I will present a personal view how in the last 30 years a backward and forward movement in concepts and experimental results took place in quasi-1D inorganic and organic conductors, taking for examples sliding density waves, low energy excitations, metastability and memory effects, and dielectric response leading to the recent results of charge ordering.

Any graduate student starting the study of quantum theory of solids, as I did using the Kittel book, knows that the evaluation of crystal vibrations, periodic boundary conditions and electron density of states are the simplest for a linear chain, before being generalized in three dimensions.

However, the first synthesis of one-dimensional or quasi-one-dimensional (Q-1D) compounds was only realized in the beginning of the 1970s. Then, all concepts developed earlier could face their experimental proofs. Among these concepts, R.E. Peierls in 1955 showed the instability of a 1D metal interacting with the lattice towards a lattice distortion and the opening of a gap in the electronic spectrum – the so-called charge density wave (CDW), a concomitant lattice and electronic modulation with the same wave vector \( q = 2k_F \). Related to this CDW state, H. Fröhlich in 1954, just before the BCS theory, described a model in which the CDW can slide if its energy is degenerate along the chain axis, yielding thus a collective current without dissipation and leading to a superconducting state. In the 1960s Fermi instabilities were already considered by A.W. Overhauser to yield a SDW in the case of chromium.

The decade 1973–1982 can be considered as a “magic” decade for the 1D physics with the first synthesis of Q-1D materials and of many other families, discovery of the Peierls instability in many of these compounds, CDW and SDW sliding, organic superconductivity, . . . . Naturally I will not forget other fundamental discoveries in adjacent fields as the quantum hall effect (QHE) which is also connected with transport properties of some organic Q-1D.

Having been asked by the editor of this volume to write a historic survey of Q-1D materials, everybody will agree to consider impossible to survey so many research activities in a few pages. So, I will present my own point of view and
how, among a great number of talentuous researchers, I have personally with many collaborators followed a research line along all these years. In the following, I will not make any reference to publications, except for the five figures.

After having obtained a Ph.D. in 1970 on microwave studies of type II superconductors, G. Waysand (Orsay) attracted our attention on publications of the research group of T.H. Geballe (Stanford) on superconductivity in layered compounds of transition metals dichalcogenides and on possible superconducting fluctuations at high temperatures (around 35 K) in intercalated 2H-TaS$_2$. Microwave is a good technique for searching such fluctuations and thus we started to interact with J. Rouxel, having recently settled his laboratory at Nantes. In the same period of time, crystals of 1D materials were just synthesized: first KCP, then TTF–TCNQ. Very soon by diffuse X-ray scattering and neutron scattering the nature of the metal-insulating transition was elucidated as being of the Peierls type. A huge peak in the conductivity just above the Peierls transition temperature of TTF–TCNQ raised a gigantic activity as being possibly due to some superconducting fluctuations. Among all the theories, J. Bardeen in 1973 revitalized the Fröhlich model of superconductivity.

Superstructures analysed as a Fermi effect with nesting properties of the Fermi surface were also discovered in the same year in transition metal dichalcogenides. By modification of the temperature conditions for growing NbSe$_2$, synthesis of a new fibre-like compound was realized at Nantes. The crystal structure made by A. Meerchaut (1975) revealed that this compound, NbSe$_3$, was formed of linear chains – six in the unit cell – running along the $b$-axis.

The first measurements we made on a bundle of fibres showed anomalies in the resistance at 145 and 59 K, change of the magnetic susceptibility at these temperatures, a peak in the specific heat and the decrease of the transition temperatures with application of pressure. These first results were accepted as a post-dead line publication at the 14th Low Temperature Conference held in Helsinki in the summer 1975.

At the end of 1975, I joined the group de A. Portis at Berkeley where N.P. Ong was measuring the Hall effect of TTF–TCNQ with a bimodal cavity to be rid off any contact effect which could disturb the measurements. The result of conductance of NbSe$_3$ we performed at 9.3 GHz is shown in Fig. 2.1. Astonishingly, the amplitude of the DC resistance peaks are nearly washed out. To corroborate these microwave studies, we performed DC and pulsed measurements with different current densities the results of which demonstrate the non-linearity in transport properties. The microwave results, in fact, make rememberings to similar results on type II superconductors in the vortex state at frequencies above the pinning frequency where the microwave resistivity is the same as that of the DC flux flow one.

It was J. Bardeen who, in 1978, assigned our results on NbSe$_3$ to the Fröhlich type conductivity resulting from sliding CDW (in his contribution to the book Physical Properties in Highly One-Dimensional Conductors edited
In the mean time, CDW was also discovered in another trichalcogenide TaS$_3$ with two polytypes, CDW superstructures observed in NbSe$_3$ by electron diffraction. It was also shown that the superlattice peaks are not suppressed in the non-linear state, excluding the destruction of the CDW order towards the normal state (at least for the amplitude of the electric fields experimentally applied), as in the mixed state of type II superconductors where the normal state is recovered above $H_{c2}$. Sliding occurs only for an applied electric field above a threshold value at which the CDW is depinned from impurities. Above this threshold, an AC voltage called NBN is generated.

