TOPICAL REVIEW

Charge-ordering transition in (TMTTF)$_2$X explored via dilatometry

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Abstract
Charge-ordering phenomena have been highly topical over the past few years. A phase transition towards a charge-ordered state has been observed experimentally in several classes of materials. Among them, many studies have been devoted to the family of quasi-one-dimensional organic charge-transfer salts (TMTTF)$_2$X, where (TMTTF) stands for tetramethyltetra-thiafulvalene and X for a monovalent anion ($X = PF_6$, $AsF_6$ and $SbF_6$).
However, the relationship between the electron localization phenomena and the role of the lattice distortion in stabilizing the charge-ordering pattern is poorly documented in the literature. Here we present a brief overview of selected literature results, with emphasis placed on recent thermal expansion experiments probing the charge-ordering transition of these salts.

(Some figures may appear in colour only in the online journal)

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1. Introduction

Charge-ordering (CO) phenomena, also frequently referred to as charge disproportionation, have been recognized as one of the main issues in the field of correlated electron systems. In particular, charge ordering has gained particular attention in transition-metal oxides, where, depending on its coupling to spin ordering, it gives rise to various exotic phenomena [1] such as ferroelectricity in spiral magnets [2] and magnetoelectric effects [3]. Also for various series of molecular conductors, such as (BEDT-TTF)$_2$X, (TMTTF)$_2$X as well as (DI-DCNQI)$_2$X, it has been recently recognized that CO plays a key role in the physics of these systems [4, 5]. However, CO effects observed in these quarter-filled organic salts is only a special realization of the so-called $4k_F$ charge-density wave (CDW) instability discovered more than
35 years ago in TTF-TCNQ [6] (here $k_F$ refers to the Fermi wave vector of the non-interacting 1D electron gas). Very soon the $4k_F$ CDW was interpreted within the framework of the extended Hubbard model as being due to a Wigner crystallization caused by the long-range Coulomb repulsions specific to organic stacking [7, 8]. In organic systems, it is the anisotropy in the hopping transfer integrals, $t_{ij}$, and mainly the inter-site Coulomb repulsion, $V_{ij}$, together with the influence from electron–lattice coupling which give rise to a very rich and diverse physics; for a recent review of all these aspects see e.g. [9]. Recently, a new type of CO with purely ferroelectric character has been reported for (BEDT-TTF)$_2$X charge-transfer salts [10]. The electronic properties of molecular conductors have been intensively discussed in several reviews, see e.g. [11–23] and more recently [24].

Here we review literature results on the CO transition occurring in the quasi-one dimensional (1D) (TMTTF)$_2$X Fabre salts. These salts are especially interesting since CO gives rise to ferroelectricity [25]. In addition, the concomitant spin–charge decoupling favors magnetic coupling, which in some cases leads to a magnetic ground state. In this framework it has been proposed [26] that the interplay between ferroelectricity and magnetism could lead to multiferroicity. As the Fabre salts are soft materials, these electronic phenomena are controlled in a subtle manner by the lattice degrees of freedom. Concerning the various structural aspects of the so-called Fabre–Bechgaard salts we refer to [27] and references therein. In this review, emphasis will be placed on high-resolution dilatometric measurements performed in these salts in the past few years in order to reveal the effects of the CO transition on the lattice counterpart.

Following this brief introduction, which includes the first section, this brief review is subsequently divided into eight sections, as follows.

- **Section 2** presents an overview of the main theoretical aspects related to the CO transition in quasi-1D organic systems.
- **Section 3** is dedicated to the structural aspects of Fabre–Bechgaard salts. In particular, we shall emphasize the coupling between the anions and the acceptors, which plays a key role in the stabilization of the CO pattern.
- **Section 4** first discusses the generic phase diagram of the Fabre–Bechgaard salts. This presentation is followed by a survey of selected literature results related to the CO phase transition of the Fabre salts.
- **Section 5** gives a general presentation of the thermodynamic quantities related to the thermal expansion.
- **Sections 6 and 7**, respectively, present and discuss the high-resolution thermal expansion results obtained in the (TMTTF)$_2$X.
- **Section 8** gives our conclusions, perspectives and an outlook.

### 2. Theoretical description of the charge-ordering ground state

In qualitative terms a CO transition, frequently referred to in the literature as charge disproportionation, can be defined as due to the self-(re)arrangement of charge carriers into a well-defined superstructure. This instability is a direct consequence of the electron–electron repulsions between charges: if the inter-site Coulomb repulsion $V_{ij}$ is sufficiently strong and sufficiently long-range, electrons will reduce their repulsion from each other by taking equidistant positions. In 1D, the reduction of the total electrostatic energy of the system is achieved by the localization of one electron every $1/\rho$ site, where $\rho$ is the average number of electrons per molecular site; $\rho = 1/2$ for a quarter-filled system. This localization wave corresponds to the $4k_F$ CDW observed in 1D systems ($4k_F = 1/\rho$ in chain reciprocal wave vector unit). If the system is metallic above the CO critical temperature ($T_{CO}$), and if $\rho$ is commensurate, the charge localization achieved at the CO transition will then be accompanied by a metal–insulator (MI) transition. This situation is, for example, achieved in (TMTTF)$_2$SbF$_6$ at $T_{CO,MI} \simeq 154$ K [28] (see curve 2 in figure 7). In quarter-filled systems, due to the spin–charge decoupling, the spin degrees of freedom of the localized electrons remain active below $T_{CO}$. At lower temperatures ($T < T_{CO}$), magnetic driven transitions such as spin-Peierls (SP) or antiferromagnetic ordering can take place.

The electronic counterpart of the CO transition has been studied using the extended Hubbard model [7]. The extended Hubbard–Hamiltonian written in second-quantization notation, is given by:

$$
H = \sum_{ij} t_{ij} a^\dagger_{i\sigma} a_{j\sigma} + \sum_i U_{n_i+1} n_i - \sum_{ij} V_{ij} n_i n_j \quad (1)
$$

where $t_{ij}$ is the hopping term from site $i$ to site $j$ in the lattice, $a^\dagger_{i\sigma}$ is the creation operator, which creates an electron on site $i$ with spin $\sigma$ and $a_{i\sigma}$ is the correspondent annihilation operator; $U$ is the on-site Coulomb repulsion potential, $n_{i\sigma}$ and $n_i$ refer to the number operator for spin up and down, respectively, i.e. $n_{i\sigma} = a^\dagger_{i\sigma} a_{i\sigma}$; and in the last term $n_i = n_{i\uparrow} + n_{i\downarrow}$.

Already in 1978 Hubbard [7] by using the Hamiltonian (1) without kinetic energy ($t = 0$) and in the absence of double site occupancy ($U$ equal to infinity) was able to discuss Wigner crystals, i.e. $4k_F$ CDW or CO for $\rho$ between 1 and 1/2. Charge ordering requires a convex repulsive potential $V_{ij}$ between the charges to be stabilized. In the quarter-filled case, which holds for the (TMTTF)$_2$X family, the $4k_F$ CDW or CO achieves a periodicity of twice the distance between the TMTTF molecules along the chain direction, i.e. charge-rich sites alternate with charge-poor sites in a 1010 pattern, where 1 and 0 refer to charge-rich and charge-poor sites, respectively (see figure 1(a)). To be complete, let us remark that a concave repulsive potential $V_{ij}$

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3 The on-site Coulomb repulsion can be seen as the energy that would be necessary to place two electrons of opposite spins in the same molecular orbital.
between the charges stabilizes the 11001100 charge pattern, referred to as a 2kF CDW or PEC, or 4kF CDW or CO. This is the pinned state which is represented in figure 1(c).

Figure 1. Schematic representations of charge and bond orders relevant for a quarter-filled band system: (a) 4kF CDW or CO, (b) 2kF CDW or PEC, (c) 4kF BOW or MD (see footnote 4), (d) 2kF BCDW and (e) 4kF CDW-SP. The large red and small blue dots represent respectively charge-rich (ρ = 1/2 + 8) and charge-poor (ρ = 1/2 − 8) sites. Gray dots represent equally charged (ρ = 1/2) sites. (4kF)−1 and (2kF)−1 periods correspond to 2 and 4 inter-site distances, respectively. The thickness of the lines linking neighboring sites is proportional to the shortening of the bond distance. In (a) and (b) all the sites are equi-spaced. Note that these ground states present different inversion symmetry, except (b) and (d) which have the same symmetry.

For a uniform chain, the bonds linking first neighbor sites in the 4kF model has been employed (see [4] and references therein). In this case, the Hamiltonian is given by:

\[ H = t_1 \sum_{i \text{ even}, \sigma} (a_{i\sigma}^\dagger a_{i+1\sigma} + \text{h.c.}) + t_2 \sum_{i \text{ odd}, \sigma} (a_{i\sigma}^\dagger a_{i+1\sigma} + \text{h.c.}) + U \sum_i n_i^c n_i^d + V \sum_i n_i n_{i+1} \]  

(2)

where \( t_1 = t(1 - \delta_1) \) and \( t_2 = t(1 + \delta_2) \) are, respectively, the inter- and intra-dimer transfer integrals and \( V \) is the nearest-neighbor Coulomb repulsion. The phase diagram of this Hamiltonian is compared in figure 2 to the one previously obtained for the uniform quarter-filled repulsive chain. The dimerization of the chain creates favorable conditions for a 4kF BOW charge localization (Mott Insulator). As this latter has a different inversion symmetry as the CO, this destabilizes the 4kF CDW instability and thus enhances the critical \( V_c \) necessary to achieve the CO ground state [32]. In the Fabre salts, because of the incipient stack dimerization a 4kF BOW progressive charge localization is generally observed at a crossover temperature \( T_{CO} \) larger than the critical temperature \( T_{CO} \) achieving the CO (see section 4).

