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TOPICAL REVIEW

Charge- and spin-density-wave superconductors

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Abstract

This review deals with the properties of superconductors with competing electron spectrum instabilities, namely, charge-density waves (CDWs) and spin-density waves (SDWs). The underlying reasons of the electron spectrum instability may be either Fermi surface nesting or the existence of Van Hove saddle points for lower dimensionalities. CDW superconductors include layered dichalcogenides, $NbSe_3$, and compounds with the A15 and C15 structures among others. There is much evidence to show that high-T_c oxides may also belong to this group of materials. The SDW superconductors include URu_2Si_2 and related heavy-fermion compounds, Cr–Re alloys and organic superconductors. We review the experimental evidence for CDW and SDW instabilities in a wide range of different superconductors, and assess the competition between these instabilities of the Fermi surface and the superconducting gap. Issues concerning the superconducting order parameter symmetry are also touched upon. The accent is put on establishing a universal framework for further theoretical discussions and experimental investigations based on an extensive list of available and up-to-date references.

1. Introduction

The concept of a Fermi surface driven structural transition due to the electron–phonon interaction (commonly called the Peierls transition) has its roots in the 1930s [1], but only became widely appreciated after the publication of the book *Quantum Theory of Solids* [2]. At the same time, Fröhlich [3] considered a possible sliding of the collective state involving electrons and lattice displacements in the one-dimensional (1D) metal as a manifestation of the superconductivity. The emergent energy gap was identified by him with a superconducting rather than with the dielectric Peierls gap [1, 2] as it should be. Even in the absence (practically inaccessible) of impurities, finite phonon lifetimes, three-dimensional (3D) ordering and the commensurability of the sliding wave with the background crystal lattice [4–9], the Fröhlich 1D metal would have really become a so-called 'ideal conductor' with a zero resistance, rather than a true superconductor exhibiting the Meissner and Josephson effects [10, 11]. It is remarkable that the concept of the electron spectrum energy gap in the superconducting state had also been proposed by Bardeen [12] almost simultaneously with Fröhlich and before the full microscopic Bardeen–Cooper–Schrieffer (BCS) theory was developed [13].

The Fröhlich point of view [3] was revived after the sensational discovery of the giant conductivity peak in the organic salt TTF–TCNQ [14]. However, the coherent transport phenomena appropriate to these quasi-1D substances appeared to be a manifestation of a quite different collective state: charge-density waves (CDWs) coupled with periodic lattice distortions [4, 6, 8, 9, 15–18]. Their coherent properties now constitute a separate interesting branch of solid-state science, but lie beyond the scope of our review and will be touched upon hereafter only in specific cases where necessary. Here we

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would only like to stress that even in the case when the CDW is depinned by an electric field and moves with a constant velocity $v_{\rm CDW}$, a possible oscillating current $J_{\rm CDW} \propto v_{\rm CDW}$ driven by impurities [19] is drastically different from the Josephson current [20]. The distinction lies in the fact that $J_{\rm CDW}$ is proportional to the *temporal* derivative of the CDW phase $\varphi_{\rm CDW}$ [9, 21, 22], whereas the supercurrent J_s and the Cooper pair velocity v_s are proportional to the *spatial* derivative of the superconductor wavefunction phase φ_s [11]. This is why the analogy [19] of the Josephson tunnelling [20] and the impurity-induced electron transitons between the macroscopic quantum-mechanical states, split by the electron gas uniform motion, is incomplete. In particular, the charge acceleration $\propto {\rm d}J_{\rm CDW}/{\rm d}t$ is involved instead with the Josephson current $J_{\rm Joseph}$.

As for superconductivity itself, it was explained in the seminal work [13] on the basis of the Cooper pairing concept [23]. Although it was not explicit in the original BCS paper, the BCS state was soon understood to be a peculiar type of a broken symmetry state, specifically a state with the off-diagonal long-range order (ODLRO). The ODLRO concept was originally developed in the context of superfluid He II [24, 25] and was later reformulated in terms of Green's functions by Belyaev [26]. The Green's function approach was extended to BCS-type superconductors by Gor'kov [27], and from this work it was recognized [28–31] that the superconducting state is characterized by the two-particle density matrix

$$\hat{\rho} = \langle \Psi^{\dagger}_{\alpha'}(\boldsymbol{r}'_1)\Psi^{\dagger}_{\alpha}(\boldsymbol{r}_1)\Psi_{\alpha}(\boldsymbol{r})\Psi_{\alpha'}(\boldsymbol{r}')\rangle \tag{1}$$

where $\Psi(\Psi^{\dagger})$ is the annihilation (creation) field operator, $\langle\cdots\rangle$ means the thermodynamical averaging and α is a spin projection. The key property of $\hat{\rho}$ in the ODLRO case is the non-zero factorization of the matrix for $|\boldsymbol{r} - \boldsymbol{r}_1| \to \infty$ while $|\boldsymbol{r}'_1 - \boldsymbol{r}_1|$ and $|\boldsymbol{r}' - \boldsymbol{r}|$ remain finite. Then

$$\hat{\rho} \to \langle \Psi^{\dagger}_{\alpha'}(\boldsymbol{r}'_1)\Psi^{\dagger}_{\alpha}(\boldsymbol{r}_1)\rangle\langle\Psi_{\alpha}(\boldsymbol{r})\Psi_{\alpha'}(\boldsymbol{r}')\rangle \tag{2}$$

i.e. the ODLRO is described by the Gor'kov's order parameter [27]. For the normal state, $\hat{\rho} \to 0$ in the same limit. It is worth mentioning, that the affinity between the ODLRO of superfluid He II and the BCS superconductor was already perceived by Bogolyiubov, whose $u - v$ transformations of field amplitudes are closely related for the Bose and Fermi cases [32, 33].

The foregoing does not mean that the close relationship between superconductivity (superfluidity) and ODLRO comprises a one-to-one correspondence. For example, ODLRO is not necessary for the occurrence of superphenomena in restricted geometries [34]. At the same time, it is generally believed that if ODLRO exists, it assures superconductivity (superfluidity) [34]. The opposite point of view [35] concerns electron–hole pairing and is touched upon below.

The possibility of the normal state Fermi surface (FS) instability at low temperatures, T, by the boson-mediated induced electron–electron attraction in superconductors [13, 27] inspired the appearance of the mathematically and physically related model called 'the excitonic insulator' [36–42]. In the original BCS model for the isotropic s-pairing the Fermi liquid instability is ensured by the congruence of the FSs for both spin projections. At the same time, the excitonic instability of the isotropic semimetal [38] is due to the electron–hole (Coulomb) attraction provided both FS pockets are congruent (nested). A similar phenomenon can occur also in narrow-band-gap semiconductors when the exciton binding energy exceeds the gap value [39] (the idea had earlier been proposed by Knox [43]).

In the excitonic insulator state the two-particle density matrix is factorized in a manner quite different from that of equation (2):

$$\hat{\rho} \to \langle \Psi^{\dagger}_{\alpha'}(\boldsymbol{r}'_1)\Psi_{\alpha}(\boldsymbol{r})\rangle\langle\Psi^{\dagger}_{\alpha}(\boldsymbol{r}_1)\Psi_{\alpha'}(\boldsymbol{r}')\rangle \tag{3}$$

where $|\boldsymbol{r}'_1 - \boldsymbol{r}_1| \to \infty$, $|\boldsymbol{r}'_1 - \boldsymbol{r}|$ and $|\boldsymbol{r}' - \boldsymbol{r}_1|$ being finite. The averages in the right-hand side (r.h.s.) of equation (3) describe the dielectric order parameter which will be specified later in the review. One sees that they correspond to the 'normal' Green's functions $\mathcal{G}$ in the usual notation [44], whereas the averages in (2) represent the 'anomalous' Gor'kov's Green's functions $\mathcal{F}$ [27] caused by the Cooper pairing [23]. The long-range order contained in (3) is called diagonal (DLRO) [36, 37, 45–47]. The classification of ODLRO and DLRO given here is expressed in the electronic representation of the operators rather than in the hole representation, where these notions should be interchanged [45, 46]. However, it is widely accepted that the difference between the two kinds of the long-range order is intrinsic and deep, leading to their distinct coherent properties [9, 46–50]. On the other hand, the formal equivalence of ODLRO and DLRO in the hole representation of the latter for the excitonic insulator or exciton gas inspired a number of investigators to suggest excitonic superfluidity for different geometries [35, 51–59]. Nevertheless, the predicted phenomena were never observed. Apparently, the point is that all electron–hole or exciton–liquid models are approximate in essence. Such an idealization allows one to practically realize more robust features of the excitonic insulator (Peierls) state, but coherent properties suffer heavy damage for any (existing in nature!) deviations from the simplest symmetric picture because the phase of the relevant order parameter is inevitably pinned [46, 48, 49, 60], to say nothing of the impurity pair breaking [37, 45, 61]. A related object was proposed theoretically to reveal superfluid properties, namely layered structures with spatially separated electrons and holes [62–72]. In such systems tunnel currents are suspected to spoil superfluidity, which in this geometry can be considered as a double-sheet superconductivity. However, the authors of the idea claim that external electric or magnetic fields may restore coherent properties [66]. Activity in this area continues and a comprehensive list of references, in particular covering the possibly related experimental effects, can be found in [72].

The excitonic insulator state covers four possible different classes of the electronic orderings [37]: CDWs, the spin-density waves (SDWs) characterized below, orbital antiferromagnetism, and spin currents. The last two states have not yet been observed to the best of our knowledge and will not be discussed here.

The low-T excitonic rearrangement of the parent electronic phase may be attended by crystal lattice transformation [37, 45] due to the electron–phonon coupling which always exists. Therefore, Peierls and excitonic insulator models are, in fact, quite similar. The main difference is the one-band origin of the instability in the former, while the latter is essentially a two- or multiple-band entity.

SDWs are marked by a periodic spin-density modulation. It can be either commensurate or incommensurate with the background crystal lattice. The SDW collective ground state cannot only come from electron–hole pairing [39] but also can be induced by the finite wavevector singularities of the magnetic susceptibility, whatever the magnitude of the underlying Coulomb electron–electron repulsion [73–77]. SDWs with the inherent wavevector $\boldsymbol{Q}$, where $|\boldsymbol{Q}|$ is related to the Fermi momentum k_F (the Planck's constant $\hbar = 1$), were first suggested by Overhauser [78] for isotropic metals. The SDW stabilization by the band structure effects, in particular by the nesting FS sections, is shown in [79, 80]. SDWs are abundant, but not so widely as CDWs, and their most common host is Cr and its alloys [76, 81].

The possibility of the simultaneous appearance of both CDW and SDW order was also studied theoretically [76, 82–85]. This case led to the notion of the band excitonic ferromagnetism [83]. It will not be treated here but it is necessary to mention the revival of the excitonic ferromagnet model to explain unusual properties of rare-earth hexaborides [86–88].

On the other hand, x-ray scattering experiments in Cr reveal second and fourth harmonics of periodic lattice distortions (strain waves) accompanied by CDWs, both with the wavevectors $2\boldsymbol{Q}$ and $4\boldsymbol{Q}$, observed simultaneously with the basic SDW magnetic peaks at the incommensurate wavevector $\boldsymbol{Q}$ [81, 89, 90]; the incommensurability being determined by the size difference between the electron and hole FSs. However there is no sign of the ferromagnetism. This controversy remains a challenge to theoreticians and the explanation may involve a proper account of the impurity effects, not only being pair breaking in the excitonic insulator phase [37, 61], but also possibly affecting the parameters [82, 85] of the complex FS of Cr [74]. It should likewise occur that the CDW magnitude in Cr is too small (see the discussion in [81]) to ensure the observability of the ferromagnetic magnetization component. Moreover, it is necessary to keep in mind that Volkov's picture [83] is based on the mean-field approximation which may be unsatisfactory here.