Pursuing the analogy with superconductors, and inspired by the work on vortices on AC–DC interference showing Shapiro steps in the $I$–$V$ characteristics, we performed similar experiments. Interference takes place when there is a locking between the RF field and the frequencies measured in the NBN and it is seen as an increase of the resistance of the sample for those frequencies, as shown in Fig. 2.2.

We associated these observations with the motion of the CDW. In the Fröhlich model, the lattice distortion moves with the electrons when the electrons are displaced in the $k$-space, so as to give a current flow $j = nev$, where $n$ is the number of electrons condensed under the gap and $v$ the velocity of the CDW. Assuming that the pinning forces are periodic with the phase of the CDW – thus the motion due to an external field is the superposition of a continuous drift and a modulation due to pinning at a recurrence frequency $\nu = (Q/2\pi)v$ with $Q$ the CDW distortion vector – we showed the linear variation between the excess current carried by the CDW when sliding and the frequency $\nu$ where interference occurs, demonstrating the validity of the Fröhlich conductivity [2].

**Fig. 2.1.** Resistivity of NbSe$_3$ at 9.3 GHz compared to the DC resistivity as a function of temperature (from [1]).
Fig. 2.2. Differential resistance $dV/dI$ of NbSe$_3$ at 47 K in sweeping the frequency of a RF current of constant amplitude superposed to the DC current above the threshold value $-I_{th} = 59 \mu A$ (from [2])

New CDW compounds were discovered: (TaSe$_4$I)$_2$I, potassium and rubidium bronze $A_0_3$MoO$_3$ with $A = K, Rb$, (NbSe$_4$I)$_{10}$I$_3$ with the Peierls transition above room temperature. A huge amount of theoretical and experimental works were performed for studying the electrodynamics of the CDW in a very broad frequency range in all these compounds, optical properties, metastability and hysteresis, screening effect, pinning effects by well-defined impurities, complete mode-locking, synthesis of high purity crystals, size effects, ... Similar depinning with very low threshold fields was also discovered in the SDW state of Bechgaard salts, (TMTSF)$_2$X, recovery of the SDW state by application of a magnetic field (field-induced SDW) on a pressured sample, plateaux in the Hall resistance, ... 1D materials are characterized by dominant valence forces between atoms along the chains. They act as restoring forces for bending. The deviation of the $T^3$ law in the specific heat at low $T$ above $T^*$ yields an estimation for the ratio between the bending force constant and the force constant between adjacent chains. Measuring this property in 1982,
that was also the starting point for searching the deviation of tranverse acoustic mode dispersion using neutron scattering. At variance with (TaSe$_4$)$_2$I and A$_{0.3}$MoO$_3$ where large crystals are available, the search for Kohn anomaly was performed only recently in NbSe$_3$ using X-ray inelastic scattering.

After many others, we measured the dielectric permittivity of CDWs, essentially TaS$_3$ and we started later with SDW. Analysis of the $T$ dependence of the real part and imaginary parts of the low frequency conductance showed that the relaxation rate has two branches: a long time one diverges near some temperature while the short time relaxation increases monotonically. We ascribed these two relaxations as $\alpha$ and $\beta$ relaxations, providing evidence for a transition of the CDW and the SDW state into a glassy-like transition at low temperature.

An appropriate technique, among others, to study the disordered state of the charge and spin DW is very low $T$ specific heat measurements. Thus, for CDW and SDW systems we showed that, as the temperature decreases, the total specific heat first follows a $T^3$ behaviour due to phonons, followed by a minimum and then at low temperatures by a $T^{-2}$ behaviour. Energy relaxation has revealed aging in the heat response in the sense that the temperature signal $T(t_\omega, \tau)$ measured at a time $t_\omega + \tau$ depends on the duration of the heat perturbation or waiting time, as well as on the time $\tau$ elapsed since $t_\omega$, as shown in Fig. 2.3 for TaS$_3$.

![Fig. 2.3](image)

**Fig. 2.3.** (a) Variation of the temperature dependence $\Delta(T)/\Delta_0(T)$ as a function of log $t$ for TaS$_3$ at $T_0 = 0.165$ K: after a heat pulse of 0.9 s (●), after that a heat flow has been applied during 5 h (13 h) and switched off (o and ▲, respectively). (b) Time dependence of the relaxation rate $d\Delta(T)/\Delta_0(T)/d\log t$ in the same conditions than in (a) (from [3])
Once the $T^3$ and the $T^{-2}$ contributions are subtracted the residual specific heat follows a power law dependence. The amplitude of the $T^{-2}$ term strongly increases when the waiting time increases. The spectrum of relaxation times shows a power-law distribution for intermediate waiting times, and interrupted aging for larger waiting times (in the sense that thermodynamical equilibrium is reached and that $T(t_w, \tau)$ does not depend on $t_w$). Finally commensurate systems relax faster than incommensurate systems. Metastability due to bisolitons occurs at a sufficiently strong pinning potential from what it is possible to define an energy two-level system with a ground state separated from a metastable state by an energy barrier, explaining the $T^{-2}$ contribution to the specific heat as the high temperature tail of a Schottky anomaly of the effective two-level system.