Figure 1 shows various \( T = 0 \) K intra-chain charge configurations resulting from the minimization of various models of the 1D interacting electron gas. The experimentally relevant 3D ground state must be stabilized by inter-chain coupling. Such inter-chain coupling involves Coulomb coupling between charges sitting on neighboring chains or effective interactions between charges mediated by lattice deformations. The effect of inter-chain Coulomb coupling has been recently considered in the Fabre salts [26]. The consideration of the lattice degrees of freedom requires the inclusion of electron–phonon coupling terms in the Hamiltonian, as done, for example, in [30]. The stabilization of the various charge modulation patterns shown in figure 1
Figure 3. The (TMTCF) molecule, which is the basic entity building the Fabre–Bechgaard salts. C (yellow circles in the bottom part of the figure) stands for S or Se atoms. The TMTTF molecule is represented in the upper part of the figure. Reproduced with permission from [16]. Copyright 2000 Nova Science.

Figure 4. Projection of the crystallographic structure of (TMTTF)₂X in the a–c plane. d₁ and d₂ are the inter-dimer and the intra-dimer spacing, respectively, with d₁ > d₂. The unit cell is outlined in black. Reproduced from [80].

Figure 5. Structure of (TMTTF)₂X projected on the b–c plane. The anion (X = PF₆, AsF₆ or SbF₆) is shown in an octahedron representation. Red lines indicate the shortest distance between the F and S atoms. Note that each anion experiences two short S–F distances related by inversion symmetry in the RT structure and only one short S–F distance in the CO state. The unit cell is outlined by yellow lines. Reproduced from [80].

requires a coupling to the intra-molecular lattice modes or to the anions (see [33]), while the various bond distance modulation patterns require a coupling to the inter-molecular lattice modes (these aspects are briefly reviewed in [9]). In the Fabre salts both charge modulation and stack deformation (this latter leading to a deformation of the cavity where the anion is located) will be coupled to the anion position and orientation, and thus transmitted to the lattice parameters via the large phononic Grüneisen parameter of the anion (see section 5).

Concluding this section, it is useful to mention that evidence for a CO phase has also been reported in many quarter-filled organic compounds other than the Fabre salts. For example, first evidence of a phase transition to a CO state was found by means of infra-red (IR) spectroscopy in the quasi-2D conductor \(\alpha-(\text{BEDT-TTF})₂\text{I}_3\) [34], and via NMR studies in the quasi-1D conductor \((\text{DI-DCNQI})₂\text{Ag}\) [35]. However, to our knowledge, the very first report of a CO transition combining both NMR and structural studies was performed in the \((\text{TMP})₂\text{X-CH}_2\text{Cl}_2\) (X = PF₆, AsF₆ or SbF₆) system [36].

3. Crystal structure of the Fabre–Bechgaard salts

The building block of the Fabre–Bechgaard family of organic conductors is the (TMTCF) molecule (shown in figure 3); here C stands for the chalcogen S or Se atoms. Irrespective of the counter-ion, all (TMTCF)₂X salts crystallize at room temperature (RT) in the centrosymmetric triclinic structure P\(\overline{1}\) with two donor molecules and one anion in the unit cell, see figure 4.

As can be seen from figures 4 and 5, the quasi-planar (TMTCF) molecules are arranged in a zig-zag configuration, forming stacks along the a-axis, where the highest electrical conductivity is observed in these materials. The stacks form layers in the a–b plane, which themselves are separated by anions along the c-axis, so that shortest separations between sulfur (for the TMTTF family) or selenium (for the TMTSF) atoms located on neighboring molecules are in the a–b plane. Figures 4 and 5 show more precisely that terminal methyl groups of successive (a, b) TMTCF layers delimit along the interlayer direction c\(^*\) soft cavities filled by anions. In such cavities the anion experiences a quite symmetric environment due to the presence of the six closest methyl groups [40].

The anions can be classified according to their symmetry. For example, X = Br (spherical); PF₆, AsF₆ and SbF₆ (octahedral) are centro-symmetrical anions, while BF₄, ClO₄, ReO₄ (tetrahedral) and SCN (linear) are non-centro-symmetrical. As we shall see below, the counter-ions are not only responsible for making the charge balance of the
(TMTTF)$_2$ donor molecule, but their structural degrees of freedom also influence dramatically the electronic properties of the Fabre–Bechgaard salts. At room temperature the anions, even centro-symmetric ones such as PF$_6$, as well as the methyl groups, are subject to considerable thermally activated motions. In this regard, NMR measurements in (TMTSF)$_2$PF$_6$[41–43] and (TMTTF)$_2$SbF$_6$[39, 44] show that both anion and methyl group rotational disorders are progressively removed upon cooling. In (TMTSF)$_2$PF$_6$ the classical motion of the PF$_6$ and of the methyl groups probed by NMR stops below about 70 K[43] and 55 K[41] respectively, but quantum tunneling of the methyl groups remains below these temperatures. The 4 K structural refinements of (TMTSF)$_2$PF$_6$[45, 46] and (TMTTF)$_2$PF$_6$[37, 47] show that each anion locks its orientation by establishing two short F–Se contact distances and four F...H–CH$_2$ bonds with four neighboring TMTCF molecules located nearly in a plane perpendicular to $a$. In (TMTSF)$_2$PF$_6$, a cooperative locking between anions and methyl groups occurs at $T \approx 55$ K[41, 46] via the formation of H-bonds between these two entities. Non-centro-symmetric anions X, located in similar methyl group cavities, are also subject to an orientational disorder at RT. The orientations of these anions order upon cooling in a staggered way through a symmetry-breaking phase transition which stabilizes a superstructure where some of the high-temperature lattice parameters are doubled[48].

In the TMTSF salts, the interstack interaction is stronger than in the TMTTF salts. This is because the shortest Se–Se interstack distances in the TMTSF family are less than twice the van der Waals’ radii of the Se atoms, whereas in the TMTTF family the corresponding shortest S–S distances are more than twice the van der Waals’ radii of the sulfur atoms. For this reason TMTSF salts are more 1D than the TMTTF salts. The ratio of transfer integrals in the $a$, $b$, $c$ directions is roughly $t_a/t_b/t_c = 100:10:1$, see[13].

The unit cell parameters of the salts (TMTTF)$_2$X (X = PF$_6$, AsF$_6$ and SbF$_6$) investigated here are listed in table 1.

| X     | PF$_6$ | AsF$_6$ | SbF$_6$ |
|-------|--------|---------|---------|
| $a$ (Å) | 7.146  | 7.178   | 7.180   |
| $b$ (Å) | 7.583  | 7.610   | 7.654   |
| $c$ (Å) | 13.218 | 13.317  | 13.51   |
| $\alpha$ (deg) | 82.69  | 82.03   | 81.24   |
| $\beta$ (deg) | 84.87  | 95.75   | 83.42   |
| $\gamma$ (deg) | 72.42  | 107.11  | 74.00   |
| $V$ (Å$^3$) | 676    | 687     | 702.9   |
| $d_1$ (Å) | 3.66   | 3.64    | 3.64    |
| $d_2$ (Å) | 3.52   | 3.54    | 3.52    |

Figure 6. Generic P–T phase diagram of the Fabre–Bechgaard salts. The position of the different compounds at ambient pressure is indicated by arrows. The various ground states are charge-ordering (CO), spin-Peierls (SP), antiferromagnetic (AFM), spin-density wave (SDW), and superconductivity (SC). The crossover to a charge localized state (loc) is indicated by the black dashed line on the left side of the phase diagram. Deconfinement crossover when the coherence of the electron gas passes from 1D to 2D or even 3D is indicated by the red dashed lines on the right side of the diagram. For details on the pressure dependence of T$_{CO}$ for the X = SbF$_6$ and AsF$_6$ salts, see figure 10. Reproduced with permission from[23]. Copyright 2007 Springer.
In these conditions the CO induces a dielectric polarization of the stack.

4. Phase diagram of the Fabre–Bechgaard salts

4.1. The generic phase diagram

The era of organic superconductors begins with the observation of superconductivity in pressurized (TMTSF)$_2$PF$_6$ by Jérôme et al [51] at the end of the 1970s. Since then, for all the anions (with the exception of X = NO$_3$) both the Bechgaard and Fabre salts were found to be superconductors under pressure. (TMTSF)$_2$X is the only ambient pressure superconductor. The Fabre and Bechgaard salts present a very rich phase diagram under pressure (see figure 6). The electronic properties of (TMTSF)$_2$X are more 1D than those of (TMTSF)$_2$X. This feature, together with the fact that TMTSF salts exhibit stronger electron repulsions than TMTSF salts, lead in the low-pressure range of the phase diagram of the Fabre salts to a charge localized behavior (below $T_D$—see figure 7) generally followed by a CO transition. The strong inter-chain coupling present in the Bechgaard salts induces a 1D to 2D then to 3D deconfinement of the electron gas upon cooling (see figure 6). Superconductivity is achieved in the 3D delocalized state.

