fluctuating electron–hole pairs can be expressed by:

$$\tau_{eh} = \xi_0/v_{eh}$$

(24)

In expression (24), $\xi_0$ is the electron–hole coherence length and $v_{eh}$ is the velocity of the electron–hole pair excitations.

$\xi_0$ given in Table 1 is obtained either from the curvature of the Kohn anomaly if it exists (42) or from the high-temperature ($\sim T_p^{MF}$) value of the CDW correlation length $\xi_0$ (42, 32). $v_{eh}$, obtained from expression (11), is expressed in Table 1 in fraction of the Fermi velocity $v_F$, this latter quantity being obtained either from ab-initio band calculations or from ARPES measurements.

In the absence of defects, only thermal fluctuations limit the electron–hole pair lifetime. In a free electron gas, one obtains with $v_{eh} = v_F$ in the thermal coherence length $\xi_0$ given by (11):

$$\tau_{eh} = \hbar v_F/\pi k_B T_p^{MF} = \sqrt{2}\tau_p^{MF}.$$
If $\omega_A T_{\text{eh}} < 1$, the electron–hole pairs fluctuate so rapidly during the phonon oscillation period that they are able to screen the coupling constant $K_q$ between the atoms. The screening is thus determined by the quasi-static electron–hole response $\chi(2k_F, \omega \approx 0, T)$ which enters in the equation of motion (19). The enhanced $q$ dependence of the response function for $q = 2k_F$ leads to the formation of a Kohn anomaly. At $q = 2k_F$, the phonon frequency $\omega_{2k_F}(T)$, which thus follows the divergence of the electron–hole response function given by expression (5), critically softens upon cooling (see Fig. 10 and the left part of Fig. 11). Upon cooling, the enhanced screening leads to a progressive flattening of the potential, in which the atoms oscillate (Fig. 9b). This drives a lattice instability of displacive type where the deviation of atomic position with respect to their high temperature position, $u(x)$, takes a continuum of values. This generally stabilizes a sinusoidal PLD $u(x)$ in the Peierls ground state. A giant $2k_F$ Kohn anomaly is already formed at RT in the acoustic mode polarized in chain direction of KCP [33]. In the blue bronze $\text{K}_0.3\text{MoO}_3$, the $2k_F$ Kohn anomaly, which progressively softens upon cooling [34], is located in a pre-existing soft phonon branch. This branch corresponds to Einstein-like pre-existing soft phonons due to an incipient ferroelectric instability of individual $\text{Mo}_4\text{O}_{12}$ segments of a 4-corner-sharing octahedron that form the repeat unit of 1D chains (see Fig. 13a). Similar underlying ferroelectric instabilities are found in several others families of 2D metallic oxides and bronzes that are subject to $2k_F$ Peierls–like instabilities [50] (see also the end of this section).

If $\omega_A T_{\text{eh}} > 1$, the $2k_F$ phonon fluctuates too rapidly during the living time of the electron–hole pairs so that the phonon mode cannot efficiently couple with the electron–hole condensate. There is no screening and thus no critical softening of $\omega_{2k_F}$ when the Peierls transition is approached (Fig. 10). The long-living electron–hole condensate induces via the electron–phonon coupling a quasi-static local $2k_F$ PLD of amplitude $\omega_0$ quite well decoupled from the $2k_F$ “critical” phonon. This gives rise above the Peierls transition to a quasi-elastic response in inelastic scattering processes (right-hand part of Fig. 11). The long-time-living structural fluctuations exhibit a Lorentzian-like relaxation (expression (A13) in the Appendix) whose associated dynamics is typical of an order–disorder transition. Such a dynamics connects, through a double-well potential shown in Fig. 9c, two local atomic deformations $\pm \omega_0$ or two PLD/CDW cluster configurations, each deformation or configuration achieving a Peierls distortion on a local scale. The change in the conformation of the individual PLD/CDW cluster requires a jump above the potential barrier separating the $\pm \omega_0$ ground states. This jump process controls the life-time $\tau_{2k_F}(T)$ of individual clusters. The long-range static order stabilized below the Peierls transition is achieved by the critical slowing down of $\tau_{2k_F}(T)$ (together with the divergence of the cluster size $\xi_1(T)$). The slowing down of the dynamics gives rise to a “divergence” of the damping constant $\Gamma_{2k_F}(T)$, defined by expression (A14), which enters the Lorentzian response (A13) calculated in the Appendix. The non-detection of a Kohn anomaly associated with the $2k_F$ Peierls instability of $\text{NbSe}_3$ [37] and the $4k_F$ instability of $\text{TTF–TCNQ}$ [36] suggests the presence of such a relaxation dynamics, which remains to be studied.

Between these previous regimes, one has, by continuity, when $\omega_A T_{\text{eh}} \sim 1$, an incomplete softening of the frequency of the Kohn anomaly at the Peierls transition (Fig. 10). Such a dynamics is observed in $\text{TTF–TCNQ}$ [35] and $\text{BaVS}_3$ [38]. In $\text{TTF–TCNQ}$, a weak $2k_F$ Kohn anomaly develops below about 150 K ($T_{1D}$) in an acoustic branch polarized transversally with respect to the stack direction [35].
In the case of the free electron gas where $\tau_{eh}$ is given by (25) and for typical dimensionless electron–phonon coupling constants $\lambda \sim 0.2$–0.4, one finds that the adiabatic–anti-adiabatic crossover condition $\omega_{A} \tau_{eh} = 1$ occurs (see expression (A.12) of Appendix) for:

$$\left( k_{B} T_{P}^{MF} / \hbar \Omega_{2k_F} \right)_{c} = \frac{\sqrt{\lambda / 2}}{\pi} \approx 0.1–0.14 \quad \text{or} \quad \left( \Delta_{MF} / \hbar \Omega_{2k_F} \right)_{c} \approx 0.2–0.25 \quad (27)$$

This condition agrees with the numerical calculations shown in Fig. 11. Note that the adiabatic condition for the formation of a Kohn anomaly is more restrictive than the one, $\Delta_{MF} / \hbar \Omega_{2k_F} \approx 1$, obtained in section 2.2.

KCP and K$_{3}$MnO$_{5}$, which both exhibit a well-defined Kohn anomaly, are in the adiabatic limit. Consistently, their $k_{B} T_{P}^{MF}/\hbar \Omega_{2k_F}$ ratio is above the critical condition (27). However, for the other 1D conductors quoted in Table 1, whose Peierls dynamics exhibits either the incomplete softening of a Kohn anomaly or a relaxation dynamics, one still obtain a $k_{B} T_{P}^{MF}/\hbar \Omega_{2k_F}$ ratio that remains above the condition (27). This means that the quantity $\tau_{eh}$ to compare with $\omega_{A}$ should be longer than the thermal time $\tau_{T}$ obtained for free electrons in the weak electron–phonon coupling limit. Following our previous discussion on the electron–hole life time, this means that the velocity of the electron–hole pair excitations $v_{eh}$ should be smaller than the Fermi velocity $v_{F}$. $v_{eh} < v_{F}$ imply that the electron gas coupled with the lattice is somewhat localized; the localization being due either to strong electron–electron repulsions (case of TTF–TCNQ and BaV$_{3}$) or to strong electron–phonon coupling (case of NbSe$_{3}$).