The goal of this review is to examine the current experimental and theoretical understanding of the coexistence between superconductivity and CDW or SDW ordering. Bearing in mind the similarities and differences between DLRO and ODLRO ground states, it is quite natural that both theoreticians and experimenters have extensively investigated the coexistence between superconductivity on the one hand and CDWs [22, 45, 91–117] or SDWs [45, 73, 91, 105–107, 118–140] on the other hand. Our review aims to cover the main achievements obtained to date, both experimental and theoretical, and to provide a comprehensive and up-to-date set of references. It should be stressed that from the theoretical point of view the problem of the coexistence between superconductivity and DWs (hereafter we use the notation DW for the common case of CDW or SDW) in quasi-1D metals is very involved and even in its simplest set-up (the so-called g-ology [141, 142]) is far from being solved [91, 143–147]. On no account is the mean-field treatment, which is the usual theoretical method, fully adequate in this situation. Nevertheless, the experiment clearly demonstrates that in real 3D, although anisotropic, materials in the superconducting and electron–hole pairings do coexist in a robust manner, so that the sophisticated peculiarities introduced by the theory of 1D metals remain largely only of academic interest. The only, but very important, exception is the organic family $(TMTSF)_2X$ and its relatives [143–146, 148]. Thus, the predictions of the mean-field theory for these very materials should be considered with a certain degree of caution.

At the same time, for the overwhelming majority of superconductors, suspected or shown to undergo another transition of the spin-singlet (CDW) or spin-triplet (SDW) type, the main question is not about the coexistence of Cooper and electron–hole pairings (it can be relatively easily proved experimentally), but whether the gapping of the FS is favourable or destructive of superconductivity. Partial dielectrization (gapping) was demonstrated to cause a detrimental effect on superconductivity [6, 92, 93, 143, 145, 146, 149–154]. However, there is also an opposite standpoint [155–161] arguing that the superconducting critical temperature, T_c, is enhanced by the singular electron density of states near the dielectric gap edge. This conjecture is based on the model of the doped excitonic insulator with complete gapping [45] and has not been verified so far. In contrast, the model of partial gapping [73, 95, 105–109, 118–120, 126–135, 162–168], as described below, explains many characteristic features of different classes of superconductors and is consistent with the principal tendency inherent to those substances. Namely, in the struggle for the FS, superconductivity is most often found to be the weakest competitor. Therefore, the most direct way to enhance T_c is to avoid the gapping of the DW type [98, 104, 169, 170]. It is, however, necessary to mention the possibility of the stimulation of d-wave or even p-wave superconductivity by DW-induced reconstruction of the electron spectrum [160, 171–175] or by renormalization of the electron–electron interaction due to a static incommensurate CDW background [176].

In addition to DW instabilities, highly-correlated metals may undergo a transition into some kind of a phase-separated state [177–180]. This idea is an old one and was originally applied both to antiferromagnetic systems [181–183] and to the electron gas in paramagnets [184, 185]. For cuprates there is evidence that charged and magnetic stripes appear at least dynamically (see section 2.3). The striped phase may include not only an antiferromagnetic environment for doped holes but also CDWs along the charged stripes [179, 186]. A final theoretical point of view on the role of an interplay between superconductivity and phase separation in oxides has not yet been established. In [178] it was proposed that the very existence of the static phase separation is incompatible with superconductivity, while an intermediate doping is necessary to suppress the separation. The same strategy is suggested to look for possible high-T_c polymeric superconductors. These considerations seem quite reasonable. On the other hand, the model in [179] is based on the Cooper pairing of holes from charged stripes in the process of hopping into magnetic regions. In this connection the so-called spin gap observed in different cuprates is considered to have a superconducting origin, which does not agree with the experimental data (see section 2.3).

Up to this point feasible DWs have been tacitly attributed to nesting-driven instabilities. Nevertheless, there is another

plausible source of DWs, namely Van Hove saddle points, which are especially important in systems with reduced dimensionality [187]. Unless specified, such a feasibility is also borne in mind. More details on both mechanisms of the electron spectrum instabilities are given below.

Irrespective of utilitarian goals, the physics of DW superconductors is very rich and attractive. In one review it is impossible to consider all sides of the problem or cover all substances which claim to belong to the DW types concerned. Nevertheless, we try at least to mention examples of every sort of DW superconductor and describe their characteristics. Special attention is given to oxides, including high-T_c oxides. To the best of the authors' knowledge, this aspect of high-T_c superconductivity has not previously been examined in detail. In this review we do not consider the different alternative scenarios of superconductivity for low- or high-T_c superconductors, because much of the corresponding comprehensive reviews can be easily found (see, e.g., [186, 188–209]). In any case it seems premature to nominate specific pairing mechanisms as the true ones for many of the most recently discovered and interesting classes of superconductors, since the experimental situation changes very rapidly. Hence, the real advantage of our attitude towards the problem concerned is a semi-phenomenological approach. In those places where it is necessary to indicate the relationships between our approach and other treatments we often cite reviews rather than original papers while describing the latter, because otherwise the list of references would become too lengthy. As for low-T_c superconductors, it seems they have been undeservedly left aside in recent years since the discovery of the superconducting cuprates. Below, we try to include both groups of substances into consideration on an equal footing, making the whole picture more complete.

The outline of the review is as follows. First we discuss in detail the background experimental data on low- and high-T_c superconductors possessing DW instabilities of various types. Second, a short description of the key theoretical ideas is given in section 3. Some general conclusions are made at the end of the review.

2. Experimental evidence

2.1. CDW superconductors

Key quantities measured for CDW superconductors can be found in table 1. From this table it is easy to detect the unambiguous interplay between the two different collective phenomena in question. Here Δ and $|\Sigma|$ are the superconducting and dielectric gaps respectively, $\nu = N_{nd}(0)/N_d(0)$ is the degree of the FS dielectric gapping and $N_{nd(d)}(0)$ is the electron density of states on the non-distorted (distorted) FS part.

The most direct way to observe CDWs in semiconducting and metallic substances is to obtain contrast scanning tunnelling microscopy real-space photomicrographs of their surfaces [246–248]. Such pictures were obtained for many systems, for example layered dichalcogenides $1T$-$TaS_{2-x}Se_x$ [246, 247] and $2H$-$NbSe_2$ [248], quasi-1D $NbTe_4$ [249], $NbSe_3$ [211, 250], as well as for the high-T_c oxide $YBa_2Cu_3O_{7-y}$ [251–254]. At the same time the application

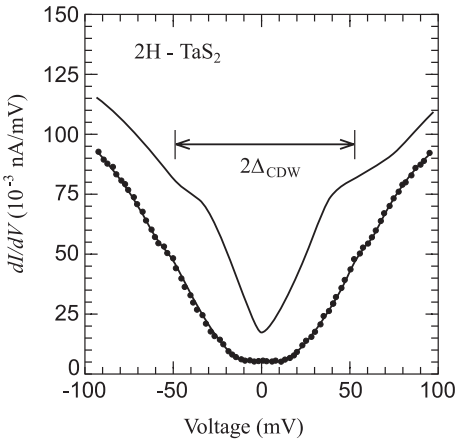

Figure 1. dI/dV (conductance) against V curves measured for $2H$-TaS_2 for two different tip–sample combinations. The upper curve shows structure dominated by the CDW with a gap edge at about ± 50 mV. The lower curve is dominated by a strong zero-bias anomaly (ZBA) with only weak structure at about ± 50 mV and the conductance is substantially reduced by the ZBA. (Reproduced by permission from [218]).

of scanning tunnelling microscopy enables one to determine the respective dielectric energy gaps. They were unequivocally found by this method and in related tunnel and point-contact measurements for a number of CDW superconductors: $NbSe_3$ [211–213, 255, 256], $2H$-$NbSe_2$ [218, 248], $2H$-$TaSe_2$ and $2H$-TaS_2 [218]. In the purple bronze $Li_{0.9}Mo_6O_{17}$, which reveals a resistivity rise below 25 K and superconductivity below $T_c \approx 1.7$ K [231, 257–261], the CDW-driven gap was identified in addition to the superconducting one of the conventional BCS type, which was long ago clearly seen in tunnel spectra of $(Li_{0.65}Na_{0.35})_{0.9}Mo_6O_{17}$ with the same T_c as the parent compound [232]. The metal–insulator transition in $Li_{0.9}Mo_6O_{17}$ was found [233] to be one of the nesting-induced type with $|\boldsymbol{Q}_{\rm nest}| = 2k_F = 0.56$ Å^{-1}, contrary to the recent assignment [262] of the substance concerned to the Luttinger liquid.

Figures 1 and 2 illustrate two kinds of tunnel spectra for $2H$-TaS_2 [218] and $NbSe_3$ [212] in the normal CDW state. Both of them were obtained in the asymmetrical set-up with only one of electrodes being the CDW metal. We want to attract attention to the striking similarity between such a manifestation of the CDW gap and that of its superconducting counterpart.

Since CDWs are usually interrelated with crystal lattice distortions [6, 8, 37, 45, 151, 154, 186, 258–260], the detection of the latter often serves as an indicator of the former. Such displacements, incommensurate or commensurate with the background lattice, were disclosed by x-ray diffraction (as extra or modified momentum-space diffraction spots) for the perovskite $Ba_{1-x}K_xBiO_3$ [263]. This remains a candidate for a possible CDW superconductor, although its high $T_c \approx 30$ K with respect to $T_c \leqslant 13$ K of its partially gapped superconducting relative $BaPb_{1-x}Bi_xO_3$ [98] may imply that the CDW is totally suppressed [264–266]. X-ray diffraction was also helpful to investigate CDWs in layered superconductors $2H$-$TaSe_2$, $4Hb$-$TaSe_2$, $2H$-TaS_2, $2Hb$-TaS_2 and $2H$-$NbSe_2$ [152, 154, 267, 268].

Electron diffraction scattering by $Ba_{1-x}K_xBiO_3$ and $BaPb_{1-x}Bi_xO_3$ compounds displayed even more clear-cut

Table 1. CDW superconductors. Note that in the table ρ denotes resistance measurements, STM denotes scanning tunnelling microscopy, TS denotes tunnelling spectroscopy, C_P denotes specific heat measurements, TP denotes thermopower measurements, R_H denotes the Hall effect, χ denotes magnetic susceptibility measurements, TE denotes thermal expansion measurements, MR denotes magnetoresistance measurements, ARPES denotes angle-resolved photoemission spectroscopy, NS denotes neutron scattering, ORS denotes optical reflection spectroscopy, PCS denotes point-contact spectroscopy and OTS denotes optical transmission spectroscopy.