Figure 7. Resistivity versus temperature for several (TMTCF)$_2$X salts. Upon cooling, a continuous charge localization, marked by a broad minimum around $T_D = 200–250$ K, is observed for the (TMTTF)$_2$AsF$_6$ (curve 1) and (TMTTF)$_2$PF$_6$ (curve 5) salts before the occurrence of the CO phase transition at much lower $T_{CO}$. For the (TMTTF)$_2$SbF$_6$ salt (curve 2), a CO transition accompanied by a MI transition takes place at $T_{CO,MI} \approx 154$ K. In (TMTTF)$_2$Br salt (curve 6) one has $T_D \approx 100$ K before the occurrence of the AFM ground state at $T_N = 13$ K. (TMTSF)$_2$PF$_6$ (curve 7) remains metallic until the 12 K SDW M–I transition. The (TMTSF)$_2$ClO$_4$ salt (curve 8) remains metallic down to $T_D = 1.2$ K, a temperature below which the resistance vanishes and superconductivity appears. Reproduced with permission from [23]. Copyright 2007 Springer.

Here the discussion will be mainly focused on the properties of the (TMTTF)$_2$X family, which exhibits CO transitions. It is well known that quasi-1D conductors are inherently more susceptible to sustain density wave instabilities than 2D or 3D conductors. Due to the combination of the 4ky charge localization instability and of the 2ky nesting instability of the correlated electron gas in 1D, together with the interplay of substantial electron–phonon interactions, the phase diagram of the Fabre–Bechgaard salts covers a rich variety of ground states.

4.1.1. Centro-symmetric anions. The phase diagram of the (TMTTF)$_2$X salts, where X is centro-symmetric, has been extensively studied. The most recent version of their generic $P–T$ phase diagram is shown in figure 6 (note that in the earlier versions of the phase diagram [14, 52, 53] the CO phase was not established). As figure 6 highlights, the ground states can be tuned by anion substitution, exchange of the chalcogen atom of the donor molecule (C = Se or S) and/or external pressure application. The phase diagram represented in figure 6 shows in particular that the ground states of the TMTTF family evolve towards those of the TMTSF family by applying pressure.

By cooling (TMTTF)$_2$PF$_6$ under ambient pressure, a progressive Mott–Hubbard charge localization is observed around $T_D \approx 240$ K (see curve 3 in figure 7). Upon further cooling, a CO phase transition coinciding with the onset of a ferroelectric phase takes place at $T_{CO} \approx 65$ K. Cooling down to lower temperatures, a SP ground state accompanied by a stack tetramerization occurs at $T_{SP} \approx 17$ K. By applying pressure, the CO phase and the SP ground state are suppressed. The SP ground state transforms into an antiferromagnetic (AFM) one, similar to the one found in the (TMTTF)$_2$Br salt at ambient pressure. Applying additional pressure (~15 kbar), $T_D$ vanishes, showing that the Mott–Hubbard localized (loc) state is suppressed and that the compound becomes metallic on a large temperature range. At low $T$, an incommensurate spin-density wave (SDW) ground state, coinciding with a MI transition, replaces the commensurate AFM order. Under a pressure of 52–54 kbar the SDW is then removed and superconductivity occurs at $T = 1.4–1.8$ K [54], closing the full sequence of various ground states exhibited by the generic phase diagram of salts with centro-symmetric anions.

4.1.2. Non-centro-symmetric anions. In the Fabre–Bechgaard salts incorporating non-centrosymmetrical anions, other structural phase transitions due to the ordering of the anions (AO transition), not shown in the generic phase diagram (figure 6), occur. At RT, the anion cavities delimited by the methyl groups of the TMTCF molecules are slightly disordered. Upon cooling, the change of the spacing between TMTCF molecules is altered, implying thus a shortening of contact distances between the anions and its vicinity. Due to the gain of energy by reinforcing the short contact distances with the TMTCF, the non-centrosymmetrical (tetrahedral) anions such as ClO$_4$, ReO$_4$ and the (linear) SCN anion order by choosing one of their two possible orientations in the methyl groups cavity. These two possible orientations...
are related by inversion symmetry in the double potential\(^5\) originating from the anion surroundings. The barrier height between the two potential minima controls the kinetics of the AO transition [48]. The AO transition breaks the inversion symmetry of the methyl group cavity. Also the associated deformation of the cavity perturbs the TMTTF stacking in the \(a-b\) layers, which changes drastically the electronic structure of the Fabre–Bechgaard salts with non-centro-symmetric anions. For example, in (TMTSF)\(_2\)ReO\(_4\) and BF\(_4\) the AO transition drives a MI transition stabilizing a 2\(k_F\) BCDW ground state. In (TMTSF)\(_2\)ClO\(_4\) the kinetics of AO drives the salt to either a SDW ground state (quenched samples) or a superconducting ground state (relaxed samples); for more details see [13, 27, 48].

4.2. The symmetry-breaking CO transition

The AO transition of the SCN salt has a subtle connection with the CO transition, which is the main purpose of this review. The story starts 30 years ago with the report in (TMTTF)\(_2\)SCN of an AO transition accompanied by a sharp MI transition stabilizing at \(T_{\text{CO}} = 160\ K\) with formation of a superstructure with a new 4\(k_F\) site periodicity [56]; a result which was very soon interpreted as the first evidence of a 4\(k_F\) charge localization (now labeled CO) triggered by the potential due to the ordering of the SCN anion [57, 58]. However, due to the inter-chain staggered AO process the CO does not remove all the inversion centers of the structure. Thus the SCN salt achieves antiferroelectricity below \(T_{\text{CO}} = 160\ K\). It takes a much longer time to establish that (TMTTF)\(_2\)X salts with octahedral anions can also achieve CO where the removal of all the inversion centers leads to ferroelectricity. Two years after the work on (TMTTF)\(_2\)SCN, electrical measurements evidence a similar sharp MI in the \(X = \text{SbF}_6\) salt at a critical temperature of 154 K, which significantly shifts in the solid solutions of \(\text{SbF}_6\) with \(\text{AsF}_6\) and \(\text{PF}_6\) [28]. These transitions were found to coincide with a dramatic change in the thermopower [59] and a peak divergence in the real part of the dielectric constant [60]. However, neither superstructure formation nor a significant change in the Bragg intensity was found at these transitions, in contrast to the finding in the SCN salt, so that the transition was labeled structureless in the literature. The first evidence of a symmetry breaking was found in 2000 when NMR measurements performed by Chow et al [61] revealed a splitting of the spectral line below the structureless transition, see figure 8.

This spectral splitting is brought about because the TMTTF molecules, which are equivalent above \(T_{\text{CO}}\), become differentiated below \(T_{\text{CO}}\) into charge-rich alternating with charge-poor molecules (see inset of figure 8 and figure 1 (a)). This differentiation gives rise to two inequivalent hyperfine couplings and a doubling of the spectral lines. The spectral splitting associated with the CO is the order parameter of the transition. Hence, based on this observation, Chow et al deduced that the so-called structureless transition in the Fabre salts with octahedral anions is in fact associated with a symmetry-breaking CO phase transition.

Near the same time, dielectric measurements [25, 62] were probing unambiguously the ferroelectric character of the transition. As a matter of fact, the first observation of a divergence of the dielectric constant at the structureless transition was reported much earlier in [60], but the data were not interpreted in relation to the ferroelectricity. The features observed in the dielectric constant are due to the presence of electric dipoles generated by the charge disproportionation along the dimerized stacks.

Later, Dumm et al [63] studied the influence of charge disproportionation on the vibrational spectra of the \(X = \text{PF}_6\) and \(\text{AsF}_6\) salts via mid-infra-red optical conductivity as a function of temperature, with the light polarized along the stacks (\(a\)-axis) (figure 11). They found that the inter-molecular \(a_g\) \((\nu_3)\) mode, which becomes infra-red active through coupling of electron–molecular vibrations, splits below \(T_{\text{CO}}\). This feature is explained by the strong dependence of this vibronic mode on the degree of ionization of the TMTTF molecule [64]. From this study, it is estimated that there is a charge disproportionation ratio of 5:4 and 2:1 for \(X = \text{PF}_6\) and \(\text{AsF}_6\) salts, respectively.

The absence of structural effects accompanying the CO transition was particularly puzzling as atomic displacements, breaking the inversion symmetry, are prerequisite for ferroelectricity to occur. It is only recently that a structural modification was detected at the CO transition of the \(\text{PF}_6\) salt using neutron diffraction [65, 66], since it was realized that in conventional structural investigations the CO is rapidly destroyed by irradiation defects induced by the x-ray diffraction beam [67]. As the CO structure could not be

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\(^5\) A similar model to treat the orientational degrees of freedom of the ethylene end-groups of the ET molecules in the quasi-2D organic (ET)\(_2\)X charge-transfer salt family was proposed by Ravy et al [55] for the \(\beta\)-phase and by Müller [55] for the \(\epsilon\)-phase. See also Pouget [55].
refined, the expected shift of the anion from the inversion centers could not be quantified. However, the key role of the anions, already pointed out in earlier investigations [28], is evidenced by the fact that \( T_{\text{CO}} \) varies significantly with the nature of the anion [68], see figures 8–10. Note that only recently a structural refinement was able to prove that an anion shift stabilizes the CO pattern in the parent salt \( \delta-(\text{EDT-TTF-CONMe}_2)_2\text{Br} \) [69].