New techniques often developed for high $T_c$ superconductors were applied to one-dimensional systems, in particular ARPES, high resolution diffraction using synchrotron radiation, ultra-vacuum STM, photo-induced effects, tunneling, ....

The interlayer tunneling method has been very useful since the last decade in studies of layered HTS materials. Recently this method has been extended to other classes of layered materials as manganites and CDWs. In NbSe$_3$ and TaS$_3$, the elementary conducting layers are formed by elementary conducting chains assembled in a layer well separated from each other by a double barrier of insulating prism bases. By the interlayer tunneling technique on mesoscopic stacked junctions fabricated by ion focused beam, we have identified [4] the CDW gap and a zero bias conductance peak (ZBCP). The CDW gap values found are consistent with the data obtained by other techniques as STM, optics, ARPES and point contact spectroscopy. By application of a high magnetic field parallel to the layers which narrows the ZBCP, we found, in addition with the peak at $2\Delta$ an additional peak in the gap at $V = 2\Delta/3$ [Fig. 2.4]. Due to the degeneracy of the CDW ground state, a non-uniform ground state can be realized by local change of the phase by $\pi$ and simultaneous acceptance of one electron from the free band to conserve electro-neutrality. The resulting state is known as the amplitude soliton (AS). The AS energy $E_s = 2\Delta/\pi = 0.65\Delta$ is lower than the lowest energy of electron in the free band $\Delta$. Therefore free electrons near the band edge tend to self-localized into AS states. Experimentally, the existence of the AS states has been reliably demonstrated only for dimeric compounds like polyacetylene. Then the additional peak in interlayer tunneling has been interpreted as resulting of transition of band carriers into AS levels.

Another remarkable feature is that onset of interlayer tunneling conductivity occurs above a sharp voltage $V_t$ at low energies within the CDW gap. We ascribed $V_t$ to the energy of the CDW phase decoupling between neighboring layers via the formation in the weakest junction of an array of dislocation lines (DL) – CDW phase topological defects. The first DL enters the junction at $V_t$ and the staircase structure above $V_t$ evidences the sequential entering of these CDW vortices in the junction area. There is a remarkable similarity
between layered superconducting and CDW systems that manifests itself in similar mechanisms of phase decoupling via formation of phase vortices. In both cases a threshold energy for phase decoupling associated with $H_{c1}$ for superconductors or $V_t$ for CDW is much less than the value of the energy gap.

Low dimensional charge transfer compounds are known to be subject of strong electronic correlations. One of the best examples is found in the Bechgaard–Fabre salts. In the course of our thermodynamic measurements, we found that the magnitude of the anomaly in the specific heat at the SDW transition temperature of (TMTSF)$_2$X salts was too large to be explained by the electron spin contribution alone, implying that the lattice is involved. Our original idea was to detect in the dielectric permittivity any contribution of the diffuse one-dimensional $2k_F$ scattering revealed previously in (TMTTF)$_2$PF$_6$ and (TMTTF)$_2$Br which grows critically below 70 K. The huge surprise was to measure in the conductivity the opening of a new charge gap and a huge peak in the real part of the permittivity, $\varepsilon'$ reaching $10^5$–$10^6$ [Fig. 2.5]. Our results on (TMTTF)$_2$PF$_6$ and (TMTTF)$_2$Br were presented at the ECRYS 1999 workshop, where we interpreted [5] this huge polarizability as reflecting the realization of a new charge ordered state of Wigner crystal type due to long range Coulomb interactions.

Charge disproportionation was then proved by NMR. The generality of this transition in the whole family of Fabre salts was established as well as the ferroelectric character of this charge ordered state. Many other compounds exhibit charge order, in particular two-dimensional organic quarter-filled compounds, for which charge patterns occur along stripes oriented along different axis depending on the anisotropy of the Coulomb interactions and of the
transfer integrals. Dielectric permittivity could be a nice tool for determination of the stripe orientation by applying the AC field parallel or perpendicular to the stripes.

I will not make any conclusions, because the future is unknown. However, the period of time covered by this short historical review has been exhuberant, totally exciting when dealing with collective properties having some similarity with superconductivity in a temperature range never reached before – till above room temperature. The occurrence of superconductivity with critical temperatures as high as 150K has tremendously enlarged and opened these new perspectives. Even if CDW and SDW sliding do not yield a superconducting state and if, up to now, there is no increase of the conductivity when the DW slides above the extrapolation of the high temperature normal conductivity, quantum condensed states are known now to be stable in the high temperature range.

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