Compound	Source	Pressure (kbar)	T_c (K)	Δ (meV)	T_d (K)	$\lvert\Sigma\rvert$ (meV)	ν	Methods
$NbSe_3$	[210]	8	2.5	—	53	—	—	ρ
	[211]	ambient	—	—	—	80	—	STM
	[212]	ambient	—	—	145[a]	—	—	TS
					59[a]	9		
	[213]	ambient	—	—	145[a]	—	—	STM
					59[a]	35		
	[214]	ambient	—	—	145[a]	—	4	ρ
					59[a]	—	0	
	[215]	ambient	—	—	145[a]	—	3	C_P
					59[a]	—	0.84	
$Fe_{0.01}NbSe_3$	[213]	ambient	—	—	59	25	—	STM
$Co_{0.03}NbSe_3$	[213]	ambient	—	—	59	48	—	STM
$Gd_{0.01}NbSe_3$	[213]	ambient	—	—	53	0	—	STM
Nb_3Te_4	[216]	ambient	1.7	—	92[a]	—	—	ρ, TP
					42[a]	—	—	
	[217]	11	2.15	—	92[a]	—		ρ
					36[a]	—	10–11.5	
$Hg_{0.4}Nb_3Te_4$	[216]	ambient	5.4	—	absent	—	—	ρ
$2H$-$TaSe_2$	[151]	ambient	0.15	—	120	—	—	ρ
	[218]	ambient	—	—	—	80	—	STM
$4Hb$-$TaSe_2$	[6]	ambient	1.1	—	600	—	—	ρ
$2H$-TaS_2	[151]	ambient	0.65	—	77	—	—	ρ
	[218]	ambient	—	—	—	50	—	STM
$2Hb$-TaS_2	[151]	ambient	2.5	—	22	—	—	ρ
$4Hb$-TaS_2	[6]	ambient	1.1	—	22	—	—	ρ
$2H$-$NbSe_2$	[151]	ambient	7.2	—	33.5	—	—	ρ
	[218]	ambient	—	—	—	34	—	STM
$Eu_{1.2}Mo_6S_8$	[219]	ambient	0	—	110	—	0.25	ρ, TP
	[219]	3.2	1.1	—	—	—	0.72	ρ, TP
	[219]	7.07	4	—	82	—	1.86	ρ, TP
	[219]	9.01	6.4	—	—	—	3.55	ρ, TP
	[219]	11.06	8.5	—	66	—	6.7	ρ, TP
	[219]	13.2	9.8	—	—	—	∞	ρ, TP
$Sn_{0.12}Eu_{1.08}Mo_6S_8$	[219]	ambient	—	—	120	—	0	ρ, TP
	[219]	6	1.5	—	100	—	1.22	ρ, TP
	[219]	8	3.2	—	78	—	1.86	ρ, TP
	[219]	10	7.5	—	—	—	9	ρ, TP
	[219]	12	10.1	—	60	—	19	ρ, TP
$Tl_2Mo_6Se_6$	[220]	ambient	6.5	—	80	—	—	ρ, R_H, TP
ZrV_2	[221]	ambient	8.7	—	120	—	—	ρ, χ
	[101]	ambient	—	—	—	7.2	0.7	C_P
HfV_2	[221]	ambient	8.8	—	150	—	—	ρ, χ
	[101]	ambient	—	—	—	8.5	1.1	C_P
	[222]	ambient	9.3	—	120	—	—	ρ
$Hf_{0.84}Nb_{0.16}V_2$	[222]	ambient	10.7	—	87	—	—	ρ
$Hf_{0.8}Ti_{0.2}V_2$	[222]	ambient	8.8	—	128	—	—	ρ
V_3Si	[149]	ambient	17	—	21	—	—	various
Nb_3Sn	[149]	ambient	18	—	43	—	—	various
	[223]	ambient	—	2.35[b]	—	—	—	TS
				1.12[b]				
				0.75[b]				
				0.18[b]				
	[224]	ambient	—	2.8	—	—	—	TS
	[225]	ambient	—	2.5	—	—	—	TS
Nb_3Al	[226]	ambient	18	—	80	—	—	various
$Nb_3Al_{0.75}Ge_{0.25}$	[149]	ambient	20	—	24	—	—	various
	[226]	ambient	18.5	—	105	—	—	various
$Nb_{3.08}Al_{0.7}Ge_{0.3}$	[226]	ambient	17.4	—	130	—	—	various
$Lu_5Ir_4Si_{10}$	[227]	ambient	3.8	—	80	—	—	TE
	[228]	20.5	3.7	—	81	—	—	ρ, χ
$(Lu_{0.9}Er_{0.1})_5Ir_4Si_{10}$	[228]	ambient	2.8	—	86	—	—	ρ, χ
	[228]	23.1	2.74	—	82	—	—	ρ, χ

Table 1. (Continued)

Compound	Source	Pressure (kbar)	T_c (K)	Δ (meV)	T_d (K)	$\lvert\Sigma\rvert$ (meV)	ν	Methods
$Lu_5Rh_4Si_{10}$	[227]	ambient	3.3	—	140	—	—	TE
	[229]	ambient	3.4	—	155	—	—	ρ, χ
$P_4W_{14}O_{50}$	[230]	ambient	0.3	—	60	—	—	ρ, χ, MR
	[230]	ambient	0.3	—	185	—	—	ρ, χ, MR
$Li_{0.9}Mo_6O_{17}$	[231]	ambient	1.7	—	25	—	—	ρ
	[232]	ambient	1.5	0.225	—	—	—	TS
	[233]	ambient	—	—	24	40	—	ARPES
$Rb_{0.25}WO_3$	[234]	ambient	5–7	—	230	—	—	ρ, R_H, TP
$Rb_{0.24}WO_3$	[235]	ambient	—	—	270	—	—	NS
$Rb_{0.22}WO_3$	[235]	ambient	—	—	200	—	—	NS
$K_{0.32}WO_3$	[236]	ambient	2	—	80	—	—	ρ, R_H, TP
$K_{0.24}WO_3$	[236]	ambient	0	—	400	—	—	ρ, R_H, TP
$K_{0.2}WO_3$	[236]	ambient	1.5	—	280	—	—	ρ, R_H, TP
$K_{0.18}WO_3$	[236]	ambient	2.5	—	260	—	—	ρ, R_H, TP
$BaPb_{0.8}Bi_{0.2}O_3$	[237]	ambient	11	—	—	4	0.9	C_P
	[238]	ambient	11	—	—	4	—	ρ
	[239]	ambient	11	—	—	610	—	ORS
	[240]	ambient	—	1.15	—	—	—	PCS
	[241]	ambient	—	1.25	—	—	—	ORS
$BaPb_{0.75}Bi_{0.25}O_3$	[242]	ambient	—	0.77	—	—	—	TS
	[243]	ambient	—	1.3	—	—	—	OTS
$BaPb_{0.73}Bi_{0.27}O_3$	[244]	ambient	—	1.71	—	—	—	TS
$BaPb_{0.7}Bi_{0.3}O_3$	[245]	ambient	—	0.95	—	—	—	TS
	[242]	ambient	—	1.5	—	—	—	TS

[a] Multiple CDW transitions.

[b] Multiple superconducting gaps.

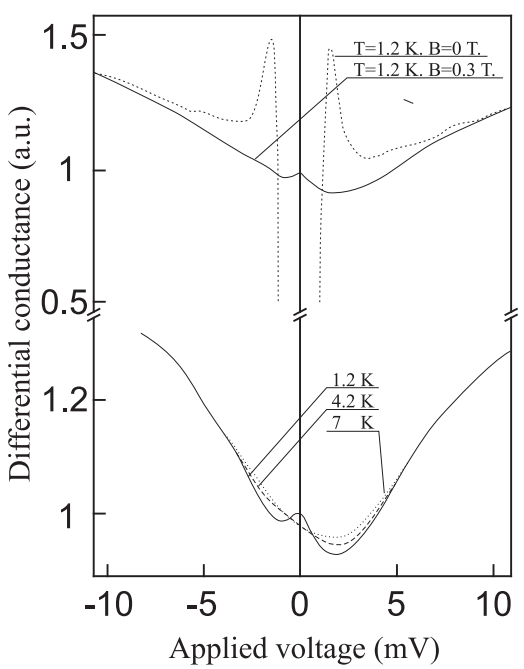

Figure 2. Upper part, the broken curve represents the tunnelling conductance Pb–I–$NbSe_3$ junction at 1.2 K, where I denotes an insulator. The full curve represents the $NbSe_3$ density of states along the a axis at 1.2 K with a 0.3 T magnetic field which suppresses the Pb superconductivity. In the lower part the magnified evolution of the density of states versus bias voltage for different temperatures is presented. (Reproduced by permission from [212]).

CDW patterns [8, 154]. The same method uncovered in $BaPb_{1-x}Bi_xO_3$ a structural cubic-tetragonal instability for $0 \leqslant x \leqslant 0.8$ and a tetragonal-monoclinic for non-superconducting compositions, but no incommensurate CDWs [269]. On the other hand, according to electron diffraction experiments, in $Ba_{1-x}A_xBiO_3$ (A = K, Rb) the diffuse scattering, corresponding to structural fluctuations of the R_{25} tilt mode of the oxygen octahedra, shows up in the cubic phase near $x = 0.4$ with the highest superconducting T_c [270]. Electron diffraction on K_xWO_3 revealed incommensurate superstructure for $0.24 < x < 0.26$ [271], where T_c has a shallow minimum [236].

Neutron diffraction measurements showed structural transitions as well as phonon softening in the oxides Rb_xWO_3 [235]. However, the x-ray diffraction method was unable to discover these anomalies, even though they are clearly seen in resistive measurements [234].

Although the direct observations of the CDW are always highly desirable, the lack of direct observation does not ensure the absence of CDWs in the investigated substance. As an example one should mention the discovery of a weak low-T ($\approx$38 K) structural CDW transition in TTF-TCNQ by measurements of the resistivity derivative $d\rho/dT$ [272]. This result was only subsequently confirmed by x-ray [273, 274] and neutron [275, 276] scattering. Thus, the existence of CDWs and their concomitant lattice distortions can be established by quite a number of methods. For superconducting layered chalcogenides, CDWs manifested themselves in resistivity [6, 8, 150–152, 154] and angle-resolved photoemission spectra (ARPES) [277]. $NbSe_3$ is a structurally unstable metal under the ambient pressure P. It has two successive structural phase transitions and becomes superconducting for $P \geqslant 0.5$ kbar [210], but is still partially gapped [212, 215]. Here CDWs were revealed by measurements of resistivity [7, 15, 214, 278] and heat capacity C_P [7, 215].

Partial gapping and/or CDWs were also observed in $BaPb_{1-x}Bi_xO_3$, both for non-superconducting and superconducting compositions, by resistivity measurements [98, 103, 162, 164, 279], C_P [98, 102, 237], optical reflection spectra [280–283], thermoelectric power [284] (here the coexistence between delocalized and localized electrons made itself evident) and extended x-ray absorption fine-structure (EXAFS) [285, 286], where the inequivalence between different Bi ions is readily seen from pair-distribution functions.

Definite evidence for CDW formation in non-superconducting and superconducting $Ba_{1-x}K_xBiO_3$ solid solutions were obtained in optical reflection spectra [287, 288] and EXAFS measurements [285]. Moreover, positron angular correlations in $Ba_{1-x}K_xBiO_3$ disclosed large nesting FS sections [289], consistent with CDW emergence.

Optical reflectance and transmittance investigations of semiconducting $BaPb_{1-x}Bi_xO_3$ at compositions with $x = 1$, 0.8 and 0.6 elucidated the band-crossing character of the metal–insulator transition there with the respective indirect dielectric gaps 0.84, 0.32 and 0.14 eV [290]. The nesting origin of the gap for the limiting oxide $BaBiO_3$ is confirmed by band structure calculations [291]. According to these the FS nesting is not perfect (see section 3), but the gapping is still possible because the BiO_6 octahedron tilting distortions make the FS more unstable against nesting-driven breathing modes. In $Ba_{1-x}K_xBiO_3$ with $x = 0.5$ similar calculations demonstrate the vanishing of both instabilities [291].