4.3. Characteristic features of the CO ground state

As figure 9 demonstrates, the transition is due to the Curie–Weiss divergence of the real part of the dielectric constant, i.e. \( \epsilon' = A/|T - T_{\text{CO}}| \), consistent with a second-order phase transition with a mean-field character. This shows that the regime of 1D pretransitional fluctuations expected in 1D conductors is removed by the 3D long-range Coulomb interactions [25]. Nevertheless, a careful analysis of the dielectric constant data reveal precursor effects already at \( T \approx 200 \text{ K} \) for the \( X = \text{PF}_6 \) salt [62]. Interestingly enough, below \( T \approx 200 \text{ K} \) the spin susceptibility continues to decrease monotonically [50, 68, 70]. Hence, the development of charge correlations in the dielectric constant together with the absence of magnetic signatures at \( T_{\text{CO}} \), offer strong evidence for the occurrence of a spin–charge separation accompanying the CO instability.

The effect of pressure on the CO transition was studied in detail via NMR measurements [44, 71], see figure 10. It was observed that by applying pressure, \( T_{\text{CO}} \) decreases dramatically. For example, for the \( X = \text{AsF}_6 \) salt (data in blue in figure 10), a pressure of about 1.5 kbar suppresses the CO phase. As can be seen from figure 10, at lower pressures (\( P < 1.5 \text{ kbar} \)) both SP and CO phases coexist in the AsF\(_6\) salt. More precisely, this figure shows that the SP transition temperature increases when the CO is depressed. This is a general behavior [9, 27] showing that there is a repulsive coupling between the SP and CO components of the 4\( k_F \) CDW-SP ground state (figure 1(e)). This is confirmed by recent accurate dielectric measurements showing a decrease of the gap of charge at the SP transition in the PF\(_6\) salt [72]. For the \( X = \text{SbF}_6 \) salt (data in red in figure 10), a pressure of roughly 5 kbar is necessary to abruptly suppress the CO phase. At low temperatures, pressure destroys the AF ordering, giving rise to the formation of local SP-like magnetic singlets [44] together with spin-liquid-like fluctuations [73]. Contrary to the expectation of the generic phase diagram.
(figure 6), a long-range SP ground state is not observed in pressurized (TMTTF)$_2$SbF$_6$, as is the case in the PF$_6$ and AsF$_6$ salts at ambient pressure. At higher pressure, however, the AF ground state is recovered in the SbF$_6$ salt [73]. All these results demonstrate that some caution must be taken in the use of the generic phase diagram, which ignores the specificity of the anions. In fact, anions influence the phase diagram by their kinetics of ordering (case of (TMTSF)$_2$ClO$_4$) or by their blockade in the methyl group cavities squeezed by the pressure. The freezing of the orientation and translation degrees of freedom of the anions prevents the development of the structural counterpart of the SP order and kills the CO in pressurized (TMTTF)$_2$SbF$_6$ (this general statement is developed in [27]).

Note (figure 9) that a rather smooth divergence of the dielectric constant occurs for the X = PF$_6$ salt at $T_{CO}$, which contrasts with the pronounced singularity observed for the AsF$_6$ and SbF$_6$ salts. For (TMTTF)$_2$PF$_6$, it has been found that with decreasing frequency, the maximum of $\epsilon'$ is enhanced and its position shifts to lower temperatures [62, 74], while for the (TMTTF)$_2$AsF$_6$ and (TMTTF)$_2$SbF$_6$ salts the peak position remains practically unaffected, but the magnitude of the anomaly decreases as the frequency is increased. This peculiar behavior of the PF$_6$ salt is well documented in the literature. It corresponds to the response of ferroelectric relaxors, see e.g. [75]. Such a frequency-dependent dielectric response indicates that ferroelectricity is probably achieved on local domains present in the PF$_6$ salt below $T_{CO}$. This means, more generally, that CO long-range order can be easily disrupted by structural defects and disorder, as previously suggested by the observation of a drastic effect of x-ray irradiation defects on the CO. Such defects should nucleate ferroelectric domain walls. Its consequence will be a smearing out of the collective charge response at $T_{CO}$ without a decrease of the CO critical temperature, see [67]. The peculiar features of the dielectric response in the Fabre salts could be also related to kinetic effects related to the order–disorder or relaxational nature of the pretransitional dynamics of the ferroelectric phase transition [76]. The dynamics of the ferroelectric transition is probably controlled by the anion shift, which stabilizes the CO pattern. In this respect, the anion shift could present the same type of kinetics at the CO transition as the anion orientation at the AO transition. The order–disorder dynamics could be related to the presence inside each methyl group cavity, where the anion is located, of a multi-well potential provided by the donor surroundings and whose minima reflect the tendency for each anion to form local bonds with the donors.

From the theoretical point of view, using the extended Hubbard model coupled to the lattice, Riera and Poiblanc [33] propose that CO could be due to a cooperative effect between the inter-site Coulomb interaction $V$ and the coupling of charges located on the TMTTF with the anions. In their model, the uniform displacement of the anions, which induce local modulation of the on-site electronic energy, is necessary to stabilize the CO phase.

Concluding this section, it is useful to recall that according to the model proposed by Riera and Poiblanc [33], and to the arguments discussed previously, anion displacement seems to play a crucial role in the stabilization of the CO pattern. However, the observation of such lattice effects accompanying the CO transition was done only recently [65, 69]. Before this observation, systematic high-resolution thermal expansion experiments carried out on the (TMTTF)$_2$X family with X = PF$_6$, AsF$_6$ and SbF$_6$ have brought the first clear-cut evidence of the involvement of the lattice in the CO instability. These experimental results will be presented and discussed in sections 6 and 7. Before doing so we introduce, in section 5, the physics deduced from thermal expansion measurements.

5. Thermal expansion and thermodynamic quantities

Thermal expansion at constant pressure quantifies the temperature ($T$) dependence of the sample volume ($V$). Upon increasing or decreasing the temperature in the vicinity of a generic phase transition, which might have its origin in magnetic or electronic effects, but should be accompanied by some structural effects, the harmonic approximation is no longer valid and the crystal expands or contracts until it finds the volume where the total free energy is minimized. In this sense, high-resolution measurements of the thermal expansion coefficient can be seen as a powerful thermodynamic experimental tool for detecting phase transitions, since phase transitions of different natures can be observed by using this method. In particular, given the high compressibility of molecular conductors, high-resolution thermal expansion experiments have been shown as an appropriate tool for exploring various intriguing physical phenomena occurring in these materials [77–82].

The volumetric thermal expansion coefficient of a solid is given by:

$$\beta(T) = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

where

$$\beta(T) = \alpha_l(T) + \alpha_o(T) + \alpha_c(T)$$

and $\alpha_l$ is the linear thermal expansion coefficient along the $i = a, b$ and $c$ crystal directions. Equation (4) holds for all lattice symmetries if $a, b$ and $c$ are perpendicular to each other [83]. The linear thermal expansion coefficient at constant pressure ($P$) reads:

$$\alpha_i = \frac{1}{l} \left( \frac{\partial l_i(T)}{\partial T} \right)_P$$

where $l$ is the sample length in the direction of measurement. The physical quantity described by equation (5) will be frequently used in this paper.

The isothermal compressibility of a solid is defined as follows:

$$\kappa_T = \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T.$$
In order to link the volumetric thermal expansion coefficient (equation (3)) of a solid and the isothermal compressibility (equation (6)), the derivative entering in equation (3) can be decomposed in the following way:

\[
\beta(T) = -\frac{1}{V} \left[ \frac{\partial V}{\partial T} \right]_V = \frac{\kappa_T}{\partial T} \left[ \frac{\partial P}{\partial T} \right]_V.
\]

(7)

The volumetric thermal expansion coefficient can still be linked with the entropy \(S\) where \(U\) is the internal energy of the system. Taking the partial derivatives of equation (8), one obtains:

\[
\frac{\partial F}{\partial T} \bigg|_V = -S,
\]

(9)

\[
\frac{\partial F}{\partial V} \bigg|_T = -P.
\]

(10)

Including equation (10) into (7) results in:

\[
\beta(T) = -\kappa_T \left[ \frac{\partial^2 F}{\partial T \partial V} \right]_V = \kappa_T \frac{\partial S}{\partial V} \bigg|_T.
\]

(11)

Interchanging the derivative in the above equation and substituting equations (6) and (9), results in:

\[
\beta(T) = -\kappa_T \frac{\partial^2 F}{\partial T \partial V} = \kappa_T \frac{\partial S}{\partial V} \bigg|_T.
\]

(12)

Equation (12) shows the direct connection of the volumetric thermal expansion coefficient to the volume dependence of the entropy. In the following, the volumetric thermal expansion coefficient will be related to the specific heat, which is defined as the amount of heat \(Q\) necessary to increase the temperature of the sample, as follows:

\[
C(T) = \frac{\Delta Q}{\Delta T}.
\]

(13)

The specific heat at constant volume is defined from the Helmholtz free energy by:

\[
CV(T) = -T \frac{\partial^2 F}{\partial T^2} \bigg|_V = T \frac{\partial S}{\partial T} \bigg|_V.
\]

(14)

Equation (12) can be rewritten as follows:

\[
\beta(T) = -\kappa_T \frac{\partial S}{\partial T} \bigg|_V \left[ \frac{\partial T}{\partial V} \right]_S.
\]

(15)

Substituting the last part of equation (14) into equation (15) and using the identity \((V/T)\partial T/\partial V = \partial \ln T/\partial \ln V\) the desired relation between \(C_V(T)\) and \(\beta(T)\) is thus obtained:

\[
\beta(T) = -\kappa_T \cdot C_V(T) \frac{1}{V} \bigg[ \frac{\partial \ln T}{\partial \ln V} \bigg]_S.
\]

(16)

By defining the new quantity

\[
\Gamma = -\frac{\partial \ln T}{\partial \ln V} \bigg|_S,
\]

(17)

equation (16) becomes

\[
\beta(T) = \Gamma \frac{\kappa_T}{V_{\text{mol}}} C_V(T).
\]

(18)

The latter equation is called the Gruneisen relation [84], where \(V_{\text{mol}}\) stands for the molar volume and \(\Gamma\) is the effective Gruneisen parameter. In general, \(\Gamma\) is weakly temperature dependent.