From the quantitative analysis of the $2k_{F}/4k_{F}$ critical X-ray diffuse scattering, $v_{eh}$ estimated in Table 1 for the donor [52] and acceptor [32] stacks of TTF–TCNQ and for BaV$_{3}$ [53] are significantly reduced with respect to $v_{F}$ [54]. The strong reduction of $v_{eh}$ with respect to $v_{F}$ leads to a $\omega_{A} \tau_{eh}$ product closer to 1. This can qualitatively explain why only a weak softening is observed for the $2k_{F}$ Kohn anomaly (on the TCNQ stack) of TTF–TCNQ and of V chain of BaV$_{3}$. Also the non-adiabatic dynamics (i.e. absence of Kohn anomaly) of the $4k_{F}$ CDW instability of TTF–TCNQ is consistent with the observation of a $4k_{F}$ Wigner-PLD instability on the TTF stack [21,22] of TTF–TCNQ. Note that the presence of sizeable electron–electron repulsions in TTF–TCNQ is assessed by the detection of a pseudo-gap of correlation in infrared conductivity [55].

The dynamics of the Peierls transition calculated in the strong-electron–phonon coupling limit does not exhibit a Kohn anomaly, but a $2k_{F}$ quasi-static lattice response [56]. The PLD instability consists of the formation of atomic clusters where the displaced atoms form quite well-defined local chemical bonds with their surroundings. In consequence, there is a large gain in energy to achieve the $\pm u_{0}$ lattice displacement and any deviation of $u(x)$ with respect to these optimal bond distance costs energy. This is consistent with the double-well potential representation shown in Fig. 9c. In each cluster, the atomic displacement $\pm u_{0}$ should be a sizeable fraction of the interatomic distances. Then the CDW consists of a modulation of the electron occupancy of these well-defined bonds so that the excess or deficit of charge of the density wave must be trapped in local atomic clusters. Because of the formation of such atomic clusters, the PLD should be non-sinusoidal. The overall energy gain due to cluster formation relies on a well-defined phasing of atomic displacements with respect to their surroundings. Thus the PLD, which could incorporate a succession of clusters differing by their relative phase shift, generally forms long-period superstructures. Fluctuations among such trapped configurations are controlled by an order–disorder or relaxation dynamics. Such a dynamics exhibits a critical slowing down of the cluster inverse life time when the Peierls transition is approached from above.

Good examples of such "$2k_{F}$" PLD and long-period superstructures can be found for $m \geq 7$ in the family of (PO$_{2}$)$_{4}$W$_{3m}$O$_{9}$ tungsten bronzes built with a segment of a $m$-corner-sharing WO$_{6}$ octahedron [57]. For example, in the “Peierls” superstructure of the $m = 10$ member, the amplitude of the modulation amounts to $u_{0} \sim 0.2$ Å, which represents one tenth of a typical W–O bond distance [58]. In this superstructure, clusters exhibiting maxima of PLD are made with correlated W displacements principally aligned (i) in a ferroelectric manner in the direction of the segment of the $m$-octahedron, and (ii) in the opposite (i.e. anti-ferroelectric) manner between neighboring segments. This displacement pattern realizes a good compromise between the “$2k_{F}$” PLD/CDW instability of the metallic bronze related to its quasi-1D electronic structure and the incipient anti-ferroelectric lattice distortion of the insulating oxide WO$_{3}$, which represents the limit of this series when $m \rightarrow \infty$.

### 3. Inter-chain Coulomb coupling between CDWs

As the $2k_{F}$ PLD modulates the charge density in chain direction, the basic inter-chain coupling mechanism between CDWs is of Coulomb origin. Coulomb coupling of the Madelung type has been calculated by Šab, Barisić and Friedel (SBF) assuming a linear charge modulation [59]. In the SBF model, the coupling between two CDWs, expressed by (6b), located on chains $i$ and $j$ distant of $R_{ij}$, and whose origin is shifted by $eb$, is given by:

$$W_{ij}(2k_{F}, R_{ij}, \varphi_{i–j}) = \frac{\delta \rho_{i} \delta \rho_{j}}{b} \sum_{G \in RR} \cos(\varphi_{i–j} - Geb)K_{0}(R_{ij}|2k_{F} + G|)$$

In expression (28) $\delta \rho_{i}$ and $\delta \rho_{j}$ are the amplitude of the $i$th and $j$th CDWs and $\varphi_{i–j}$ is their relative phase shift. $G$ is a vector of the reciprocal lattice (RR) of the chain of period $b$. $K_{0}(x)$ is the modified zeroth-order Bessel function, which rapidly decays with $R_{ij}$ ($x$ below) as:

$$K_{0}(x) \sim e^{-x}/\sqrt{x}$$

(29)
The exponential spatial decay means that the phase shift $\varphi_{j-i}$ between CDWs is basically fixed by first-neighbor interactions $|j-i|=1$. Assuming $\varepsilon = 0$, $W_{j-i}=1$ is minimum for a phase shift of $\pi$ between first-neighbor chains. This brings an excess of charge, $+\delta \rho$, in regard of a deficit of charge, $-\delta \rho$ as shown in Fig. 12a. This CDW’s phase shift is observed in the two transverse directions of the Peierls ground state structure of KCP.

In chains made of atomic clusters or of molecules, the CDW is spread on these entities and thus has a lateral extension. Thus one has to go beyond the SBF approximation of a linear charge modulation to calculate the Coulomb coupling. However in many cases, simple arguments based on electrostatic coupling between first-neighbor charged entities can account for the optimal phase shift $\varphi_{j-i}$.

In molecular compounds where the CDW modulates the electron occupancy of the LUMO (lower unoccupied molecular orbital) or the hole occupancy of the HOMO (higher occupied molecular orbital) between successive molecules in acceptor or donor stacks respectively, the optimal CDW phase shift results from the minimization of Coulomb interactions between the closest charge distributions in inter-chain directions. This is illustrated by Fig. 13a, giving the optimal phasing in the CDW ground state of the organic TMA–TCNQ-I salt. Here the dominant CDW Coulomb interaction $W_d$ occurs between the cyano groups of neighboring zigzag stacks of TCNQ in regard along the $a/2+c$ diagonal direction (note that in this direction the zig-zag TCNQ stacks are shifted by $eb$).