Metal–insulator transitions for superconducting hexagonal tungsten bronzes Rb_xWO_3 and K_xWO_3 are observed in resistive, Hall and thermoelectric power measurements [234, 236]. It is remarkable that the x-dependence of the critical structural transition temperature, T_d, anticorrelates with $T_c(x)$ in Rb_xWO_3 [234] and, to a lesser extent, in K_xWO_3 [236]. On the other hand, such anomalies are absent in superconducting Cs_xWO_3, where $T_c(x)$ is monotonic [292]. For sodium bronze Na_xWO_3 superconductivity exists in the tetragonal I modification, and T_c is enhanced near the phase boundary with the non-superconducting tetragonal II structure [293]. It may be the case that the recent observation (both by ρ and magnetic susceptibility, χ, measurements) of $T_c \approx 91$ K in the surface area of single crystals of $Na_{0.05}WO_3$ [294] is due to the realization of an optimal crystal lattice structure without reconstructions detrimental to superconductivity. In this connection one should bear in mind that the oxide Na_xWO_3 is a mixture of two phases at least for $x \geqslant 0.28$ [295].

The two-dimensional (2D) $PW_{14}O_{50}$ bronze is an example of another low-T_c oxide with a CDW background [230]. Here $T_c \approx 0.3$ K after an almost complete FS exhaustion by two Peierls gaps below $T_{d1} \approx 188$ K and $T_{d2} \approx 60$ K.

The onsets and developments of the CDW instabilities in layered dichalcogenides are very well traced by $\rho(T)$ measurements [6, 8, 150, 151, 154]. The characteristic pressure dependences of T_c and T_d are shown in figure 3 [151]. From figure 3 one can see clearly once more that CDWs suppress superconductivity, so that for sufficiently high P, when $T_d < T_c$, the dependence $T_c(P)$ saturates. For $2H$-$NbSe_2$, the ARPES spectra showed a nesting-induced CDW wavevector $\boldsymbol{Q} \approx 0.69$ Å^{-1} [277, 296]. This is consistent with diffraction data [152] and rules out the Rice–Scott scenario of the CDW appearance due to the saddle points of the Van Hove type [186, 187]. In the latter case the magnitude of the wavevector $\boldsymbol{Q}_{sp}$ connecting saddle points is bound to be $|\boldsymbol{Q}_{sp}| \approx 0.97$ Å^{-1}. ARPES studies of the related layered superconductor $2H$-$TaSe_2$ [297] led to the opposite conclusion from that of [277, 296], namely that the CDW gap is predominantly associated with extended saddle points of the FS, and not with the nested segments found for the Γ-centred FS pockets.

Resistive experiments revealed a gapping in $NbSe_3$ as well [15, 210]. The addition of Ta was shown to suppress both the Peierls instabilities observed in $\rho(T)$ for this substance [278].

Electrical resistivity and thermoelectric power investigations of the quasi-1D Nb_3Te_4 single crystals and similar crystals inserted with mercury $Hg_xNb_3Te_4$ demonstrated a very convincing evidence of the CDW and superconducting gap competition for the FS [216]. Specifically, in the pristine crystals two CDW-like features are observed at about 92 K and about 42 K with a weak superconductivity below 1.7 K. Alloying leads to the nonmonotonic deformation of the upper and lower anomalies, so that they finally disappear at $x \approx 0.15$ and $x \approx 0.26$ respectively. At the same time, T_c grows and attains 5.4 K (by a factor of three larger!) for $x \approx 0.4$. Applied pressure leads to the same effect, reducing the lower resistively determined T_d down to about 36 K and increasing T_c up to 2.15 K for $P \approx 11$ kbar [217]. The effect might have been even more pronounced if not for the reduction of T_c due to other effects not connected with CDWs. It was proved by the associated measurements for related superconducting compounds Nb_3S_4 and Nb_3Se_4, which do not show CDW anomalies and for which $T_c(P)$ is a decreasing function [217].

Measurements of ρ and χ under ambient and enhanced pressure clearly displayed CDW instabilities for $Lu_5Rh_4Si_{10}$ [227, 229], $(Lu_{1-x}Sc_x)_5Ir_4Si_{10}$ [228], $R_5Ir_4Si_{10}$ (R = Dy, Ho, Er, Tm, Yb, Sc) [227, 298], $Lu_5Ir_4Si_{10}$ [227]. The dependences $\rho(T)$ for different members of these families with CDW features are shown in figure 4, taken from [298]. CDWs manifest themselves here as broad humps of $\rho(T)$ near the corresponding T_ds.

The interrelation between T_d, T_c and the reduced CDW anomaly amplitude $\Delta\rho/\rho(300\ \mathrm{K})$ for different compositions of the alloy $(Lu_{1-x}Sc_x)_5Ir_4Si_{10}$ are exhibited in figure 5, taken from [228]. One sees that the reduction of resistive anomalies with the concomitant depression in T_d anticorrelates with the increase in T_c.

In the anisotropic compound $Tl_2Mo_6Se_6$, the CDW instability at $T \approx 80$ K was observed by Hall, thermoelectric power and magnetoresistive measurements [220].

In the Chevrel phases, it was shown by ρ and thermoelectric power experiments that $Eu_{1.2}Mo_6S_8$ and its modification $Sn_{0.12}Eu_{1.08}Mo_6S_8$ are partially-gapped superconductors [219]. Applied pressure led to the suppression of T_d, a decrease in the extent of the structurally-driven FS gapping, and a concomitant growth of T_c [219].

Two well known structurally unstable superconductor families, namely the A15 [92–94, 97, 149, 226, 229] and C15 [94, 149, 226, 229] compounds (Laves phases), had been investigated in detail before the discovery of high-T_c oxides. Among the A15 superconductors there is a compound, Nb_3Ge, with the highest $T_c \approx 23.2$ K achieved before

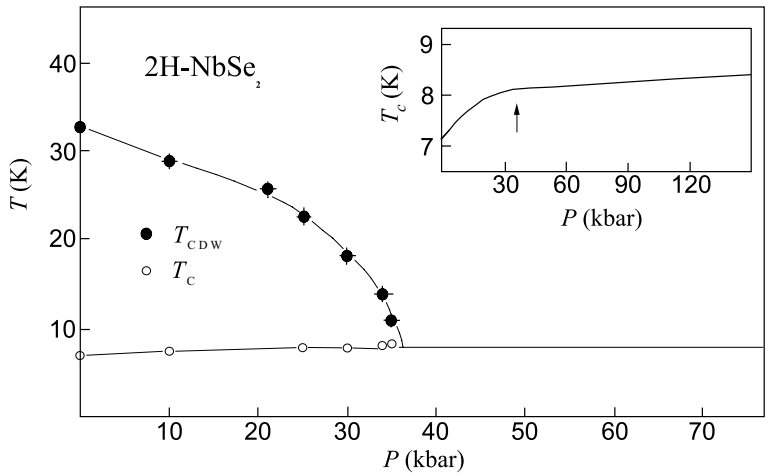

Figure 3. Phase diagram of the CDW state and of the superconducting state in $2H$-$NbSe_2$. Inset, pressure dependence of T_c after Smith T F 1972 *J. Low Temp. Phys.* **6** 171. (Reproduced by permission from [151]).

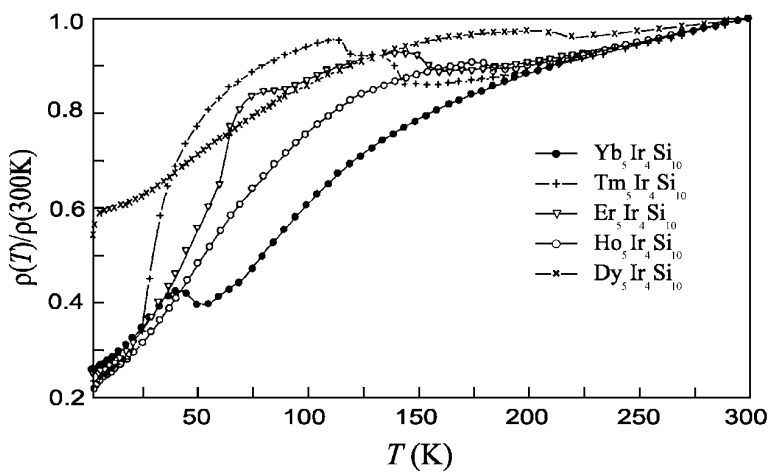

Figure 4. Normalized resistivity as a function of temperatures between 2.6 and 300 K for $R_5Ir_4Si_{10}$ (R = Dy–Yb). (Reproduced by permission from [298]).

1986. Many A15 substances with the highest T_c's exhibit martensitic transitions from the cubic to the tetragonal structure with T_d slightly (for Nb_3Sn and V_3Si) or substantially (for Nb_3Al and $Nb_3Al_{0.75}Ge_{0.25}$) above T_c. Many lattice properties show strong anomalies at T_d. It was established that the structural transformations essentially influence the superconducting properties. Theoretical interpretations of the electronic and lattice subsystems, electron–phonon interaction and the interplay between superconductivity and structural instability are based mostly on the assumed quasi-1D features of these compounds [92–94, 97, 108, 109, 149, 226, 229–304] and will be discussed in the subsequent sections.

In the C15 compounds HfV_2 ($T_c \approx 9.3$ K) or HfV_2-based pseudobinaries and ZrV_2 ($T_c \approx 8.7$ K) structural anomalies are also present at $T_d \approx 150$ K and ≈120 K, respectively [101, 149, 221]. They are detected, for example, in $\rho(T)$ [221, 222] and $\chi(T)$ [221]. In figure 6 the latter is shown for HfV_2 [221]. The suppression of the electronic density of states by the one-particle spectrum gapping is conspicuously reflected in the drop of $\chi(T)$ below T_d. Heat capacity measurements [101] gave one the possibility to observe the corresponding features and even to determine the parameters of the partial-gapping theory [108, 162, 164, 279].

Competition between CDWs and superconductivity is inherent not only to inorganic substances. For example, in $TTF[Ni(dmit)_2]_2$, $\rho(T)$ curves measured at various pressures, $P < 14$ kbar, demonstrate that at intermediate $P \geqslant 5.75$ kbar the activated regime above $T_c \approx 2$ K precedes the superconductivity [305]. The suppression of superconductivity by CDWs is also seen in the β_L-phase of quasi-2D $(ET)_2I_3$ with $T_c \approx 1.2$ K and $T_d \approx 150$ K [148, 153]. At the same time, $T_c \approx 8.1$ K for β-$(ET)_2I_3$ without traces of CDWs and superconductivity disappears for α-$(ET)_2I_3$ which undergoes a metal–insulator transition at 135 K [306].

2.2. SDW superconductors

A number of interesting systems exhibit coexisting superconductivity and SDW order. For example, this is observed in the quasi-1D organic substance $(TMTSF)_2ClO_4$ at ambient P [73, 145, 146, 148]. Specifically, the physical properties of the low-T phase depend on the cooling rate for $T \leqslant 22$ K, as shown in resistive [122, 307], nuclear magnetic resonance (NMR) [308], electron paramagnetic resonance (EPR) [307]

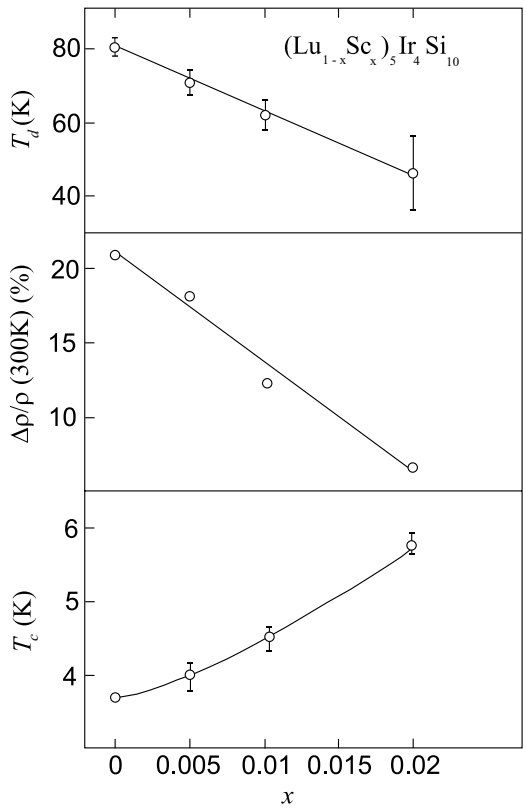

Figure 5. Alloy concentration dependence of CDW transition temperature T_d, amplitude of anomaly $\Delta\rho/\rho(300\ \mathrm{K})$ and superconducting transition temperature T_c for the pseudoternary system $(Lu_{1-x}Sc_x)_5Ir_4Si_{10}$ ($x = 0$, 0.005, 0.01 and 0.02). (Reproduced by permission from [228]).