In the frame of the Debye model, the phononic specific heat reads:

\[
C_V = \frac{9Nk_B}{\Theta} \left( \frac{T}{\Theta} \right)^3 \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} \, dx,
\]

(19)

where \(x = \Theta/T\), \(\Theta\) stands for the Debye temperature, \(N\) is the number of atoms taken into account and \(k_B\) is the Boltzmann constant. To fit the thermal expansion data shown in figure 12 (see section 6), we combined equations (18) and (19), as follows:

\[
\beta(T) = \Gamma \frac{\kappa_T}{V_{\text{mol}}} 9Nk_B \left( \frac{T}{\Theta} \right)^3 \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} \, dx.
\]

(20)

In such fits (figure 12), the pre-factor \((\Gamma \frac{\kappa_T}{V_{\text{mol}}} 9Nk_B)\) of the integral in equation (20) and \(\Theta\) were considered as fit parameters.
The lattice (or phononic) Grüneisen parameter $\Gamma_{\text{ph}}$ is given by:

$$\Gamma_{\text{ph}} = -\frac{d \ln \Theta_D}{d \ln V}.$$  \hspace{1cm} (21)

According to equation (21), the bigger the lattice Grüneisen parameter, the higher the volume dependence of the vibration modes of the lattice. Strictly speaking, the lattice Grüneisen parameter is a measure of the volume dependence of the anharmonicity of the lattice vibrations, which in turn is responsible for the lattice contribution to the thermal expansion in a solid. If the vibrational free energy, entropy, specific heat and thermal expansion are the sum of contributions $f_i$, $s_i$, $c_i$ and $\alpha_i$ due to independent vibration modes of frequency $\omega_i(V)$, respectively, it is convenient to define the Grüneisen parameter of the phonon mode $i$ in the following way:

$$\Gamma_i = -\frac{d \ln \omega_i}{d \ln V}.$$  \hspace{1cm} (22)

Thus, according to equation (22), vibration modes whose frequency, $\omega_i$, decreases or softens as the volume of the solid decreases will lead to a negative Grüneisen parameter and, from equation (18), these modes will be responsible for a negative contribution to the overall thermal expansion of the material [85].

More generally, in addition to the phonon contribution to the thermal expansion of a material, other contributions, whose origin might be electronic or magnetic, have to be included. This is especially the case at low temperatures, where such contributions may dominate the thermodynamic properties [83]. Hence, the total volumetric thermal expansion coefficient can be generally expressed as:

$$\beta = \beta_{\text{ph}} + \beta_{\text{el}} + \beta_{\text{mag}}$$

$$= \frac{\kappa T}{V_{\text{molv}}} (\Gamma_{\text{ph}} C_{\text{ph}} + \Gamma_{\text{el}} C_{\text{el}} + \Gamma_{\text{mag}} C_{\text{mag}}).$$  \hspace{1cm} (23)

where $\beta_{\text{ph}}$ ($C_{\text{ph}}$), $\beta_{\text{el}}$ ($C_{\text{el}}$) and $\beta_{\text{mag}}$ ($C_{\text{mag}}$) refer to the phononic, electronic and magnetic contributions to $\beta$ (C), respectively, while $\Gamma_{\text{ph}}$, $\Gamma_{\text{el}}$ and $\Gamma_{\text{mag}}$ are the respective Grüneisen parameters.

If the Grüneisen parameter, which measures the volume dependence of a characteristic temperature, is constant and if in the temperature range of interest only one of its contributions is predominant, then it is expected that $C_V(T)$ and $\beta(T)$ will have the same temperature dependence. For this reason thermal expansion measurements provide a good test of the mean-field (jump of $C_V(T)$) or critical ($\lambda$-type divergence of $C_V(T)$) character of a second-order phase transition. In the latter case critical exponents can be obtained via thermal expansion measurements [81].

Interestingly, from the volume dependence of the critical temperature of the superconducting transition in $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ one obtains, by analogy with equation (17), $\Gamma \approx 40$ [86], a value which roughly exceeds by a factor of twenty the values of $\Gamma$ obtained for ordinary superconductors such as in Pb ($\Gamma = 2.4$ [87]) and which is very much larger than $\Gamma$ obtained for the layered cuprate YBa$_2$Cu$_3$O$_7$ ($\Gamma = (0.36-0.6)$ [88]). These findings reveal the strong sensitivity of the superconductivity to lattice parameters in the family of $\kappa$-(BEDT-TTF)$_2$X, as discussed in more detail in [89].

Very recently it has been reported [46] that in the Bechgaard salt (TMTSF)$_2$PF$_6$ the phononic Grüneisen parameter $\Gamma$, defined by expression (22), is dominated by the anion rotation ($\Gamma(\text{PF}_6) \approx 28$). As this finding remains true for the Fabre salts with octahedral anions, the lattice expansion data of section 6 should reveal the electronic instabilities on the TMTTF stack via the modification of the anion vibrational spectra (generally caused by a modification of the volume and shape of the methyl group cavity where the anion is located or by a modification of the linkage of the anion with the neighboring organic molecules).

6. Thermal expansion measurements on (TMTTF)$_2$X salts

The focus of this section is the direct observation of structural changes associated with the CO via high-resolution thermal expansion experiments. Thermal expansion measurements were carried out along three orthogonal axes, namely along the $a$-, $b$- and $c$-axes. The $a$-axis is along the stacks, the $b$-axis is perpendicular to the $a$-axis in the $a$-$b$ plane and the $c$-axis is perpendicular to the $a$-$b$ ($a$-$b'$) plane. The crystals of (TMTTF)$_2$X ($X = \text{PF}_6$, AsF$_6$ and SbF$_6$) have the following shape: the long crystal axis is parallel to the $a$-axis, the intermediate axis is parallel to the $b$-axis and the short one is parallel to the $c$-axis. As the crystal structure is triclinic, the three orthogonal directions previously defined are not the eigen directions of the thermal expansion tensor. Earlier measurements of the eigen components of this tensor using less accurate neutron diffraction methods, have shown, both for (TMTSF)$_2$PF$_6$ [45] and (TMTTF)$_2$PF$_6$ [37, 47], that the eigen directions change considerably with temperature and thus deviate significantly from the orthorhombic set used in the present study.

6.1. Overall thermal behavior of the lattice expansion coefficient

Figures 12–14 show the uniaxial expansivity for the $X = \text{PF}_6$, AsF$_6$ and SbF$_6$ salts, respectively. As can be seen from figures 12 and 13, the data show that the lattice expansivity is anisotropic at high temperature and quite isotropic at low temperature, let us say below 100 K. The largest expansivity is along the $a$ (stack) direction and the smallest one is in the $c^*$ direction, along which planes of TMTTF molecules alternate with planes of counter-anions X. An intermediate lattice expansivity is measured along the interstack $b'$ direction. The anisotropy is due to the fact that the rate of increase of the expansion coefficient upon heating saturates first along $c^*$, then along $b'$ and finally along $a$, before becoming negative at higher temperature for all the directions. For the $X = \text{PF}_6$ (figure 12) and $X = \text{AsF}_6$ (figure 13) salts, an anomalous thermal dependence is observed along the $c^*$-axis for $T > T_{\text{CO}}$. The data reveal a striking negative slope, $da_{\text{c}}(T)/dT <$
0, starting from about the CO transition temperature \( T_{CO} \). Less pronounced effects are observed along the \( a \)- and \( b' \)-axes. A negative slope, \( d\alpha_i(T)/dT < 0 \), is also observed in the AsF\(_6\) salt (figure 14) above about 75 K, well below \( T_{CO} \). At this point, it is interesting to remark that the negative slope regime is not observed for the uniaxial expansivity measured along \( c^* \) in (TMTTF)\(_2\)Br, see [90]. In addition, this lattice expansivity is one order of magnitude smaller in the Br salt than in the PF\(_6\), AsF\(_6\), and SbF\(_6\) salts. Thus the unusual features previously described are probably due to the rotational degrees of freedom of the octahedral anions which do not exist in the Br salt.

As expected from these unusual features, attempts to fit the data employing a Debye-like behavior along the three axes were unsuccessful. Along the chain axis up to \( \sim 100 \) K (red dashed line in figure 12) a Debye dependence fits (equation (20)) the data relatively well, with a Debye temperature \( \Theta_D \approx 158 \) K. We observed, however, that by changing the temperature range of the fits, \( \Theta_D \) varies markedly. For example, a fitting up to 24 K along the \( a \)-axis results in \( \Theta_D = 102 \) K. However, due to the anomalous lattice effects, depicted in figures 12 and 13 along the \( b' \) and \( c^* \) axes, the Debye model fails to describe the data, see for example the blue dashed line in figure 12.