In inorganic compounds such as the blue bronze, where the $2k_F$ CDW modulates the amplitude of polarization of each linear segment of 4-corner-sharing MoO$_6$ octahedra forming the chain repeat unit, the inter-chain coupling occurs between the $2k_F$ modulated electric dipoles of the segments. The anisotropy of the electrostatic coupling between polar CDWs in the dipole direction ($\sim a+2c$) and in the perpendicular direction $c^*$, shown in Fig. 12b, explains respectively the uniform and staggered CDW transverse orders (Fig. 14a) found in the Peierls ground state of K$_2$MoO$_3$. Coupling between dipolar CDW can also account for the CDW transverse orders observed in NbSe$_3$ (Fig. 14b; see also Ref. [61] for a more complete discussion). In this compound, the dipolar CDWs originate from pairs of strongly coupled type-I or type-III chains in which the individual CDWs primarily order with a $\pi$ phase shift.

The Ginzburg–Landau formalism introduced in section 2.1 can be generalized to include the inter-chain coupling $W$. The treatment of the inter-chain coupling term in the mean-field approximation leads a 3D Peierls transition at finite
Fig. 14. Structures of \(K_{0.3}\text{MoO}_3\) (a) and \(\text{NbSe}_3\) (b) projected along the stack direction b. Lateral phasing between the dipolar CDWs in (a) \(K_{0.3}\text{MoO}_3\) (red arrows) and (b) \(\text{NbSe}_3\) (red and blue arrows) represent dipoles located on pairs of type-I and type-III chains, respectively. The anisotropy of the inter-chain couplings \(W\) given in the figure is obtained from the square of the anisotropy of the transverse correlation lengths \(\xi_{\perp}\). (Fig. 14b is adapted from Ref. [61].) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 15. Variation of \(T_P\) scaled to \(T_P^{\text{MF}}\) as a function of the inter-chain coupling \(W\) for the amplitude and phase \((n=2)\) domain wall \((n=1)\) fluctuation regimes relevant for complex \((n=2)\)/real Ising-type \((n=1)\) order parameters. The variation of \(T_P\) with \(W\) in the amplitude fluctuation regime is the same for complex- and real-order parameters.

temperature \(T_P\). \(T_P\) is an increasing function of the amplitude and correlation length of the 1D fluctuations and of the magnitude of \(W\). The variation of \(T_P\) with \(W\), shown in Fig. 15, depends on whether the 3D Peierls transition occurs in the regime of fluctuation of the amplitude or of the phase of the 1D order parameter (see Fig. 5). In the regime of (Gaussian) amplitude fluctuations, one gets [62]:

\[
T_P = T_P^{\text{MF}} e^{-C/\sqrt{W}}
\]

(30)

Fig. 13b shows that \(T_P\) calculated using expression (30) with \(W\) being the dominant \(W_d\) inter-chain Coulomb coupling nicely accounts for the variation of the experimental \(T_P\) in the Y-TCNQ-I series [60]. As for the Y-TCNQ-I series, Table 1 shows that the \(T_P\) of Peierls compounds remains a sizeable fraction of \(T_P^{\text{MF}}\).

4. Elasticity, plasticity and pinning of CDW

Below \(T_P\), collective excitations of the 3D PLD sublattice are those of the amplitude and of the phase of the modulation \(u(x)\) expressed by (8). The dynamics of the amplitude and of the phase modes of the PLD of \(K_{0.3}\text{MoO}_3\) have been measured by neutron [34] and X-ray [63] inelastic scatterings, Raman [64] and femtosecond [65] spectroscopies. Phase and amplitude excitations are relatively well decoupled in energy: the amplitude mode is optic-like, while phase excitations are acoustic-like. When \(2k_F\) is incommensurate, the vanishing of this acoustic dispersion for \(q = 2k_F\) corresponds to the degree of freedom of collective sliding of the phase of the PLD first considered by Fröhlich. For low-energy deformations, the variation of the amplitude of the order parameter can be neglected. In this case, CDW deformations are described by an elastic medium involving continuous long-range deformations of the phase of the PLD for \(q\) close to \(2k_F\). This assumption is however not valid when large stresses break phase continuity. In that case, plastic deformations nucleate dislocation loops. Also the variation of the amplitude of the order parameter cannot be neglected when large strains, induced for example by strong pinning centers, lead to the formation of Friedel oscillations (FOs).
This section is built on the works by Feinberg and Friedel (F&F), who have first introduced phase elasticity and plasticity of the CDW [66]. They also considered the deformation of the PLD in the presence of various imperfections using local models [67]. Their pioneering work will be illustrated by recent experimental findings.

4.1. CDW phase elasticity

Low-energy deformations are those of the phase $\psi(r)$ of the PLD modulation defined by expression (8). By analogy with conventional elasticity, F&F have introduced in Refs. [66,67] the elasticity of the phase $\psi(r)$ of the PLD. Fig. 16 introduces the basic ingredients of the phase elasticity in the case of (a) a compression/dilatation deformation of the PLD and (b) a shear deformation of the PLD.

The compression/dilatation of the phase in the chain direction corresponds to a local change of $2k_F$. Since there are two electrons per $2\pi$ CDW period, a phase variation along $x$ induces a modulation of the electronic charge of:

$$
\delta \rho(x) = \frac{1}{\pi} \frac{\delta \psi(r)}{\delta x}
$$

The charge modulation $\delta \rho(x) (= (\delta \rho_\psi)_x = \rho\delta e_{xx})$ in Fig. 16a) caused by the deformation along $x$ induces Coulomb forces. If Coulomb forces are dynamically screened by normal carriers excited through the Peierls gap, the compression/dilatation mode is acoustic. In the regime of perfect screening, the acoustic dispersion is governed by the longitudinal elastic constant:

$$
K^x_\psi = \frac{h v_F}{2 \pi}
$$

If the dynamical screening is not efficient, the longitudinal deformation of the phase induces an optical response. This response corresponds to a plasma frequency $\sqrt{3/2} v_F$ due to the rigid displacement of the CDW with respect to the ionic background. Such a regime where the CDW becomes extremely rigid occurs in $K_{0.3}\text{MoO}_3$ below $\sim 40$ K. Upon cooling $K_{0.3}\text{MoO}_3$ from $T_P$ to $\sim 40$ K, the reduction in the number of carriers thermally excited through the Peierls gap reduces the screening effect of Coulomb forces induced by the longitudinal phase variation. This causes a sizeable enhancement of the longitudinal elastic constant from the perfectly screened value $K^x_\psi$ given by expression (32). This effect has been observed in $K_{0.3}\text{MoO}_3$ [68,63].