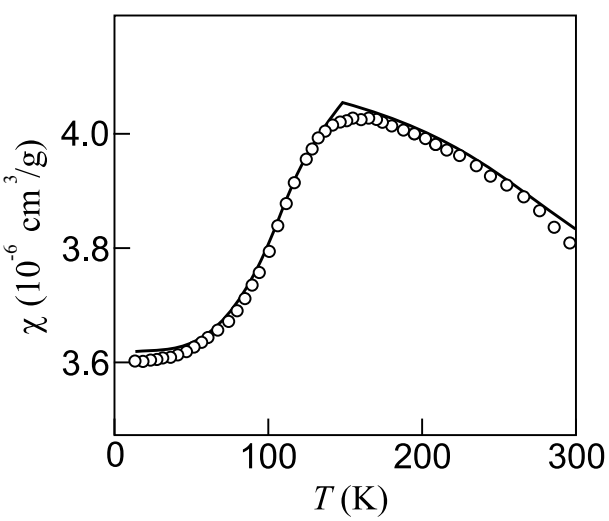

Figure 6. Magnetic susceptibility of HfV_2 against T; the full curve represents the theoretical results. (Reproduced by permission from [221]).

and specific heat [309, 310] measurements. Rapid cooling (10–30 K min^{-1}) leads to the quenched Q-phase with $T_c \approx 0.9$ K, a negative temperature coefficient of resistance and SDWs for T smaller than the Néel temperature $T_N \approx 3.7$ K. A reduction in the cooling rate to 0.1 K min^{-1} results in the relaxed R-phase with $T_c \approx 1.2$ K, positive temperature coefficient of resistance and SDWs existing at $T < 6$ K [311]. The emergence of an SDW state in the R-phase was verified by the broadening of the NMR line for ^{77}Se with cooling [308] and the existence of the $C_P(T)$ singularity at $T \approx 1.4$ K for the magnetic field $H \approx 63$ kOe [309, 310].

On the other hand, recent polarized optical reflectance studies of $(TMTSF)_2ClO_4$ show a broad band with a gap developed below the frequency 170 cm^{-1} [312] and corresponding to a collective charge transport [7, 9, 15] by a sliding CDW rather than a SDW. Other reflectance measurements in $(TMTSF)_2ClO_4$ allowed the authors to extract the gap feature with the energy in the range 3–4.3 meV [311] or 4.3–6.2 meV [313], associated with the SDW gap and substantially exceeding the corresponding BCS weak-coupling value (see the relevant data set in table 2).

It has been argued [144] that $(TMTSF)_2ClO_4$ may exhibit an unconventional pairing, of spin triplet type. However, the thermal conductivity, κ, measurements are consistent with a conventional s-like character of the superconducting order parameter [314]. On the other hand it was shown [315] that the electronic contribution to κ is linear in T for the organic quasi-2D superconductor κ-$(ET)_2Cu(NCS)_2$, so that unconventional superconductivity is possible there [144]. It also seems quite plausible that this relatively high-T_c ($\approx$10.4 K) superconductor is partially gapped well above T_c [316]. In reality, $\rho(T)$ has a broad peak at 85–100 K with ρ_{peak} being three to six times as high as $\rho(300\ \mathrm{K})$. At lower temperatures, T, resistivity becomes metallic before the superconducting transition.

On the basis of the currently available data it is impossible to prove or reject the possibility that the SDW persists in the superconducting state of $(TMTSF)_2X$ (X = PF_6, AsF_6) under external pressure. However, the clear SDW-type pairing correlations below $T_N \approx 15$ K were revealed in optical reflectance spectra [317].

The interplay of SDWs and superconductivity is also apparent in heavy-fermion compounds [318, 319]. In particular, the magnetic state in URu_2Si_2 is really of the collective SDW type, rather than local moment antiferromagnetism observed in a number of Chevrel phases and ternary rhodium borides [73, 299, 320–322] insofar as the same 'heavy fermions' are responsible for both collective phenomena [323]. Therefore, the electron subsystem of URu_2Si_2 can be considered below $T_N \approx 17.5$ K (see table 2) as a partially-gapped Fermi liquid [108, 126–129] with appropriate parameters determined by $C_P(T)$ [325–327, 329], thermal expansion in an external magnetic field [329] and spin-lattice relaxation [339]. The partial gapping concept is supported here by the correlation between the increase in T_c and the decrease in T_N with uniaxial stress [353, 354]. It is interesting that the magnetic neutron scattering Bragg peak (100) exhibits a cusp near T_c, reflecting the superconducting feedback on the SDW, which is noticeable notwithstanding $T_N \gg T_c$ [355].

It is well known that the superconducting order parameter in the related uranium-based heavy-fermion compounds UBe_{13} and UPt_3 is non-conventional [318, 356–358]. For the latter the analysis of the thermal conductivity in a magnetic field led to the conclusion [358] that due to the different dependences of the density of states in a field for s- and d-wave symmetry systems the power law observed in thermal conductivity as a

Table 2. SDW superconductors. See table 1 for notations and, furthermore, H_{c2} denotes upper critical magnetic field measurements, NSLR denotes nuclear spin-lattice relaxation measurements and NMR denotes nuclear magnetic resonance measurements.

Compound	Source	Pressure (kbar)	T_c (K)	Δ (meV)	T_N (K)	$\lvert\Sigma\rvert$ (meV)	ν	Methods
U_6Co	[324]	ambient	2.5	—	90–150	—	—	ρ
U_6Fe	[324]	ambient	3.9	—	90–150	—	—	ρ
URu_2Si_2	[325]	ambient	1.3	—	17.5	9.9	0.4	C_P, χ, H_{c2}
	[326]	ambient	1.3	—	17.5	11.1	1.5	C_P, ρ, H_{c2}
	[327]	ambient	1.2	—	17.5	2.3	—	C_P
	[328]	ambient	1.37	—	17.7	5.9	—	TS, PCS
	[329]	ambient	—	—	17.5	9.9	—	C_P, TE
	[330]	ambient	1.25	—	—	—	—	C_P
	[331]	ambient	1.3	0.3	—	—	—	PCS
	[332]	ambient	—	—	17.5	10	—	PCS
	[333]	ambient	—	—	—	9.5	—	TS
	[334]	ambient	—	0.2	—	—	—	PCS
	[335]	ambient	—	0.35	—	—	—	PCS
	[336]	ambient	—	0.17	—	—	—	PCS
	[337]	ambient	—	0.25 (a-axis) 0.7 (c-axis)	—	—	—	PCS
	[338]	ambient	—	0.35–0.5	—	—	—	TS
	[339]	ambient	—	—	—	12.9	—	NSLR
$LaRh_2Si_2$	[340]	ambient	3.8	—	7	—	—	C_P, ρ, χ
YRh_2Si_2	[340]	ambient	3.1	—	5	—	—	C_P, ρ, χ
$Tm_2Rh_3Sn_5$	[341]	ambient	1.8	—	2.3	—	—	C_P, ρ, χ
UNi_2Al_3	[342]	ambient	1	—	4.6	—	—	C_P, ρ, χ
	[333]	ambient	1.2	—	4.8	10	—	TS
UPd_2Al_3	[343]	ambient	1.9	—	14.3	—	—	C_P, ρ
	[343]	ambient	1.9	—	13.8	—	—	χ
	[333]	ambient	—	—	—	13	—	TS
	[344]	ambient	1.35	0.18	—	—	—	TS
	[345]	ambient	—	—	—	4.5	—	PCS
$Cr_{1-x}Re_x (x > 0.18)$	[346]	ambient	3	—	160	—	7.3	ρ, χ, NMR
$CeRu_2$	[347]	ambient	6.2	—	50	—	—	ρ,TP,MR,χ, R_H
	[348]	ambient	5.4–6.7	0.95–1.3	40–50	—	—	TS
	[349]	ambient	6.2	0.6	—	—	—	PCS
$TmNi_2B_2C$	[350]	ambient	10.9	1.3	1.5	—	—	PCS
$ErNi_2B_2C$	[350]	ambient	10.8	1.7	5.9	—	—	PCS
$HoNi_2B_2C$	[350]	ambient	8.6	1.0	5.2	—	—	PCS
$DyNi_2B_2C$	[350]	ambient	6.1	1.0	10.5	—	—	PCS
R-$(TMTSF)_2ClO_4$	[308]	ambient	1.2	—	1.37	—	—	NMR
	[311]	ambient	—	—	6	3–4.3	—	ORS
	[313]	ambient	—	—	—	absent	—	ORS
Q-$(TMTSF)_2ClO_4$	[308]	ambient	0.9	—	3.7	—	—	NMR
	[313]	ambient	—	—	4.3	6.2	—	ORS
β-$(BEDT\text{-}TTF)_2I_3$	[351]	ambient	1–1.5	—	20	—	—	R_H
	[352]	ambient	1.5	—	22	—	—	C_P

function of the field can be explained by an anisotropic E_{2u} hybrid order parameter with quadratic point nodes along the c-axis rather than by an anisotropic E_{1g} one. Bearing in mind the existing similarity between UBe_{13} and UPt_3 on the one hand and URu_2Si_2 on the other hand, the pairing symmetry of URu_2Si_2 was under suspicion from the very beginning. It was recently shown that the presence of line nodes of the order parameter seems plausible, because the T-dependence of the spin-lattice relaxation rate T_1^{-1} does not show the Hebel–Slichter coherence peak [208, 359] and is proportional to T^3 down to 0.2 K. One should stress, however, that the interplay with SDWs, strong-coupling effects [194], mesoscopic non-homogeneities [360] and other complicating factors might lead to the same consequences.

There are two other U-based antiferromagnetic (AFM) superconductors: UNi_2Al_3 and UPd_2Al_3 [318, 361]. Here the transitions into the magnetic states were revealed by studies of ρ, χ and C_P for both substances, elastic measurements for UPd_2Al_3 [362] and thermal expansion for UNi_2Al_3 [363]. The ordered local magnetic moments in UPd_2Al_3 and UNi_2Al_3 are $(0.12–0.24)\mu_B$ and $0.85\mu_B$ respectively, as opposed to $(10^{-3}–10^{-2})\mu_B$ for URu_2Si_2 [318, 364]. Thus the SDW nature of the AFM state for the two former compounds remains open to question. The local-moment picture is also consistent with the $d\rho/dT$ continuity for UPd_2Al_3 [365], whereas $d\rho/dT$ for UNi_2Al_3 manifests a clear-cut singularity [366]. Taking into account the distinctions and likenesses [333] between the various properties of URu_2Si_2, UNi_2Al_3 and UPd_2Al_3, one can conclude that all three compounds are SDW superconductors but with different degrees of magnetic moment localization.