**6.2. Lattice anomalies at the CO transition**

Figures 12–14 show that the uniaxial thermal expansion exhibits an anomaly at the CO transition of PF\(_6\) (\( T_{CO} \approx 65 \) K), AsF\(_6\) (\( T_{CO} \approx 100 \) K) and SbF\(_6\) (\( T_{CO} \approx 154 \) K) salts, respectively. The strongest anomaly is observed for measurements performed along the \( c^* \)-axis. Interestingly, along the chain direction (\( a \)-axis)\(^6\), almost no effects are observed at the CO transition. The anomalous behavior along the \( c^* \) direction, where the stacks are separated by anions, provides strong evidence that the anions play a crucial role in the stabilization of the CO phase. For the \( X = \text{PF}_6 \) (figure 12) and \( X = \text{AsF}_6 \) (figure 13) salts, one observes a rapid decrease of \( \alpha_{c^*} \) upon cooling at about \( T_{CO} \). This is indicative of a broadened step-like anomaly, i.e. a mean-field-like transition, with \( \Delta\alpha_{c^*}\big|_{T_{CO}} = \alpha(T \to T_{CO}^c) - \alpha(T \to T_{CO}^p) < 0 \). Indeed, a broad anomaly is expected in the PF\(_6\) salt due to the smooth divergence of the dielectric constant at \( T_{CO} \) (see figures 9 and 16), but not in the case of the AsF\(_6\) salt, where the dielectric constant diverges at \( T_{CO} \) (figure 9). \( \Delta\alpha_{c^*}\big|_{T_{CO}} \) enters the Ehrenfest relation for second-order phase transitions:

\[
\left( \frac{d\alpha_i}{dT} \right)_{P_i \to 0} = V_{mol} \cdot T_e \cdot \frac{\Delta\alpha_i}{\Delta C} \tag{24}
\]

where \( \Delta\alpha_i \) and \( \Delta C \) refer to the thermal expansion and specific heat changes at the transition temperature (\( T_e \)), respectively. In expression (24), the index \( i \) refers to the crystallographic direction along which pressure is applied. Strictly speaking, the Ehrenfest relation is valid only for mean-field-like phase transition, where \( \Delta\alpha \) and \( \Delta C \) present step-like behavior.

\(^6\) Data along the \( a \)-axis for the \( X = \text{AsF}_6 \) salt are missing because the sample simply cleaved as soon as a small force was exerted by dilatometer.
According to this relation, the sign of the volumetric thermal expansion coefficient jump, i.e. $\Delta \beta = \Sigma_i \Delta \alpha_i$, defines the pressure dependence of the corresponding second-order phase transition. Hence, the negative jump anomaly in $\alpha_i(T)$ at $T_{CO}$ is consistent with $dT_{CO}/dP < 0$, which agrees with NMR data under hydrostatic pressure [71], see figure 10.

This behavior should be contrasted with the huge negative $\lambda$-type anomaly observed at $T_{CO,MI} = 154$ K (figure 14) for the $X = $ SbF$_6$ salt. This anomaly coincides nicely with the peak in $\epsilon'$. Its shape is quite distinct from the broadened step anomaly observed at the CO transition in the $X = $ PF$_6$, AsF$_6$ salts. Interestingly, the anomaly at $T_{CO,MI}$ in $X = $ SbF$_6$ exhibits the same shape as the anomaly observed at the MI Mott–Hubbard transition in $\kappa$-D8-Br [79]. This agrees also with the fact that in the $X = $ SbF$_6$ salt, the charge localization does not occur gradually, as in the $X = $ PF$_6$ and AsF$_6$ salts, but abruptly at the MI transition. As can be seen from figure 15, the $\lambda$-type anomaly of figure 14 corresponds to an abrupt change of the (001) interlayer spacing with a relative jump of about $3.3 \times 10^{-4}$ at $T_{CO,MI} = 154$ K (solid line in figure 15). This strikingly different behavior of the lattice expansivity at the CO transition between the various Fabre salts, already commented upon in [90], probably relies on the presence of screened electron–electron repulsions above $T_{CO}$ in the SbF$_6$ salt, while these interactions begin to be unscreened below $T_{p}$, well above $T_{CO}$, in the AsF$_6$ and PF$_6$ salts. It is also worth mentioning that the shape of the anomalies at $T_{CO}$ of the SbF$_6$ salt bears some resemblance to the sharp negative $\lambda$-type anomaly observed at the transition temperature of conventional ferroelectric insulators such as tri-glycine sulfate (TGS) [91] and BaTiO$_3$ [92].

### 6.3. Lattice anomalies at the SP and AF transitions

The insets of figures 12 and 13 show that thermal expansion measurements exhibit a well-defined $\lambda$-type anomaly at the SP transition of the PF$_6$ and AsF$_6$ salts, occurring at 17 and 11.4 K, respectively. The anomaly is the strongest for measurements performed along the $c'$ direction, weaker for those performed along $b'$ and very weak for those performed along $a$. The $\lambda$-type anomaly is positive for all directions of measurements in the PF$_6$ salt. Surprisingly, it is negative along the $b'$ direction in the AsF$_6$ salt. Measurements performed with the same PF$_6$ sample show that the lattice expansion anomaly reflects the critical divergence of the specific heat at the SP transition [93]. Note that the anomalies at $T_{CO}$ and $T_{SP}$ differ markedly by their shapes. While kinks observed at $T_{CO}$ are consistent with a mean-field-type transition, as discussed above, the $\lambda$-type anomalies at $T_{SP}$ for both salts are compatible with the presence of significant critical fluctuations, complying with SP fluctuations observed for both compounds by x-ray diffuse scattering studies [28, 94]. As for the CO transition, more pronounced effects are observed for the uniaxial thermal expansion coefficient measured along the $c'$-axis. This means that the tetramerization of the TMTTF stacks achieved by the SP pairing is accompanied by important elastic deformations perpendicular to the stack direction, which could be induced by the transverse shift of the TMTTF along their long molecular axis. Since the TMTTF molecules form cavities...
where the anions are located, the SP distortion of the TMTTF sublattice should also cause a shift of the anions. The involvement of the anion in the SP transition is assessed by the measurement of a critical divergence of the NMR $^{75}\text{As}$ relaxation rate at the SP transition of (TMTTF)$_2\text{AsF}_6$ [95].

The inset of figure 14 reveals that a negative anomalous contribution in $\alpha_{\text{c*}}$ shows up with an extremum around $T_N$, achieving the AF ground state in (TMTTF)$_2\text{SbF}_6$. Interestingly, a similar negative anomalous contribution in $\alpha_{\text{c*}}$ also occur near $T_N$ in the Br salt [90]. These behaviors should be contrasted with the observation of a clear $\lambda$-type anomaly at the SDW and MI transition of (TMTSF)$_2\text{PF}_6$ [46, 96]. Although very small, this negative contribution indicates that $dT_N/dP_{\alpha^*} < 0$. This is in line with NMR measurements on the $X = \text{SbF}_6$ salt under hydrostatic pressure, which reveal a negative pressure dependence of $T_N$ [71], see figure 10. Hence, such results also provide evidence that for the $X = \text{SbF}_6$ the variation of the $c^*$ lattice parameter should control the pressure-induced dependence of $T_N$.

6.4. The lattice anomaly at $T_{\text{int}}$

Upon cooling below $T_{\text{CO}}$, a kink is observed in the uniaxial thermal expansion coefficient at $T_{\text{int}} \simeq (39 \pm 2)$ K and (65 $\pm$ 3) K for $X = \text{PF}_6$ and $\text{AsF}_6$, respectively. The observed kink in $\alpha_{\text{c}}(T)$ at $T_{\text{int}}$, again more pronounced along the $c^*$-axis, indicates the existence either of an additional phase transition or of a crossover in the intermediate temperature range $T_{\text{SP}} < T_{\text{int}} < T_{\text{CO}}$. These anomalous features can be better visualized in figure 16, where the volumetric thermal expansion coefficient $\beta$, divided by $T$ for (TMTTF)$_2\text{PF}_6$, is shown together with dielectric constant data extracted from the literature [74] for the same salt. Very sharp kinks in $\beta(T)/T$ are observed at $T_{\text{CO}}$ and $T_{\text{int}}$. Note that the shapes of the anomalies are very similar, indicating therefore that both features are likely to have the same origin. Interestingly enough, a small bump at $T_{\text{int}}$ can also be observed in the real part of the dielectric constant $\epsilon'(T)$, a feature which has been overlooked so far.