The shear deformation of the phase along $y$ does not induce any charge redistribution, $(\delta \rho_\psi)_y = 0$, because $2k_F$ remains unchanged. Thus the dispersion of shear modes, which involves the transverse elastic constant $K^y_\psi$ and $K^z_\psi$, remain acoustic whatever the temperature. The elastic constant, $K^i_\psi$, is proportional to the square of the phason acoustic velocity $v^i_\psi$ measured in the $i$ direction. Their anisotropy follows also the square of the anisotropy of CDW coherence length $\xi_i$. The anisotropy of shear deformation elastic constants amounts also to the anisotropy of the inter-chain coupling energy $W_i$:

$$
\frac{K^y_\psi}{K^x_\psi} = \left( \frac{v^y_\psi}{v^x_\psi} \right)^2 = \left( \frac{\xi_y}{\xi_z} \right)^2 = \frac{W_y}{W_z}
$$
Phason velocities $v^p_i$ have been measured below $T_P$ along the three principal lattice directions of $K_{0.3}MoO_3$ by inelastic neutron scattering [68]. As expected, their anisotropy follows the anisotropy of the CDW coherence lengths $\xi_i$ of the pre-transitional CDW fluctuations measured above $T_P$.

An electric field ($E$) applied in chain direction couples with the local phase $\varphi$ of the CDW or to the CDW “displacement $u_x$” defined in Eq. 16. This coupling induces the Fröhlich-type collective sliding of the phase of the electronic CDW accompanied by an oscillating movement of the atomic positions of the PLD. In real systems where the CDW is locally pinned to lattice defects (see section 4.3 below), the collective sliding is only observed when $E$ exceeds a threshold field $E_T$, as demonstrated in NbSe$_3$ [12] and $K_{0.3}MoO_3$ [13]. In the presence of pinning defects, the competition between elasticity and disorder leads to a generic phase diagram including three dynamical regimes (see for example [69]):

- the creep regime at small electric fields ($E < E_T$), where the CDW is polarized through local phase displacements $u_x$,
- the CDW de-pinning regime around $E_T$,
- the collective flow regime for $E > E_T$ when the CDW moves as a whole with a finite velocity $V_D$.

Figs. 17a and 18 give, in the presence of boundary pinning effects, two illustrations of the CDW elastic response to an external stress caused by the application of a longitudinal electric field $E$. In these figures, CDW pinning at the electrodes or on sample surface induces respectively a compression/dilatation or a shear deformation of the phase of the CDW.

Fig. 17a illustrates the effect of longitudinal compression ($\epsilon_{xx} > 0$) and dilatation ($\epsilon_{xx} < 0$) of the phase $\varphi(x)$ resulting from the coupling of CDW with an electric field applied in the chain direction $x$. The CDW-strain that results has been directly observed using spatially resolved X-ray diffraction measurement of $2k_F(x)$ for sliding CDW in NbSe$_3$ [70,71]. Far from the contact currents, $2k_F(x)$, proportional to $\partial \varphi / \partial x$ varies linearly with $x$, as predicted by a simple elastic theory: $\varphi(x)$ shown in Fig. 17a has a parabolic dependence on $x$ and vanishes at the electrode positions in $x = 0$ and $L$. However, this simple picture has to be modified in the blue bronze where it has been surprisingly observed that, above $E_T$, the $2k_F$ sliding CDW develops an extra-long period modulation in the chain direction, which could be due to the formation of a soliton lattice [72].

Fig. 18 shows that surface pinning leads to a shear deformation of the CDW coupled with an electric field applied in chain direction $x$. The shear deformation induces a bending of CDW fronts accompanied by a tilt of the $2k_F$ modulation wave vector along $y$. A shear deformation of the moving CDW along the 2a*−c* weakest inter-layer coupling direction of $K_{0.3}MoO_3$ ($W_{\perp}$ in Fig. 14a) was first reported more than 30 years ago [73]. Sizeable shear deformations and rotations of the CDW wave vector have been imaged above $E_T$ by monochromatic X-ray topography in ribbon-like NbSe$_3$ presenting pinning surface steps in the chain direction [74]. Recent coherent X-ray diffraction experiments [75] performed below $E_T$ in the creep regime of NbSe$_3$ reveal local shear deformations of the polarized CDW, probably nucleated by domain walls delimiting the more strongly pinned domains where the CDW phase does not move under $E$. These local shear deformations break the lateral coherence of the CDW sub-lattice.

4.2. CDW dislocation

When the bending angle $\theta$ of the shear deformation represented in Fig. 18 exceeds a critical value, the continuity of CDW wave fronts should be broken by nucleation of mixed loop dislocations [66]. For a sliding CDW, the transformation of free carriers into CDW condensed carriers at the electrode implies the creation of new CDW phase wave-fronts. This occurs via a
Earlier (4.3. of coherence intensity to in CDW with K0.3MoO3 [76] (Fig. 19). The top of the figure gives a representation of the PLD in direct space and the bottom of the figure shows the corresponding diffracted speckle spectra. Because of the tilting of the CDW wave vector $q_{CDW}$ with respect to chain direction, $b$, the dislocation mixes edge and screw wave front deformations (from Ref. [77]).

so-called phase slippage phenomenon, which is probably achieved by nucleation and growth of edge loop dislocations [67]. However, it was only recently that an isolated CDW dislocation has been directly imaged using coherent X-ray diffraction in K0.3MoO3 [76] (Fig. 19). The introduction of an abrupt $\pi$ phase shift in the regular PLD sub-lattice by a dislocation leads to a negative interference term that manifests in the speckle spectra (right side of Fig. 19) by a vanishing of the diffracted intensity at the Bragg position of the regular PLD (left side of Fig. 19). The recent observation of a well-defined multi-peak speckle spectrum in transverse reciprocal direction in the creep regime of NbSe3 [75] shows that the loss of transverse coherence in the CDW sublattice polarized under the application of an electric field should be accompanied by nucleation of CDW dislocations that cause abrupt CDW phase shifts.

4.3. CDW pinning

Non-linear CDW and SDW conductivity phenomena that are observed for $E \geq E_T$ in the density-wave ground state ($T < T_F$) of 1D inorganic and organic conductors such as NbSe3, K0.3MoO3, TTF–TCNQ and (TMTSF)$_2$PF$_6$ are now well documented [78]. However, the detailed understanding of these electronic phenomena requires a microscopic description of the textured 3D PLD pattern in the presence of pinning centers, a question that is still incompletely settled. The present section reviews the more recent “structural” aspects of this topic.