As for the superconducting order parameter symmetry, it

should be noted that, similarly to URu_2Si_2, the dependence $T_1^{-1}(T)$ for UPd_2Al_3 exhibits no Hebel–Slichter peak below T_c and $T_1^{-1} \propto T^3$ for low T [367]. The heat capacity for $T \leqslant 1$ K also has a non-conventional contribution proportional to T^3 compatible with an octagonal d-wave state [365]. The different behaviours of the thermal conductivity for UPt_3 and UPd_2Al_3 in a magnetic field is explained in [358]. However, the problem is far from being solved.

High-pressure investigation of two more heavy-fermion compounds, U_6X (X = Fe, Co), uncovered an anomalous form of $T_c(P)$, in particular a kink of $T_c(P)$ for U_6Fe [324]. The authors suggest that these materials undergo transitions into some kind of the DW state and identify the kink with the suppression of T_N (or T_d) to a value below T_c.

The compounds $LaRh_2Si_2$ and YRh_2Si_2 have been also classified as SDW superconductors, according to the measurements of their ρ, χ and C_P [340]. Partial gapping of the SDW type was also displayed by the investigations of ρ, χ and C_P for the related substance $Ce(Ru_{1-x}Rh_x)_2Si_2$ when $x = 0.15$ [368]. However, superconductivity is absent there. This is all the more regrettable because the results of [368] demonstrate that the object concerned can be considered the ideal toy substance for the theory [126–129], much like URu_2Si_2 [325, 326]. The FS nesting and SDWs in $Ce(Ru_{1-x}Rh_x)_2Si_2$ and $Ce_{1-x}La_xRu_2Si_2$ were observed in [369] by neutron scattering.

The cubic compound $CeRu_2$ with the C15-type structure was also found to be an SDW superconductor from magnetoresistive, Hall, thermoelectric power and χ measurements [347]. Similarly, resistive, magnetic and heat capacity techniques revealed a coexistence between superconductivity and SDWs in $Tm_2Rh_3Sn_5$ [341].

Recently, the large family of quaternary borocarbides was discovered, which have separate phases of AFM, superconductivity and coexisting AFM-superconductivity [350, 370–373]. It is possible to study the interplay of AFM and superconductivity for both of the cases $T_c > T_N$ and $T_c < T_N$. Incommensurate magnetic structures (SDWs) with the wavevector ($\approx$0.55, 0, 0), originated from the FS nesting were found for $LuNi_2B_2C$ [374–376], YNi_2B_2C [375], $TbNi_2B_2C$ [377], $ErNi_2B_2C$ [373, 378, 379], $HoNi_2B_2C$ [373, 380], $GdNi_2B_2C$ [381], and with the wavevector ($\approx 0.093, 0.093, 0$) for $TmNi_2B_2C$ [373]. It is natural to make an extrapolation that other members of this family may possess the same property. Especially interesting is the situation in $HoNi_2B_2C$ with $T_N \approx 8.5$ K and $T_c \approx 8$ K [373]. Here superconductivity tends to be almost re-entrant near 5 K, which is revealed, for example, by $H_{c2}(T)$ measurements. However, full re-entrance is not achieved and the incommensurate spiral SDW locks in to a commensurate AFM structure coexisting with superconductivity.

There is a diversity of results regarding superconducting order parameter symmetry in borocarbides. Namely, $T_1^{-1}(T)$ for $Y(Ni_{1-x}Pt_x)_2B_2C$ with $x = 0$ and 0.4 exhibits a Hebel–Slichter peak and an exponential decrease for $T \ll T_c$ [382], which counts in favour of isotropic superconductivity. On the other hand, the T-linear term in the specific heat of $LuNi_2B_2C$ measured under magnetic fields H in the mixed state shows $H^{1/2}$ behaviour [383] rather than the conventional H-linear dependence for the isotropic case. Hence, for this class of superconductors the question of symmetry is still open.

Finally, another important class of SDW superconducting substances are the alloys $Cr_{1-x}Re_x$ [76, 346], where the partial gapping is verified by ρ, χ and NMR measurements.

2.3. High-T_c oxides

In [98, 238], while studying $BaPb_{1-x}Bi_xO_3$, the conclusion was made that structural instability is the main obstacle to high T_c's in oxides. The validity of this reasoning was supported by the discovery of 30 K superconductivity in $Ba_{1-x}K_xBiO_3$ [266]. The same interplay between lattice distortions accompanied by CDWs and Cooper pairing is inherent to cuprates, although the scale of T_c is one order of magnitude larger. However, notwithstanding the efficiency of the acting (and still unknown!) mechanism of superconductivity, the existence of the structural instability prevents even higher T_c's simply because of the partial FS destruction. This key point is soundly confirmed by experiment, as we shall show below.

The abrupt change of the unit cell volume as a function of the charge transfer parameter in $HgBa_2CuO_{4+y}$ arrests the T_c growth [384], as is demonstrated in figure 7.

Thermal expansion measurements on insulating La_2CuO_{4+y} and $La_{2-x}M_xCuO_4$ (M = Ba, Sr) with non-optimal doping show two lattice instabilities having $T_{d1} \approx 32$ K and $T_{d2} \approx 36$ K, while the underdoped $YBa_2Cu_3O_{7-y}$ with $y = 0.5$ and $T_c = 49$ K has a single instability at $T_d \approx 90$ K [385]. Both T_{d2} and T_d are close to maximal T_c's in the corresponding optimally doped compounds. Anomalies of the lattice properties above T_c in $La_{2-x}M_xCuO_4$ were also observed in ultrasound experiments ($x = 0.14$, M = Sr) [386] as well as in thermal expansion, $C_P(T)$ and infrared absorption measurements [387]. Resistive measurements of $La_{2-x}Sr_xCuO_4$ demonstrated an anomalous peak above T_c for superconducting samples with $x = 0.06$ and 0.075, persisting also for the semiconducting composition with $x = 0.052$, where the resistive upturn appears just below this peak [388]. These authors consider the anomalies as a clear indication both of the structural and the electronic phase transitions to the more ordered charge stripe phase. Such anomalies in the vicinity of T_c were shown to be a rule for $La_{2-x}Sr_xCuO_4$, $YBa_2Cu_3O_{7-y}$ and Bi–Sr–Ca–Cu–O [389] and cannot be explained by the superconducting transition *per se* [390]. Rather they should be linked to a structural soft-mode transition attendant to the former [389]. The analysis of the neutron scattering in $La_{2-x}Sr_xCuO_4$ shows that the above-T_c structural instabilities reduce T_c for the optimal-doping composition, so that its maximum for $x = 0.15$ corresponds, in fact, to the underdoped regime rather than the optimally doped one [391].

It should be noted that in addition to the doping-independent transitions [385] in $La_{2-x}Ba_xCuO_4$ there are also successive transitions from high-temperature tetragonal (HTT) to low-temperature orthorhombic (LTO) and then to low-temperature tetragonal (LTT) phase [186, 202, 392, 393] with T_c suppressed to zero in the intermediate doping regime centred at $x = \frac{1}{8}$, the superconducting region becoming doubly connected. At the same time, the $La_{2-x}Sr_xCuO_4$ phase diagram does not include a LTT phase and its superconducting region is not broken by the normal state intrusion [393]. $La_{2-x}Sr_xCuO_4$ doped with Nd leads to the LTT phase, and this kind of doping is widely claimed

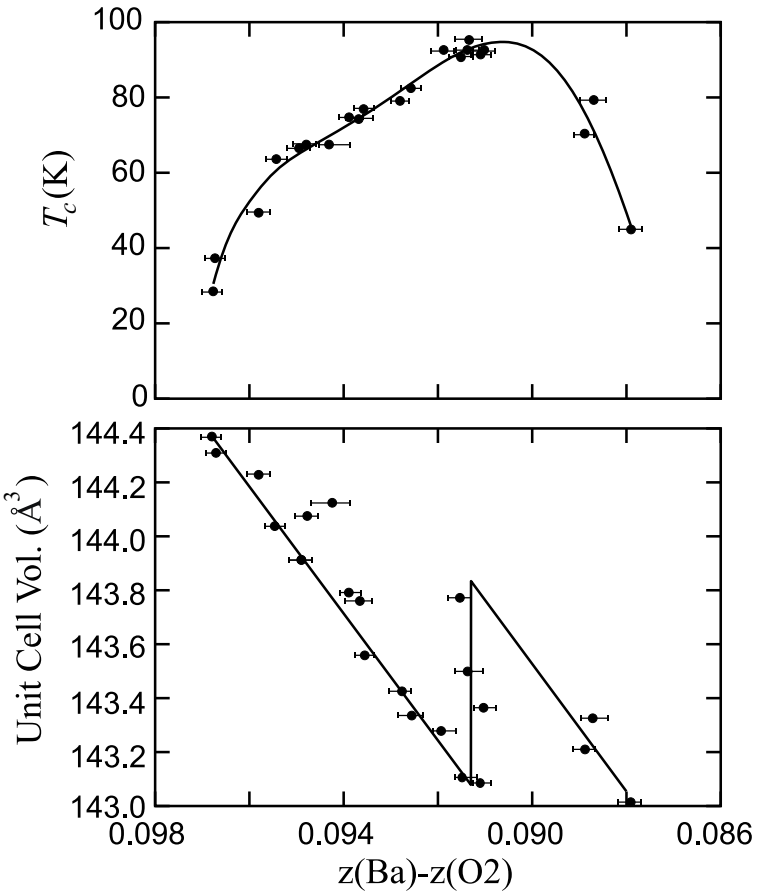

Figure 7. T_c (a) and unit cell volume (b) of $HgBa_2CuO_{4+y}$ against the structural parameter [z(Ba)-z(O2)], which is a measure of the charge transfer. (Reprinted by permission from Springer-Verlag, Berlin Heidelberg 2001 [384]).

to provoke phase separation with either static or dynamic charged and magnetic stripes [186, 394–396]. Stripes of a nanoscale width were also detected by EXAFS, x-ray, neutron, and Raman scattering as well as inferred from ARPES data in $La_{2-x}Sr_xCuO_4$ [397–399], La_2CuO_{4+y} [394, 395, 400], $YBa_2Cu_3O_{7-y}$, $Y_{1-x}Ca_xBa_2Cu_3O_{7-y}$ [401] and $Bi_2Sr_2CaCu_2O_{8+y}$ [402, 403]. ^{63}Cu and ^{139}La NMR and nuclear quadrupole resonance (NQR) measurements for $La_{2-x}Sr_xCuO_4$ with $x = 0.06$ and $T_c \approx 7$ K show that a cluster spin glass emerges below $T_g \approx 5$ K [404]. The authors of [404] made a conclusion on the freezing of hole-rich regions related to charged stripes below T_g, thus coexisting with superconductivity. The anomalies of κ dependences on the planar hole concentration p at $p = \frac{1}{8}$ in $YBa_2Cu_3O_{7-y}$ and $HgBa_2Ca_{m-1}Cu_mO_{2m+2+y}$ [405, 406] give indirect evidence that the charged stripes (if any) are pinned, probably by oxygen vacancy clusters.

As was mentioned in section 1, the concept of phase separation was introduced long ago for structurally and magnetically unstable systems [185, 407] and later revived for manganites, nickelates and cuprates [182, 408–410]. As a microscopical scenario for high-T_c oxides there are many proposals, for example: (i) a Van Hove singularity-driven phase separation with the density of states peak of the optimally doped phase electron spectrum split by the Jahn–Teller effect [186, 411], (ii) droplet formation due to the kinetic energy increase of the doping current carriers at the dielectric gap edge with density of states peaks [412] in the framework of the isotropic model [45]; and (iii) instability for the wavevector $\boldsymbol{q} = 0$ in the infinite-U Hubbard–Holstein model where the local charge repulsion inhibits the stabilizing role of the kinetic energy [413]. In the last case, $\boldsymbol{q}$ becomes finite when the long-range Coulomb interaction is taken into account. The origin of such incommensurate CDWs has little to do with the nesting-induced CDWs we are talking about. In practice, nevertheless, ICDWs or charged stripes are characterized by widths similar to CDW periods in the Peierls or excitonic insulator cases and can be easily confused with each other [186], especially as the local crystallographic structure is random [202, 392, 393, 401].