The analogy between the anomalies at $T_{\text{CO}}$ and $T_{\text{int}}$ is better illustrated by the inset of figure 16, where $\alpha_{\text{c*}}/T$ is plotted as a function of $T/T_{\text{CO}}$ for the $X = \text{PF}_6$ and $\text{AsF}_6$ salts. A remarkable phenomenological result obtained from this plot is that the anomalies at $T_{\text{int}}$ and $T_{\text{CO}}$ for both salts are linked by $T_{\text{int}} \simeq 0.6T_{\text{CO}}$. Interestingly enough, dielectric measurements as a function of $T$ on the mixed-stack charge-transfer salt TTF-CA, which is recognized as a prototype system exhibiting the NI transition, reveal a similar behavior [97]. Upon cooling TTF-CA through the NI transition, two distinct peaks are observed in the real part of the dielectric constant. The authors assigned these features to the dynamics of the NI domain pairs and ionic domains in the neutral lattice. Amazingly, the thermal position of the peaks is also scaled by the factor 0.6, i.e. the same factor that links $T_{\text{int}}$ and $T_{\text{CO}}$ in the (TMTTF)$_2X$ salts with $X = \text{PF}_6$, $\text{AsF}_6$. This similarity indicates that there is a common origin between these behaviors which probably relies on a somewhat similar texture of the ferroelectric medium.

An enhancement of the $c^*$-axis compressibility modulus below 40 K (i.e. below $T_{\text{int}}$) in (TMTTF)$_2\text{PF}_6$ has recently been observed [98]. Such a behavior is reminiscent of the enhancement of the $a$-axis Young modulus observed below 55 K in (TMTSF)$_2\text{PF}_6$ [99] and recently attributed to the H-bond linkage of the $\text{PF}_6$ to the methyl groups [46]. It is thus tempting to suggest that a similar linkage of the $\text{PF}_6$ to the TMTTF should occur at $T_{\text{int}}$ in (TMTTF)$_2\text{PF}_6$. In this scenario, structural modifications brought by this linkage should modify the CO pattern on the TMTTF. In this respect a change of the $^{13}\text{C}$ NMR spectra below about 40 K in (TMTTF)$_2\text{PF}_6$ has been observed [100]. However the optical spectra do not exhibit sizable modifications around $T_{\text{int}}$ [101]. However, the thermal dependence of the expansion coefficient of the $\text{SbF}_6$ salt measured along the $c^*$ direction (figure 14) does not reveal any clear additional anomaly between its broad maximum located around 50–90 K and $T_{\text{CO}}$. But the dielectric constant of this salt exhibits a small bump at about 100 K (figure 14), which is reminiscent of the one observed at $T_{\text{int}}$ in the $\text{PF}_6$ salt (figure 16). In conclusion, much work is necessary to determine if there is any relation, via a modification of the CO pattern, between the various anomalies revealed by dielectric measurements and the static and dynamic properties of the anion sublattice essentially probed by thermal expansion measurements.

7. Anomalous lattice properties of the Fabre salts in relation with the anion sublattice

The thermal dependence of the uniaxial expansivity measurements performed in the Fabre salts with octahedral anions exhibits a negative slope at high temperatures. This negative contribution is observed whatever the direction of measurement. However, this effect is the most pronounced for measurements performed along the interlayer direction $c^*$, where $\alpha_{\text{c*}}(T)$ begins to decrease upon heating from about 75 K (PF$_6$ and $\text{SbF}_6$) and 100 K (AsF$_6$). Hence, this negative contribution may indicate some kind of unconventional lattice dynamics in the Fabre salts, which can be understood within the ‘rigid-unit-mode’ (RUM) scenario, introduced by Goodwin et al [102]. In this scenario, the thermal population of local (dispersion-less) low-energy vibrational modes of independent rigid units which are coordinated in a flexible fashion induces a shrinking of their surroundings (especially in the direction perpendicular to the RUM displacement). In this framework it is tempting to suggest that rotational or translational modes of rigid $\text{PF}_6$, $\text{AsF}_6$ or $\text{SbF}_6$ units, trapped in centrosymmetrical anion cavities delimited by the methyl groups [27, 48], could play the role of these RUM or translational modes of rigid $\text{PF}_6$, $\text{AsF}_6$ or $\text{SbF}_6$ units, trapped in centrosymmetrical anion cavities delimited by the methyl groups [27, 48], could play the role of these RUM modes.

Furthermore, $^{19}\text{F}$ NMR studies [39, 43, 44] were able to show that octahedral anions are disordered at high temperatures by thermal activated jump over a potential height between RT and $\sim 135$ K and by rotation above $\sim 70$ K. In particular, measurements performed in (TMTTF)$_2\text{SbF}_6$ [39, 44] show...
that anions rotate in the temperature range where the $c^*$ thermal expansion coefficient exhibits a negative contribution (see figure 14). In addition, figure 14 shows that $\alpha_{c^*}(T)$ is drastically reduced below $50\,\text{K}$ when the anion is frozen in its cavity.

Our interpretation is also corroborated by the fact that the magnitude of the thermal expansion coefficient is drastically reduced and its negative contribution is suppressed by substitution of octahedral anions ($X = \text{PF}_6^-$, $\text{AsF}_6^-$, $\text{SbF}_6^-$) by the Br [90], which does not possess rotational degrees of freedom. This observation is complemented by a recent study [46] of the thermal dependence of the lattice expansivity of (TMTSF)$_2\text{PF}_6$ below $200\,\text{K}$, which exhibits also high-temperature negative contributions [96], and whose analysis shows that anion rotation exhibits a huge Gruneisen parameter of $\Gamma(\text{PF}_6) \approx 28$. A similar value of $\Gamma(\text{PF}_6)$ is expected in (TMTTF)$_2\text{PF}_6$ because the thermal expansion coefficients have the same magnitude in (TMTSF)$_2\text{PF}_6$ and (TMTTF)$_2\text{PF}_6$.

In general, such RUM are likely the driving force of the negative thermal expansion (NTE) phenomenon observed in several materials [80, 102, 103]. As pointed out above, the CO transition seems to affect dramatically the overall behavior of the $\alpha_{c^*}(T)$ expansivity. For the $X = \text{PF}_6^-$ and $\text{AsF}_6^-$ salts, $T_{\text{CO}}$ coincides roughly with the temperature below which the negative contribution to $\alpha_{c^*}(T)$ is no longer active. Above $T_{\text{CO}}$, CO pretransitional fluctuations cause positional fluctuations of the anions towards their new off-center equilibrium position, providing an effective damping/softening of these modes. Upon achieving the structural distortion at $T_{\text{CO}}$, the anion motions become strongly reduced, which suppress the negative contribution in $\alpha_{c^*}$ for $T < T_{\text{CO}}$. In fact, data obtained for the $\text{SbF}_6^-$ salt shows that the situation could be a little bit more subtle than the one previously described. Figure 14 shows indeed that the thermal expansion coefficient along $c^*$ has a negative slope above $T_{\text{CO}}$, but also that the negative dependence continues below $T_{\text{CO}}$ until about $85\,\text{K}$. In the RUM scenario, this means that the anion fluctuations do not stop at the CO transition of the $\text{SbF}_6^-$ salt, a statement in perfect agreement with $^{19}\text{F}$ NMR studies performed in (TMTTF)$_2\text{SbF}_6$ [39, 44]. Thus, a more elaborated scenario should be that the Fabre–Bechgaard salts possess an incipient off-centering anion instability and that the $4k\pi$ CDW or CO electronic instability uses this structural instability to stabilize at $T_{\text{CO}}$ a 3D pattern of localized charges on one site out of two (figures 1(a) and 17). The non-freezing of all the anion degrees of freedom at $T_{\text{CO}}$ is sustained by the experimental observation that the Fabre salts incorporating tetrahedral anions, such as $\text{ReO}_4^-$ and $\text{BF}_4^-$ (whose orientation is disordered at RT), the CO transition leaves unaffected the orientation degree of freedom of the anion, which thus remains available for their ordering at an AO transition with a $T_{\text{AO}}$ [48] significantly lower than $T_{\text{CO}}$ [74].

In the CO process, however, the size of the anion should also play an important role. As discussed in [68], for anions of same symmetry $T_{\text{CO}}$ increases with the anion size. For example, $T_{\text{CO}}^{\text{X-\text{SbF}_6}} = 154\,\text{K} > T_{\text{CO}}^{\text{X-\text{AsF}_6}} = 105\,\text{K} > T_{\text{CO}}^{\text{X-\text{PF}_6}} = 65\,\text{K}$. This can be simply rationalized if the anion size defines its free rotational/translational volume in the methyl group cavity as well as the intensity of the electron–anion coupling necessary to stabilize the CO pattern.

The off-centering anion displacements accompanying the CO transition have been presented in [104], as a direct consequence of Earnshaw’s theorem, which states that a classical system of point charges under the interaction of Coulomb forces alone is unstable, since there is no minimum in the electrostatic potential. However, this statement requires great caution because if the shift of the anion induces some chemical bonding, with the methyl groups for example (see the end of this section), we are faced with a quantum phenomenon going beyond the validity of Earnshaw’s theorem.