The delicate question of CDW pinning by randomness begins to be addressed in the 1970s (for a recent review, see [79]). Earlier theories assumed, when the CDW is well developed below $T_F$, that the main effect of the potential defect is to interact with the phase of the PLD/CDW. The most important effect occurs when defects, located on the conducting path,
strongly perturb the 1D electronic motion. Along a 1D conducting path, the impurity potential induces two scattering processes of the incoming $k_F$ wave function corresponding to the $q \sim 2k_F$ backward scattering process ($k_F \rightarrow -k_F$ reflection of the wave function on the potential barrier; $U$ term below) and to the $q \sim 0$ forward scattering process ($k_F \rightarrow k_F$ transmission of the wave function through the potential barrier; term $V$ below). With the long-range elastic energy term previously considered in section 4.1, the interaction between the phase of the CDW, given by (6b), and disorder potentials (located in $m$) is described by the Hamiltonian:

$$H_{\psi \text{-dis.}} = \frac{1}{2} \int d\mathbf{r} \left[ K_x^\psi \left( \frac{\partial \psi}{\partial x} \right)^2 + K_y^\psi \left( \frac{\partial \psi}{\partial y} \right)^2 + K_z^\psi \left( \frac{\partial \psi}{\partial z} \right)^2 \right]$$

$$+ \sum_m \left[ U \cos(2k_F x + \psi(\mathbf{r})) \delta(\mathbf{r} - \mathbf{r}_m) + V(\mathbf{r} - \mathbf{r}_m) \frac{1}{\pi} \frac{\partial \psi}{\partial x} \right]$$

(34)

The term $U$ describes the interaction between the impurity and the $2k_F$ oscillating part of the electronic density. The backscattering process causes the individual pinning of $2k_F$ CDW, since the minimization of the cosinus term tends to impose a well-defined phase of the CDW on each impurity site. Such “phase-locking” terms, also present for the PLD, give rise to an asymmetry of intensity between pairs of $+2k_F$ and $-2k_F$ satellite reflections in the diffraction pattern [80]. The backscattering process breaks also the $2k_F$ electron–hole pairing and thus limits the condensate lifetime (see section 2.3). The term $V$ describes the interaction between the impurity and the $q \sim 0$ long-wave-length oscillation of the electronic density given by expression (31). The phase shift that results from the forward scattering process elongates or compresses locally the phase of the CDW (see Fig. 22a below). Concomitant local variations of the phase of the PLD induce an asymmetry of profile of individual $2k_F$ satellite reflections [81].

The $U$ term alone was considered in earlier theories with the effect to pin the phase of the PLD/CDW. As a function of the relative values of the pinning energy gain and of the elastic energy cost, two extreme situations are found:

- when the individual pinning energy gain dominates, the phase of the CDW is adjusted on each impurity site (Fig. 20a). The coherence of the CDW pattern is broken by the randomness of the impurity distribution along both chain and transverse directions (the phase adjustment on impurities induces local shear deformations of the CDW sub-lattice, which also break the optimal inter-chain phasing due to $W$). In the situation of strong pinning, each CDW coherent domain contains few impurities;

- when the elastic energy cost dominates, there is collective adjustment of the phase of the CDW on the impurity distribution (Fig. 20b). The CDW pattern remains coherent in large domains containing a sizeable number of impurities. In this case the possibility to obtain a Bragg glass with a quasi-long-range CDW order has been considered [83].

The real texture of the pinned CDW pattern is more subtle than those of these two extreme descriptions. In particular, it was suggested on the basis of earlier structural studies of irradiated organic salts [84] that the CDW pattern could be the superimposition of weakly pinned regions, where the phase fluctuates slowly, and strongly pinned domains where the phase is locked (Fig. 20c). In this situation the domain walls play the role of pinning surface as a source of shear deformation of the CDW (see Fig. 18).

The phase of the CDW pinned on an impurity site can be probed by the so-called “white line” effect [80] illustrated in Fig. 21. Such a “white line” effect is revealed by an asymmetry of intensity between pairs of $+2k_F$ and $-2k_F$ satellite reflections in the diffraction pattern from the PLD. This effect, analogous to holography in optics, is due to interference ($I_A$ term) between diffracted beams by impurities ($I_{\text{sub}}$) and by the PLD modulation ($I_{\text{dis}}$) [82]. The “white line” effect observed in solid solutions of organic conductors as well as in substituted inorganic conductor allows one to probe size and/or charge effects of impurities in the pinning process [85]. Using this effect, it has been possible to follow upon heating the thermal de-pinning of the phase of the CDW by thermally excited phasors in doped K$_{0.3}$MoO$_3$ [86].

Earlier pinning theories ignored local variations of the phase (Fig. 22a) and of the amplitude (Fig. 22b) of the CDW/PLD around impurities. A local variation of the phase, $\delta \psi(x)$, generally occurs when non-isoelectronic impurities induce a local

**Fig. 20.** CDW patterns for strong impurity pinning (a), weak impurity pinning (b) and weak pinning between strongly pinned CDW domains (c). In (a), the arrows show local shears of the CDW lattice due to individual phase adjustments on impurities. In (a) and (b), the dots represent local impurities and in (c) the boxes materialize strongly pinned domains. Parts (a) and (b) are from Ref. [82] and part (c) is from Ref. [84].
variation of the charge of the CDW, \(\delta \rho(x)\); these two quantities being connected through expression (31). Local variation of the amplitude of the CDW, \(u_1(2k_F)\), is expected in response to an impurity potential \(V_{imp}\) via the 1D divergent \(\chi(q, T)\) electron–hole response function – see Fig. 22b [87]. Both charge screening of non-isoelectronic impurities by a phase shift (not yet considered in the literature until recently [88]) and amplitude [87] variation in response to an impurity potential are the two basic components of Friedel oscillations (FOs). With the same critical \(2k_F\) wave vector, 1D FOs should superimpose above \(T_P\) to regular 1D \(2k_F\) CDW fluctuations and below \(T_P\) to the 3D CDW modulation pattern, with however a delicate problem of phase matching between the FOs and the regular CDW that will be considered below.

In response to strong lattice defects, such as those created by X-ray irradiation, 1D FOs can be induced well above \(T_P\). The intensity diffracted by the FOs, which is proportional to the square of the induced PLD \(u_1(2k_F)\), defined in Fig. 22b, superimposes on the intensity diffracted by the regular \(2k_F\) CDW fluctuations \(I_{dis}\) in Fig. 21. As \(|u_1(2k_F)|^2\) is proportional to the square of \(\chi(q, T)\), the intensity diffracted by the FOs strongly varies as a function of temperature. This thermal dependence has been measured above \(T_P\) in irradiated TMTSF–DMTCNQ [89] and TTF–TCNQ [32] and analyzed in this framework.