Returning to the $La_{2-x}M_xCuO_4$ family, it is important to point out that the atomic pair distribution functions in real space, measured by neutron diffraction both for M = Ba and Sr, revealed local octahedral tilts surviving even at high T deep into the HTT phase [414]. For $La_{2-x}Sr_xCuO_4$ with $x = 0.115$, electron diffraction disclosed that a low-T structural transition is accompanied by the CDWs of the $(\frac{1}{2}, \frac{1}{2}, 0)$ type that lead to the suppression of superconductivity [415]. Raman scattering investigations indicated that in the underdoped case there is a pseudogap $E_{ps} \approx 700$ cm^{-1} without any definite onset temperature, which competes with a superconducting gap for the available FS [416], whereas for the overdoped samples the pseudogap is completely absent [417]. On the other hand, EXAFS measurements for $La_{2-x}Sr_xCuO_4$ with $x = 0.15$ and La_2CuO_{4+y} with $y = 0.1$ demonstrated that

CDWs and superconductivity coexist, but with the clear-cut onset temperature T_{es} revealed from the Debye–Waller factor [418]. T_{es}'s are doping dependent and coincide with the corresponding anomalies of the transport properties.

In $YBa_2Cu_3O_{7-y}$, lattice and, in particular, acoustic anomalies were observed just above T_c soon after the discovery of these oxides [389, 419–421]. $C_P(T)$ measurements also demonstrated a concomitant structural anomaly at 95 K besides the smeared superconducting jump at $T_c \approx 90$ K [422]. NMR data for $YBa_2Cu_3O_{7-y}$ and $YBa_2Cu_4O_8$ confirmed the conclusion that the actual gap below T_c is a superposition of the superconducting and dielectric contributions [115, 423–426]. The same can be inferred from optically determined ac conductivity [427]. The absence of the (^{16}O–^{18}O)-isotope effect in the normal state pseudogap and its presence in T_c for $YBa_2Cu_4O_8$ [423] cannot be a true argument against the CDW origin of the normal state gap because the latter may be predominantly of Coulomb (excitonic) nature (see the discussion in sections 1 and 3). On the contrary, the sought after isotope effect was actually found with the help of the inelastic neutron scattering in $HoBa_2Cu_4O_8$ [428], where the electronic density of states depletion begins at $T \approx 170$ K for ^{16}O and $I \approx 220$ K for ^{18}O, thus being huge in comparison with the 0.5 K shift of T_c. Recent comparative Raman and NMR investigations [429] of the isotope dependence for different quantities in the normal and superconducting states of $YBa_2Cu_4O_8$ showed, in particular, that a Cu isotope effect does exist both for T_c and the ^{89}Y Knight shift. However, the isotope effect for the latter changes its sign to negative above T_c as contrasted with the positive Cu isotope effect for T_c itself.

In $YBa_2Cu_3O_{7-y}$, the back bending of the Hall number density as a function of T exhibits the anomaly at about twice or three times T_c [430], attributed to an electronic structural transition. This is in agreement with the onset of superconducting fluctuations at $T \approx 2.5T_c$ revealed by very precise measurements of the paraconductivity behaviour [431]. Moreover, this can be related to an anomalous self-diffusion coefficient behaviour of oxygen in the incomplete planes at a so-called 'low temperature', as discussed in [432]. Immediately this supports the arguments on the existence of Cooper pair-like systems at high T, determining the fluctuation character near T_c and the pseudogap onset temperature [433].

There also exists direct scanning tunnelling microscopy evidence of the occurrence of a CDW in the CuO_3 chains of $YBa_2Cu_3O_{7-y}$ [251–254, 434]. CDWs in metallic quasi-1D chains were observed by NMR in the related compound $PrBa_2Cu_3O_7$, where the CuO_2 planes are AFM with $T_N \approx 280$ K [435].

In $Bi_2Sr_2CaCu_2O_{8+y}$, lattice anomalies above T_c were observed in the same manner as in $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$ [389]. It is remarkable that in $Bi_2Sr_2CaCu_2O_{8+y}$ with $T_c = 84$ K the lowest structural transition is at $T_d = 95$ K, while for Bi–Sr–Ca–Cu–Pb–O with $T_c \approx 107$ K the respective anomaly is at $T_d \approx 130$ K [436], much like the T_c versus T_d scaling in $La_{2-x}[Sr(Ba)]_xCuO_4$, $YBa_2Cu_3O_{7-y}$ discussed above and electron–doped cuprates [385]. Local atomic displacements in the CuO_4 square plane of $Bi_2Sr_2CaCu_2O_{8+y}$ due to incommensurate structure modulations were discovered by EXAFS [437]. The competition between superconducting and normal state gaps for the FS in $Bi_2Sr_2CaCu_2O_{8+y}$ was detected in [438] when analysing the impurity suppression of T_c. The other possibility, appropriate to a number of approaches, comprises a smooth evolution between the gaps while crossing T_c (see, e.g., [439, 440] and the discussion below), but is discarded by the experimental data [438].

There exists also an indirect indication [441] of the charge inhomogeneities appearance in cuprates (hypothetically attributed to stripes such as observed in nickelates [442]). Specifically, infrared optical conductivity in $YBa_2Cu_3O_{7-y}$ and $Pr_{1.85}Ce_{0.15}CuO_4$ [441] revealed sharp features from unscreened optical phonons, impossible for conventional metals. On the other hand, this behaviour is similar to the occurrence of the phonon peaks in the CDW metal η-Mo_4O_{11} conductivity found below a higher $T_d \approx 110$ K, but above lower $T_d \approx 35$ K in the partially-gapped (however, still metallic) state.

The analysis of the relevant experimental data would be incomplete if one did not mention incommensurate spin fluctuations revealed by inelastic neutron scattering in $La_{2-x}Sr_xCuO_4$ [443, 444], La_2CuO_{4+y} [444] and $YBa_2Cu_3O_{7-y}$ [445], which change from commensurate ones on cooling to the neighbourhood of T_c. The phenomenon might be connected, for instance, with the stripe phase state [179, 182, 186, 394, 395, 409, 410, 446, 447] or reflect an underlying mechanism of d-wave superconductivity based on the AFM correlations [197, 203, 320, 408, 446–453]. The dynamic susceptibility found in $La_{2-x}Sr_xCuO_4$ strongly resembles that of the paramagnetic state for a dilute alloy Cr+0.2 at.% V near the Néel temperature [76, 90, 454, 455]. It is worth noting that the famous resonance peak with the energy of about 41 meV observed by the inelastic neutron scattering in the superconducting state of $YBa_2Cu_3O_{7-y}$ is often considered as intimately related to the very establishment of superconductivity [391, 452, 453]. Moreover, *elastic* neutron scattering showed that there is a long-range SDW order of the mean-field type in La_2CuO_{4+y} appearing simultaneously with the superconducting transition [456]. Thus, a third player is involved in the game between Cooper pairing and CDWs, making the whole picture rich and entangled. According to [456], it might happen that the claimed phase separation in $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ [394, 395, 442] is actually a real-space coexistence between superconductivity and SDWs. Zero-field and transverse-field muon spin resonance investigations of the same La_2CuO_{4+y} samples that had been used in [456] confirmed the coexistence of the static incommensurate SDWs below T_N coinciding with T_c [457]. These static spin correlations are condensed from the dynamic spin correlations inelastically probed above T_N. According to the authors of [457], the static non-homogeneous structure developed below T_N is identical to that in $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ [394, 395, 442]. However, it still remains unclear whether the comcomitant superconductivity occurs in locations associated with 'non-magnetic' or 'magnetic' muon sites.

Recently ARPES investigations in $Bi_2Sr_2CaCu_2O_{8+y}$ established an extra 1D narrow electronic band with a small Fermi momentum $k'_F \approx 0.2\pi$ in units of a^{-1}, where $a = 3.8$ Å, in the $\Gamma - M_1 = (\pi, 0)$ direction [458, 459]. For this band the charge (CDW) fluctuations with the nesting wavevector $\boldsymbol{Q}_c = 2\boldsymbol{k}'_F$ are expected. The authors of the [459] associate

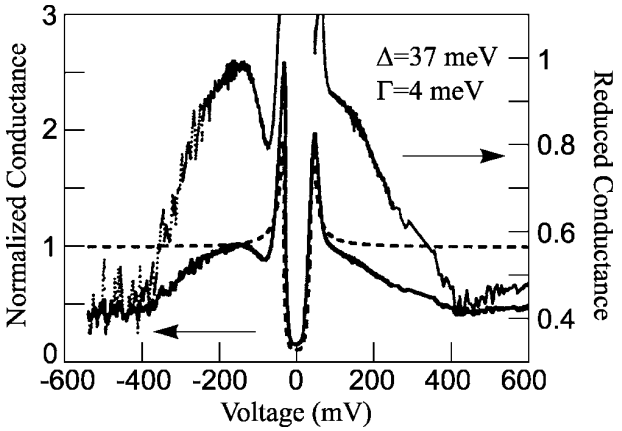

Figure 8. A representative superconductor–insulator–normal metal normalized point-contact tunnelling conductance (full curve) for optimally doped $Bi_2Sr_2CaCu_2O_{8+y}$ at 4.2 K and smeared BCS fit (broken curve) with the gap $\Delta = 37$ meV and the damping factor $\Gamma = 4$ meV. The uppermost curve shows the reduced conductance which is the normalized conductance divided by the smeared BCS density of states. (Reproduced by permission from [467]).

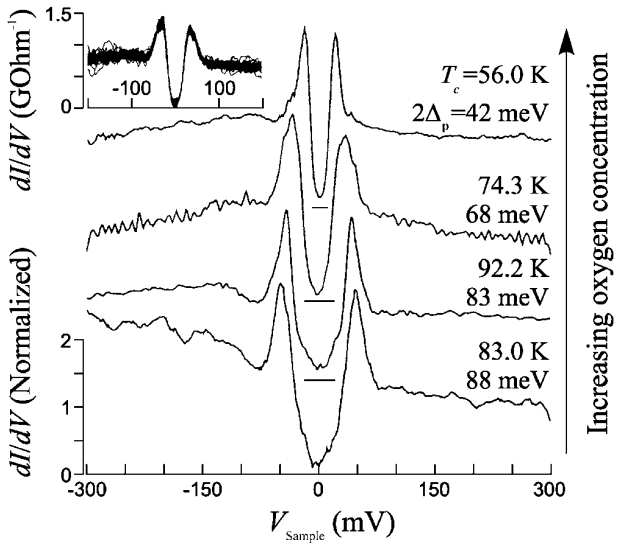

Figure 9. Tunnelling spectra for $Bi_2Sr_2CaCu_2O_{8+y}$ measured at 4.2 K for different oxygen doping levels. The curves are normalized to the conductance at 200 mV and offset vertically for clarity (zero conductance is indicated for each spectrum by the horizontal line at zero bias). The estimated error on the gap values ($2\Delta_p$) is ± 4 meV. The inset shows 200 superposed spectra measured at equally spaced points along a 0.15 μm line on overdoped $Bi_2Sr_2CaCu_2O_{8+y}$ ($T_c = 71.4$ K), demonstrating the spatial reproducibility. (Reproduced by permission from [463]).

spin fluctuations of the wavevector $\boldsymbol{Q}_s \approx (0.2\pi, 0)$, observed for $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ and $La_{2-x}Sr_xCuO_4$ [442, 444], with charge fluctuations of the wavevector $2\boldsymbol{Q}_s$ coinciding with the deduced $\boldsymbol{Q}_c$. Later [460] they rejected the allegations [461] that the observed asymmetry of the directions $\Gamma - M = (0, \pi)$ and $\Gamma - M_1$ [459] is an artifact of the misalignment between the rotation axis and the normal to the samples. In addition to this, the high-precision ARPES measurements for $Bi_2Sr_2CaCu_2O_{8+y}$ clearly show the existence of nested FS sections [462].