The present findings (see figures 12–14) provide strong evidence that the interstack $c^*$-axis plays a crucial role in the stabilization of the CO phase. The $c^*$ direction is distinct in that it incorporates the anions $X$ (see figures 4 and 5), while the $a$-$a$-axis lattice parameter, which is determined by the intrastack interactions between neighboring TMTTF molecules, remains practically unaffected by the CO, see figure 12. Hence, according to the anisotropy observed in

Figure 17. Schematic representation of the 3D ferroelectric pattern in the (TMTTF)$_2X$ family. (a) Charge pattern in ($b^*, c^*$) plane. Black and white hexagons are used to represent charge-rich and charge-poor sites, i.e. (TMTTF)$^{0.5\pi+\rho}$ and (TMTTF)$^{0.5\pi-\rho}$, respectively. Dashed black hexagons are used to represent (TMTTF)$^{0.5\pi+\rho}$ molecules located in another layer. Anions are represented by full and dashed circles. Arrows indicate displacements of the anions from their centrosymmetric positions towards positive charged nearest-neighbor (TMTTF)$^{0.5\pi+\rho}$ molecules, necessary for the stabilization of the CO phase. Green line exemplarily indicates short S–F contacts. (b) View of the ferroelectric pattern in the $(a, b^*+c^*)$ plane, indicated by orange dotted line in (a). Adapted from [78, 80].
α, with a dominant effect in α∗, anion displacements and their coupling to the TMTTF molecules play a crucial role in the CO transition, as previously predicted [33]. Such a scenario, taking into account both the charge degrees of freedom on the TMTTF stacks as well as their coupling to the anions, is illustrated in Figure 17 [78]. In this figure the arrangement of TMTTF (hexagons) and the anions (circles) in the (b′, c′) plane (top panel) and the (a, b′+c′) planes (bottom panel) are shown schematically. Upon cooling through TCO, the charge ρ on the TMTTF molecule changes from a homogeneous distribution with ρ = 0.5 (in units of e) holes per TMTTF, above TCO to a modulated structure whose charges alternate by ±δ along the TMTTF stacks below. For deriving the resulting 3D charge pattern, we start by considering a stack of anions along the a-axis and the two nearest-neighbor stacks of TMTTF molecules linked via short S–F contacts (green line in Figure 17). For a fixed charge modulation on one of the stacks, the electrostatic energy of the whole array can be reduced if one of the anions’ nearest-neighbor TMTTF molecules is charge-rich (TMTTF)0(δ−1) (black symbols), and the other one is charge-poor (TMTTF)0(δ−1) (white symbols), while the anions perform slight shifts towards the charge-rich molecule. The resulting anion displacements, indicated by the arrows in Figure 17, which are uniform for all anions and lift the inversion symmetry, together with the minimization of Coulomb energies of adjacent stacks along the b-axis, determine the 3D charge pattern unambiguously.

Thus, the CO transition achieving ferroelectricity requires a shift of the anions from the high-temperature inversion centers. The direction of shift of the anions has not yet been determined for the Fabre salts, but is known in the parent salt δ-(EDT-TTF-CONMe2)2Br [69]. In this respect, two possible scenarios can be considered [27, 66]: either (1) a shift of the anion towards the S atom of the TMTTF, shortening one S–F contact distance (this is the scenario illustrated in Figure 17) or (2) a shift of the anion towards the methyl group of one of the TMTTF molecules delimiting the methyl group cavity, forming F· · · H–CH2 bonds with this molecule. In each case the anion shift stabilizes an excess of holes in the molecule towards which the anion moves. However, the location of charge-rich TMTTFs is different in these two scenarios because the direction of displacement of the anion is different. Arguments in favor of scenario (2) are given in [27]. In this last scenario, the shift of the anion and its H-bonding with the methyl groups of one TMTTF out of two will form a H-bond ferroelectric [105]. H-bond ferroelectricity explains both the strong H/D isotopic effect leading to a significant increase of TCO when D substitutes H in TMTTF [68] and the order–disorder, or relaxation, of the dielectric transition recently revealed by clever dielectric measurements [76]. In the order–disorder scenario, the two relevant configurations correspond to the two ways in which the MF6 anion can form F· · · H bonds with the neighboring methyl groups. As methyl groups rotate easily, this ferroelectricity should be very sensitive to defects. Disorder of the methyl groups will perturb the H-bonding network with the anions. Thus an opposite F· · · H–CH2 linkage will invert the direction of the ferroelectric polarization and, since F· · · H-bonds are directed towards the hole-rich TMTTF, this will induce a phase shift in the CO pattern. Disorder will thus fragment the ferroelectric pattern into domains which achieve local polarization at the origin of the relaxor-like dielectric properties. We suspect that the PF6 salt having the lowest TCO should be more sensitive to the disorder because TCO is close to the freezing point of the rotational classical motion of the methyl groups (∼55 K in (TMTSF)2PF6 [41, 42]). In addition, x-ray irradiation defects will easily disorder the H-bond pattern, leading to a disordered CO ground state. The break of the long-range CO explains why x-ray diffraction experiments have not succeeded in revealing the symmetry breaking at TCO, and why neutron scattering, which does not induce methyl group disorder, has recently succeeded in detecting a singularity in the thermal dependence of the Bragg reflection intensity at TCO [65, 66].

8. Summary and outlook

In this review we have discussed several aspects of the CO transition.

The thermal expansion measurements reviewed here revealed, for the first time, lattice effects associated with the CO transition of (TMTTF)2X salts. Given the charge unbalancing imposed by the CO transition, uniform displacements of negative charged anions X− from their symmetric positions towards positive charged nearest-neighbor (TMTTF)0.5+p are required to minimize the electrostatic energy. Hence, expansivity results demonstrate the importance of lattice effects/anion displacements for the stabilization of the CO phase, as predicted from calculations on the basis of the extended Hubbard model including Peierls-like coupling. The anomalous expansivity observed above about 100 K along the c∗-axis, along which planes of TMTTF molecules are separated by planes of anions X, was interpreted considering the rigid-unit-mode scenario. In (TMTTF)2X salts (X = PF6 and AsF6), the thermal expansion coefficient along the c∗-axis remains positive while a dramatic change of slope occurs from dα∗/dT < 0 above TCO to dα∗/dT > 0 below TCO. Although the CO transition in (TMTTF)2X exhibits a mean-field behavior (the dielectric constant obeys the Curie law), charge-ordering fluctuations show up well above TCO. Such charge fluctuations couple to the rotational or translational shifts of the rigid PF6 or AsF6 units from the center of the cavities delimited by the methyl groups. Below the CO transition temperature (TCO = 65 K and 105 K for X = PF6 and AsF6 salts, respectively), translations or rotations of the anions are no longer critically active and, as consequence, a dramatic change of slope in the thermal expansion coefficient along the c∗-direction is observed in these salts. Based on the strong anisotropy observed, a scheme to demonstrate the 3D ferroelectric character of the CO transition, taking into account charge degrees of freedom and anion displacements, was proposed. Furthermore, evidence for a new phase transition or crossover was presented for the PF6 and AsF6 salts at Tint ∼ 0.6TCO. This unexpected finding could be caused by the linkage of the anion to the methyl groups in the same temperature range.
for (TMTSF)$_2$PF$_6$. Measurements along the $c^*$-axis on the (TMTTF)$_2$X salt with $X =$ SbF$_6$ revealed a distinct behavior. The shape and magnitude of the lattice expansion anomaly, indicative of the presence of strong critical fluctuations, differ markedly from the mean-field-like anomaly observed at $T_{CO}$ for the $X =$ PF$_6$, AsF$_6$ salts. This difference can be understood as a consequence of short-range Coulomb forces in the $X =$ SbF$_6$ salt [90], where CO coincides with a metal-to-insulator transition, i.e. $T_{CO} = T_{MI}$. This implies a more effective screening of the long-range Coulomb forces above $T_{CO}$, as compared to the $X =$ AsF$_6$ and PF$_6$ salts, where $T_{CO} < T_p$, with $T_p$ denoting the temperature of minimum of resistivity, which marks the onset of the charge localization [28, 50, 74].

In what follows, we suggest further experiments which will contribute to shed light into the CO phase. For the (TMTTF)$_2$X salts, high resolution thermal expansion measurements, both at the CO and AO transitions of the $X =$ ReO$_4$ and BF$_4$ salts, are desirable. In addition, directional-dependent thermal expansion measurements on (TMTTF)$_2$SbF$_6$ are important in order to look for anisotropic effects at the CO transition, which in turn is accompanied by a metal-to-insulator transition. In addition, systematic measurements on the TMTSF family are important in order to check the existence of a possible ‘metallic ferroelectricity’, as suggested long ago by Anderson and Blount [106], or of an incipient local and fluctuating ferroelectricity [104]. We have shown in this review that the anions play an important role in stabilizing the CO pattern. In the same spirit it should be important to determine more clearly their influence in the AO microscopic mechanism, especially in compounds such as (TMTSF)$_2$ClO$_4$, where the kinetics of ordering tunes the electronic ground state. In particular, the effect of elastic deformations of the conducting layers induced by the AO process should be clarified. In this respect, it should be important to perform high-resolution lattice parameter measurements in (TMTSF)$_2$ClO$_4$ around the AO transition in order to complete earlier measurements, which already show an influence of the cooling rate on the $a$ [107], $\gamma$ and $c$ [108, 109] triclinic parameters (see also [27]). Such measurements could also reveal whether there exist similarities between the AO and the glass-like transition observed in fully deuterated/hydrogenated salts of $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br [80], and how an inhomogeneous texture of the low-temperature phases of these organic salts could explain the strong sensitivity of their superconducting properties to cooling effects [110].

In order to gain more insights into the screening and polarization effects in the (TMTCF)$_2$X salts, systematic calculations of the Madelung energy [111] above and below the CO transition temperature, including the polarization effects induced by the anion shift, are required. Furthermore, a detailed experimental investigation of the recent proposed multiferroic character of (TMTTF)$_2$PF$_6$ [26], similar to the one proposed for TTF-CA [112], is highly desired as well.

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