Below \(T_P\), the right-hand part of Fig. 23 represents the FOs induced in the vicinity of a V defect in K\(_{0.3}\)MoO\(_3\) and gives its matching with the regular PLD present at larger distance from the impurity. The structure of the FOs is obtained by a detailed analysis of the high-resolution profile of \(\pm 2k_F\) satellite reflections shown in the left-hand part of Fig. 22 [88,86]. A V defect induces both an oscillation of amplitude of the \(2k_F\) modulation on few near neighbor Mo sites (\(2\xi_\Delta \approx 16\ \text{Å}\), where \(\xi_\Delta = hV_F/2\Delta\) is the damping length in presence of the Peierls gap [87]) and a phase shift \(2\eta = -\pi\) on the V site able to screen a difference of charge of one electron \((Z = -1)\) with the Mo [90a]. The phase shift is directly related to \(Z\) by the Friedel sum rule (see also the contribution by J. Villain, M. Lavagna, and P. Bruno in this issue) because, since in a 1D system the scattered wave is in the same direction as that of the incident one, only the \(l = 0\) term enters the Friedel sum rule. This phase shift can be simply understood in 1D since a \(2\pi\) CDW period contains two electrons, half a CDW period \((-\pi\) is required to screen the impurity charge of one hole. The screening is achieved by a phase variation of the electron density from \(+\pi/2\) to \(-\pi/2\) on a distance of about one lattice spacing corresponding to the extension of the impurity potential (right-hand part of Fig. 23). However the intra-chain CDW phase shift \(2\eta\) induces also an inter-chain phase shift of \(\pi\) with neighboring CDWs. This last phase shift cancels the optimal Coulomb inter-chain coupling energy gain, \(W\), in transverse direction (see Fig. 12a in section 3). Thus the best way to recover the optimal inter-chain coupling is to resorb \(2\eta\) by forming two solitons on each side of the impurity, as shown in the right part of Fig. 23 (each soliton recovering a \(-\eta = \pi/2\) half phase shift). The matching of the FOs on the regular PLD by formation of two \(\pi/2\) phase shifts could be responsible of the asymmetry of intensity \((-I_a'/I_b')\) of the \(+2k_F/-2k_F\) reflections observed in the diffraction processes by
the FOs (see left-hand side of Fig. 23) [90b]. Note also that by the formation of two \( \pi/2 \) solitons, the total variation of the phase of the CDW perturbed by the impurity, obtained by integration of (31) on the chain length, is zero. This finding means that \( \varphi(n) \) should vanish asymptotically on each side of the impurity when \( |n| \) becomes large (see the right-hand side of Fig. 23). On large scales, there is thus charge neutrality of defects dressed by the FOs. Thus the spatially averaged \( 2k_F \) value of the CDW consistently corresponds to \( 2k_F \) calculated from the 1D band filling obtained by electron count based on chemical formulae of the \( \text{K}_{0.3}(\text{Mo}_{1-x}\text{V}_x)\text{O}_3 \) solid solution: 2\( k_F(x) = [(3 - 10x)/4]b^* \).

5. Concluding remarks

This review is focused on the CDW/PLD instability in a 1D conductor. It covers mostly the case of the Peierls transition driven by the 2\( k_F \) divergence of the electron–hole response function. In the presence of strong electron–electron repulsions, the 1D electron–hole response function diverges also for the 4\( k_F \) critical wave vector, which corresponds to the wave number of a Wigner lattice of localized charges (one localized charge every 1/\( \rho \) sites) coupled with a PLD [21–23]. These 4\( k_F \) CDW/PLD effects, which are now well documented in 1D organic compounds, have been reviewed recently [45,91]. They are distinct from the 2\( k_F \) CDW/PLD Peierls effects that occur in the free-electron gas and that are the main object of this review. Note that for intermediate electron–electron repulsion, the 1D electron gas can exhibit simultaneously 2\( k_F \) and 4\( k_F \) electron–hole instabilities [92], as experimentally observed [45,91]. Charge localization effects are also commonly observed in oxides and organic compounds of higher electronic dimensionality. In 1D conductors, the study of quarter-filled systems is particularly interesting because 4\( k_F \) bond and 2\( k_F \) site localization phenomena, stabilizing respectively Mott dimer and charge ordered (CO) ground state of different inversion symmetry, are basically decoupled. However, a mixture of bond and charge orders without inversion symmetry can lead to electronic ferroelectricity, as observed in some organic materials [93], and could drive multiferroicity in several classes of materials [94,95].

Another field of current interest concerns the presence of CDW instability in 2D and 3D electronic systems. In 2D layered transition metal oxides and bronzes, where, because of the anisotropic overlap of \( t_{2g} \) d-wave functions, the electronic lattice can be decomposed into sub-lattices of differently oriented sets of interpenetrating weakly coupled chains, it is found that PLD/CDW transitions result from a succession of Peierls instabilities driven by the underlying 1D band electronic structure [96,97]. It has also been proposed that the crystal structure of some group V and VI simple elements and \( \text{A}^\text{V}\text{B}^\text{VI} \) compounds could be stabilized by a Peierls-like transition occurring in a prototype 3D cubic lattice, where there is an anisotropic overlap of the p-wave functions (see, for example, [98]). Note that H. Jones was the first to propose in 1934 [4] a similar stabilization mechanism for Bi; see also R.E. Peierls [1] for the column V elements. However, such a mechanism could be questioned [99] if the s–p hybridization which blurs the 1D nature of the orbital overlap cannot be neglected. This is apparently not the case for column-V, -VI and -VII elements, where the s–p hybridization is very small (see the contribution of J.-P. Gaspard in this issue). Incommensurate PLD/CDW modulations are observed in layered transition-metal di-chalcogenides \( \text{MX}_2 \) [100]. However, the origin of these CDW transitions cannot be simply rationalized by a simple FS nesting mechanism. This leaves
open the possibility of CDW instabilities driven by strong electron–phonon coupling mechanisms. CDW transitions are also observed in 3D electronic systems. For example, three distinct CDW ground states are stabilized below 43 K in $\alpha - U$ (for a recent review, see [101]), with a critical CDW wave vector nesting flat portions of the FS due to narrow f bands [102].

Some 1D systems exhibit complex intertwined orders such a mix of 2kF SDW–CDW in (TMTSF)$_2$PF$_6$ [19], or even a succession of complex orders combining charge, spin, orbital and lattice degrees of freedom as found in the t$_{2g}$ multiband BaV$_5$S$_3$ compound [53]. Complex spin, charge and orbital current modulations are also observed in 2D superconducting cuprates. However, the wide range of non-conventional mechanisms used to describe the charge effects (CDW, CO, d-wave bond order, charge and spin stripes, charge “nematicity”, etc.) together with the presence of the compounds of a meso-/nano-scale phase separation show that a clear physical picture is far to emerge (for recent reviews, see [103,104]).

CDW, SDW, orbital anti-ferromagnetism and spin currents ground states are predicted when semi-conductors/semimetals with small indirect bandgap/overlap exhibit an excitonic instability [105]. In these transitions towards an excitonic insulator, the mechanism appears to be similar to that of the Peierls transition, the wave vector $\mathbf{Q}$ that links the energy extremites of the hole and electron pockets playing the same role as the 2kF nesting wave vector of a 1D Fermi surface. Good candidates for such transitions could be the incompletely nested semi-metallic oxides and bronzes [97].

The phase diagram of many density-wave (CDW, SDW, CO) systems includes also superconductivity. In most of them, superconductivity develops under pressure at the vanishing point of the density-wave ground state. This situation is well illustrated by organic conductors [106,107]; see also the contribution of D. Jérôme in this issue. However, in multiband conductors or when Fermi level states of a single-band conductor are not completely removed by the nesting process, superconductivity could coexist with the CDW modulation. Coexistence between CDW and superconductivity is observed in cuprates, in 1T–TiSe$_2$ and in the multiband charge transfer organic conductor TTF[Ni(dmit)$_2$]$_2$ (see [41] and earlier references therein).

6. Chemical index

<table>
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<tr>
<th>Abbreviation</th>
<th>Compound</th>
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<tbody>
<tr>
<td>BCPTTF</td>
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<td>bis-dithiolate copper</td>
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<tr>
<td>dmit</td>
<td>isotrithione-dithiolate</td>
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</table>

Acknowledgements

This paper is written in memory of Prof. Jacques Friedel who has always considered the physics of low-dimensional conductors as resulting from a subtle interplay between electronic and structural degrees of freedom. The author recognizes more than 40 years of live discussions with him on that topic. Here I want to especially acknowledge our last discussions concerning the history of the Peierls transition. The part on phonon dynamics of the Peierls transition is built on discussions with the late H.J. Schulz. Several results quoted in this review have been obtained in collaboration with C. Coulon, P. Fourny-Leylekian, C. Pasquier, and S. Ravy. Finally, this paper has also benefited of fruitful discussions with C. Bourbonnais, V. Jacques, D. Lebillionch, and G. Montambaux. The author is also very grateful to H. Bouchiat and J. Villain for their comments on the manuscript.

Appendix A. Mean-field dynamics of the Peierls transition

In inelastic neutron scattering by phonons measures the $\omega$ Fourier transform $S(q, \omega)$ of the time-dependent displacement–displacement correlation function $(u_q(t)u_{-q}(0))$, which can be expressed as:

$$S(q, \omega, T) = \coth \left( \frac{\hbar \omega(q)}{2k_B T} \right) \text{Im} D(q, \omega, T)$$  \hspace{1cm} (A.1)

In (A.1) $\coth(x)$ is the Bose–Einstein occupation number of the $\omega(q)$ phonon branch and $D(q, \omega, T)$ is the phonon propagator. For the electron–phonon coupled system considered in Fig. 9a, $D(q, \omega, T)$ is expressed by the Dyson equation:

$$D(q, \omega, T) = \frac{2\Omega_q}{\omega^2 - \Omega_q^2 - 2\Omega_q\tilde{g}^2 \chi(q, \omega, T)}$$  \hspace{1cm} (A.2)
Note that expression (A.2) involves the electron–phonon coupling constant \( \tilde{g} \), which is related to the term \( g \) introduced in section 2.3 by the relationship:

\[
\tilde{g} = g \sqrt{\Omega_q / K_q}
\]

For a linearized electronic dispersion of the 1D electron gas, the \( 2k_F \) Lindhard electron–hole response function can be expressed under the compact form [18]:

\[
\chi(2k_F, \omega, T) = N(E_F) \left[ \ln \left( \frac{2 \gamma e_c}{\pi k_B T} \right) + \psi \left( \frac{1}{2} \right) - \psi \left( \frac{1}{2} - i \frac{\hbar \omega}{4 \pi k_B T} \right) \right]
\]  \hspace{1cm} (A.3)

In (A.3), \( \psi(z) \) is the digamma function. \( \psi(z) \) is the sum of real and imaginary components, which are respectively even and odd in frequency. Thus (A.3) can be generally written as:

\[
\chi(2k_F, \omega, T) = N(E_F) \left[ \ln \left( \frac{2 \gamma e_c}{\pi k_B T} \right) - \Sigma(\omega^2, T) + i \omega \tau(\omega^2, T) \right]
\]  \hspace{1cm} (A.4)

For \( \hbar \omega < 4\pi k_B T \), one has the development:

\[
\Sigma(\omega^2, T) \approx \omega^2 \tau_T^2,
\]

\[
\tau(\omega^2, T) \approx \tau_T \left( 1 - \frac{\omega^2 \tau_T^2}{8} \right),
\]

with:

\[
\tau_T = \xi_T / \nu_T = \hbar \sqrt{2 \pi k_B T}, \quad \text{and} \quad \tau_T' = 1.75 \tau_T.
\]

\( D(q, \omega, T) \) can thus be written in the general form:

\[
D(2k_F, \omega, T) = \frac{2 \Omega_{2k_F}}{\omega^2 - \omega_R(\omega^2, T)^2 + i \omega \Gamma(\omega^2, T)}
\]  \hspace{1cm} (A.6)

Expression (A.6) explicitly involves with the notations of (A.4):

- the renormalized square phonon frequency \( \omega_R(\omega^2, T)^2 = \omega_A^2 \left[ \ln \left( \frac{T_{pF}^{MF}}{T} \right) - \Sigma(\omega^2, T) \right] \)  \hspace{1cm} (A.7)

- the damping \( \Gamma(\omega^2, T) = \omega_A^2 \tau(\omega^2, T) \)  \hspace{1cm} (A.8)

In these expressions \( \omega_A = \sqrt{\Omega_{2k_F}} \) is the frequency of the amplitude mode, \( \lambda = 2 \tilde{g}^2 N(E_F) / \Omega_{2k_F} \) is the dimensionless electron–phonon coupling constant (see also expression (22)) and \( T_{pF}^{MF} \) is given by expression (23).

Neutron scattering measures the imaginary part of (A.6):

\[
\text{Im} \, D(2k_F, \omega, T) = \frac{2 \Omega_{2k_F} \omega \Gamma(\omega^2, T)}{[\omega^2 - \omega_R(\omega^2, T)^2]^2 + \omega^2 \Gamma(\omega^2, T)^2}
\]  \hspace{1cm} (A.9)

Poles of (A.9) give the dynamics of the \( 2k_F \) critical phonon. When the damping can be neglected, the frequency of the soft phonon \( \omega_{2k_F}(T) \) is the solution of the implicit equation:

\[
\left( \frac{\omega}{\omega_A} \right)^2 = \ln \left( \frac{T_{pF}^{MF}}{T} \right) + \Sigma(\omega^2, T)
\]  \hspace{1cm} (A.10)

This equation is graphically solved in Fig. 24.

If \( \omega_A \tau_T < 1 \), the intersection between the left-hand-side and right-hand-side members of (A.10) gives the frequency \( \omega_{2k_F}(T) \) of the Kohn anomaly renormalized by electron–phonon coupling. Its frequency is smaller than \( \Omega_{2k_f} \). Furthermore, when \( T \) tends to \( T_{pF}^{MF} \), \( \omega_{2k_F}(T) \) softens according to expression (21) of section 2.3:

\[
\omega_{2k_F}(T) = \omega_A \ln \left( \frac{T}{T_{pF}^{MF}} \right)
\]  \hspace{1cm} (A.11)

This situation, which corresponds to the adiabatic limit, is depicted by the numerical simulation of the left-hand part of Fig. 11. Note that when \( \omega_{2k_F}(T) \) tends to zero, one has to include the thermally-dependent damping term \( \Gamma(\omega^2, T) \) in the phonon-softening mechanism. There are also non-harmonic corrections included in the free energy (9), which are ignored in the RPA approximation. They will be considered at the end of the Appendix.
If $\omega_A \tau_T > 1$, the intersection occurs at frequencies close to $\Omega_{2k_F}$. The (weakly) renormalized frequency $\omega_{2k_F}$ is determined by the behavior of $\Sigma(\omega^2, T)$ at large values of $\omega$. There is no phonon softening. This situation corresponds to the anti-adiabatic limit.

An incomplete phonon softening occurs when $\omega_A \tau_T \sim 1$. To analyze this behavior, one must take into account the thermal dependence of $\tau_T$ through the critical dimensionless quantity $\omega_A \tau_T$ which can be written under the form:

$$\omega_A \tau_T = \left( \frac{T_{p}^{MF}}{\Omega_{2k_F}} \right) \frac{\Omega_{2k_F}}{\tau}$$  \hspace{1cm} (A.12)

In (A.12) the critical ratio $(k_B T_{p}^{MF}/\hbar \Omega_{2k_F})c$ amounts to $\frac{\sqrt{2} \pi}{\sqrt{2}} \approx 0.1-0.14$. When the temperature decreases towards $T_{p}^{MF}$, (A.12) increases. When for $T > T_{p}^{MF}$, $T/\Omega_{2k_F}$ becomes larger than the critical ratio $(T_{p}^{MF}/\Omega_{2k_F})c$ a phonon hardening, shown in Fig. 11b, results from the increase of the $\Sigma(\omega^2, T)$ term upon cooling. However, it is also possible to have a high-temperature phonon softening, when $\omega_A \tau_T < 1$, which however never vanish if, when $T$ approaches $T_{p}^{MF}$, $\omega_A \tau_T$ becomes larger than 1. Also by continuity, a phonon softening at high temperature could be followed by phonon hardening near $T_{p}^{MF}$. Fig. 10 illustrates these different behaviors. Note that the longitudinal acoustic branch of TTF–TCNQ exhibits a frequency hardening around the $4k_F$ critical wave vector upon cooling [36].

The right-hand part of Fig. 11 shows in the non-adiabatic regime that, in addition to the phonon hardening phenomenon previously discussed, Im$(D(2k_F, \omega, T))$ exhibits a quasi-elastic response that critically narrows in frequency when $T_{p}^{MF}$ is approached. To calculate this quasi-elastic response, one must consider on the same footing the low-frequency dependence of $\Sigma(\omega^2, T)$ and of the damping term $\Gamma(\omega^2, T)$ given by expressions (A.5). In the lowest order in $\omega$, (A.9) becomes a Lorentzian response:

$$\text{Im} D(2k_F, \omega, T) \sim \frac{\text{constant}}{\omega^2 + \Gamma_{2k_F}(T)^2}$$  \hspace{1cm} (A.13)

The frequency dependence of (A.13) is typical of a relaxation dynamics. Furthermore, the damping constant $\Gamma_{2k_F}(T)$ of the Lorentzian response critically decreases to $T_{p}^{MF}$ according to:

$$\Gamma_{2k_F}(T) = \frac{\text{Im}(T/T_{p}^{MF})}{T_{p}^{MF}}$$  \hspace{1cm} (A.14)

The mean-field theory of the dynamics of the SP transition gives a critical ratio $(k_B T_{p}^{MF}/\hbar \Omega_{SP})c \approx 0.45$ or $\hbar \Omega_{SP} \approx \Delta_{SP}^{MF}$ significantly larger than the one found for the Peierls chain (expressions (27) and (A.12)). This critical ratio separates adiabatic and anti-adiabatic fluctuations regimes [see [108] and Fig. 4 in Ref. [42]].

Non-harmonic terms are relevant to describe the true dynamics of the Peierls chain beyond the RPA approximation [109]. When for $\omega_A \tau_T < 1$, the dynamics includes these terms, the Kohn anomaly tends to soften at $T_{\text{eff}} \sim 0.38 T_{p}^{MF}$ defined in Fig. 5. However, because of sizeable 1D fluctuations, the Kohn anomaly becomes over-damped around $T_{\text{eff}}$. Below $T_{\text{eff}}$, when the Peierls order is established on a large correlation length $\xi(T)$, the damping diminishes and one recovers a dynamics of decoupled fluctuations of the amplitude and of the phase of the order parameter. There is no real softening and thus no true Peierls transition for an isolated Peierls chain at finite temperature in agreement with thermodynamics arguments. The dynamics of the Peierls systems quoted in Table 1 is in fact measured in real systems made of coupled chains. When $T_P$ is comparable to or larger than $T_{\text{eff}}$, pre-transitional Peierls dynamics basically follow that given by the mean-field theory with $T_P$ replacing $T_{p}^{MF}$. This is the case of the Kohn anomaly measured in K$_{6.3}$MoO$_3$ where $T_P \sim T_{\text{eff}}$. However, in this compound, the amplitude mode fluctuations already emerge from the damped Kohn anomaly at a frequency comparable to $\omega_A$ above $T_P$ [110].
References


H. Jones, Proc. R. Soc. 147 (1934) 396;


[48] C. Coulon, personal communication, 2005. A comparison of earlier measurements with the calculation of the thermal dependence of the SP pseudogap can be found in Ref. [46].


[54] For a Luttinger liquid of charge and spin velocities, vρ and vσ respectively, the velocity of the 2k electron–hole pair excitations is vρh = √vρvσ and the velocity of the 4k electron–hole pair excitations is vρh = vρ + vσ. (L Dumoulin, Thesis, Université de Sherbrooke, Canada, 1997). Theory of the pure Luttinger liquid gives vρ larger than vσ. However, a strong decrease in the collective velocity of charge fluctuations is found in presence of electron–phonon backscattering of momentum transfer ~ 2k. (J. Voit, H.J. Schulz, Phys. Rev. B 37 (1988) 10068). This goes with an enhancement of the tendency to form a CDW state in presence of this electron–phonon coupling.