One should also note that in the superconducting state of $Bi_2Sr_2CaCu_2O_{8+y}$, tunnel measurements of the non-symmetrical junctions often show the dip in the bias V dependences of the differential conductivity $G_{ns}^{diff}(V)$ (about 10% magnitude as compared to the peak height) at about $V \approx -2\Delta/e$ [463–468], whereas for symmetrical junctions the dips (or dip–hump structures) are observed at $V \approx \pm 3\Delta/e$ [469–471]. The dependences $G_{ns}^{diff}(V)$ for the junctions involving $Bi_2Sr_2CaCu_2O_{8+y}$ are shown as typical examples of asymmetrical patterns in figures 8 and 9. In the context of the previous discussion, the appearance of the pronounced dips in $G_{ns}^{diff}(V)$ may be connected with the dielectric gap [472]. It is remarkable that the dips and near-by lying smeared humps in $G_{ns}^{diff}(V)$ for $Bi_2Sr_2CaCu_2O_{8+y}$ look similar to peak–dip–hump features of the ARPES spectra for this superconductor [473, 474]. There is an alternative explanation [475] of these structures together with the resonant peaks in neutron scattering, which is based on the involvement of feedback effects on the spin fluctuation damping in d-wave superconductors.

Let us return now to the very notion of 'pseudogap' ('spin gap' or 'normal state gap' [476]). The corresponding features appear in many experiments measuring different properties of high-T_c oxides. This term means a density of states reduction above T_c or an additional contribution to the observed reduction below T_c if the superconducting gap is determined and subtracted. A formal analogy exists here with pseudogaps in the range $T_{3D} < T < T_{MF}$ for quasi-1D or quasi-2D substances, observed both for dielectric (e.g., Peierls) gaps [7, 15, 18, 477] or their superconducting counterparts [152, 359, 478–480]. T_{MF} denotes the transition temperature in the respective mean-field theory while T_{3D} is the actual ordering temperature, lowered in reference to T_{MF} by the order parameter thermal fluctuations [113, 114, 477–479].

Specifically, pseudogaps with edge energies $\leqslant 0.03$ eV were detected in $La_{2-x}[Sr(Ba)]_xCuO_4$ by NMR [481, 482], Raman scattering [483–485] and optical reflection [486]. From the analysis [484, 485] of the Raman spectra it comes about that the pseudogaps in $La_{2-x}Sr_xCuO_4$ which appear near hot spots of the FS are nodeless and are hostile to the superconductivity. Ac current susceptibility studies resulted in the cusps for the doping, p, dependences of the c-axis penetration depth λ_c at $p = 0.20$ holes/Cu atom both for $La_{2-x}Sr_xCuO_4$ and $HgBa_2CuO_{4+y}$ [487], thus indicating an opening of the normal state pseudogap. Furthermore, photoemission measurements showed that in $La_{2-x}Sr_xCuO_4$ there is in addition a 'high-energy' pseudogap structure at 0.1 eV [488]. A theoretical scenario for the Van Hove singularity-induced nesting with several coexisting DW gaps was proposed to cover the two-pseudogap situation [489].

In $YBa_2Cu_3O_{7-y}$, pseudogaps were observed in NMR [423, 424, 481, 490], Raman [483, 491–494], optical reflectance [486], neutron scattering [445, 495], time-resolved quasiparticle relaxation and Cooper pair recombination dynamics [496, 497], specific heat [498, 499] and ellipsometric [427] measurements. The observation of the anomalous crossover in the temperature T-dependence of the electrical resistivity at $T \approx 2.5T_c$ [431] was interpreted as the opening of a pseudogap [433]. Pseudogaps showed themselves for $YBa_2Cu_4O_8$ in NMR [500] and Raman [501, 502] experiments. It is remarkable and important

for possible future interpretations that similar pseudogapping also exists in the non-superconducting allied substances $PrBa_2Cu_3O_7$ [435], as was shown by NMR investigations, and $PrBa_2Cu_4O_8$ [501], as was demonstrated in resistive and Raman measurements. The same phenomenon was discovered by infrared and Raman techniques for the non-superconducting oxygenated $Nd_{1.85}Ce_{0.15}CuO_{4+y}$ [503]. Bi-based oxides revealed pseudogaps in NMR [481, 504, 505], Raman [483, 491, 493, 494, 506], optical [486, 507, 508], ARPES [458, 509–512] and resistive [513] experiments. For $Nd_{1.85}Ce_{0.15}CuO_{4+y}$ there is a conspicuous pseudogap in Raman and infrared spectra of sufficiently oxygenated AFM samples [503]. At the same time, the authors of [503] indicate that a Bragg spot in the direction $\Gamma - (\pi, 0)$ is absent, so that SDWs can be ruled out. Therefore, they consider the charge ordering instability to be the origin of the pseudogap. Finally, pseudogaps were found in Hg-based superconductors with the help of NMR investigations [514–518].

It should be noted that despite the same temperature ranges of the pseudogap manifestations and similar doping dependences, revealed in various experiments for the same objects, the analysis shows that charge-excitation and spin-excitation pseudogaps are probably nature in different [519].

Pseudogap phenomena inherent to quasi-2D cuprates were also observed by NMR and optical measurements in two-leg ladder compounds [520]. Moreover, in the particular case of $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.81}$, under external pressure pseudogapping coexists with superconductivity, with the highest $T_c \approx 14$ K attainable for $P \approx 50$ kbar.

The origin of pseudogaps in layered cuprates is far from clear [440, 476, 521]. First of all the agreement concerning a possible relationship between Δ and the pseudogap is lacking, even at the phenomenological level. The authors of [505] inferred the similarity between two quantities from their NMR measurements in $Bi_2Sr_2CaCu_2O_{8+y}$, where the anomaly of T_1^{-1} was absent at T_c in the underdoped samples but observed in the overdoped ones. It is remarkable that theoreticians [522] make the opposite conclusion from the same fact. The latter deduction is confirmed by the observation that $T_1^{-1}(T)$ in $YBa_2Cu_3O_{7-y}$ reveals a magnetic field H independent of the spin gap, although T_c is reduced by 8 K for $H = 14.8$ T [523]. A similar situation holds for the spin gap in $YBa_2Cu_4O_8$, where T_c decreases by 26% for $H = 23$ T [500]. In this connection one should also mention the close resemblance between pseudogaps for the superconducting $YBa_2Cu_4O_8$ and non-superconducting $PrBa_2Cu_4O_8$ found by Raman and resistive measurements [501, 502]. Finally, the large magnitudes of the Raman spectra anomalies in $YBa_2Cu_3O_{7-y}$ and $Bi_2Sr_2(Ca_xY_{1-x})Cu_2O_8$ at $E^* \approx 800$ cm^{-1} were considered by the authors of [494] as evidence of their magnetic origin.

From a microscopic point of view there are a great number of possible explanations of the pseudogap including: reduced dimensionality [524]; preformed pairs [478, 524, 525]; resonant pair scattering above T_c [526–530]; electron spectrum quantization due to the charge confinement in grains [531], stripe-induced Van Hove singularity splitting [532], proximity to 2D electronic topological transition at the Van Hove singularity, which also leads to the bare electron spectrum splitting [533–536]; or giant fluctuations above T_c. In particular, fluctuations should renormalize the electron density of states, manifesting themselves as a gap-like structure in the quasiparticle tunnel current–voltage characteristics [537]. For a detailed discussion of this subject see also [179, 186, 450, 530, 538–546]. On the other hand, it is natural to conceive the pseudogaps or related phenomena, observed before the pseudogap paradigm became popular, as a result of electron–hole correlations leading to a dielectric gap [169, 387, 547–550]. In accordance with this basic concept, the latter coexists with its superconducting counterpart below T_c, whereas above T_c it distorts the FS alone. Moreover, the very appearance of pseudogaps suppresses T_c's (the same conclusion stems from the other approach [527, 528, 551]).

During the last few years the point of view expressed above has received some substantial support, the calculations being widened to include anisotropy up to non-conventional, for example, d-like character of the dielectric order parameter and the fixation of its phase [115, 170–174, 480, 489, 552–560]. On the other hand, it is difficult to agree with the conclusions (see, e.g., [476]) frequently drawn from the same body of information: that the superconducting gap Δ emerges from the normal state pseudogap and that they both represent the same d-wave symmetry. A partial character of the dielectric gapping, also accepted in [476], may mimic pretty well the d-wave superconducting order parameter spatial pattern [170, 552, 553].

The possible coexistence of d-wave-like partial gapping in the normal state may complicate the interpretation of experiments which measure the anisotropy of the superconducting state order parameter in the cuprates [201, 203, 206, 208, 321, 356, 357, 360, 408, 451, 480, 552, 553, 561–571]. However it is not clear at present whether a d-wave-like normal state partial gapping could alter the identification of the d-wave superconducting state symmetry, in particular the phase-sensitive experiments [201, 572]. The only possible theoretical alternative to the d-wave state order parameter would be a highly anisotropic s-wave pairing. This might be consistent with recent twist-junction c-axis tunnelling experiments [565, 566, 568, 569]. However these appear to directly contradict the earlier in-plane phase-sensitive experiments, as reviewed in [201]. These measurements have already led to the design of the so-called π-SQUID [573] and have also recently been reproduced in electron-doped cuprates [572], previously considered as systems with an isotropic s-wave gap. Mixed s–d-pairing states are also theoretically possible, and may resolve this contradiction. In this context it is interesting to note that if the pseudogap were to be due to pairing fluctuations above T_c, then the non-trivial angular dependence of the pseudogap suggests that the pairing fluctuations should include both s- and d-wave components [574].

It should also be stressed that the predominantly $d_{x^2-y^2}$-type superconducting order parameter of cuprates, inferred mostly from the phase-sensitive measurements like those for local junctions [201, 203, 206] and from investigations of magnetic-field-dependent bulk properties such as, for example, the electrothermal conductivity [575, 576] and the thermal conductivity [577–580] (in zero magnetic field the thermal conductivity measurements are inconclusive [564, 578, 581–583]), is *not* matched one to one with the AFM spin fluctuation mechanism of pairing [203, 408, 451]. In reality, in a quite

general model including both Coulomb and electron–lattice interactions the forward (long wavelength) electron–phonon scattering was shown to be enhanced near the phase separation instability, thus leading to momentum decoupling for different FS regions [584–586]. In its turn, this decoupling can result in an anisotropic superconductivity, for example, d-wave or mixed s–d, even for phonon-induced Cooper pairing. Non-screened coupling of charge carriers with long-wave optical phonons [587] or anisotropic structure of bipolarons [540] in the framework of the approach of [195] may also ensure a d-like order parameter structure. There exists an interesting scenario involving the combined action of AFM correlations and the phonon mechanism of superconductivity [588]; namely correlations modify the hole dispersion, producing anomalous flat bands [589]. Then the robust Van Hove peak in the density of states boosts T_c, Cooper pairing being the consequence of the electron–phonon interaction [588]. In the particular case of cuprates, the buckling mode of oxygen atoms serves as an input quantity of the employed Holstein model [590].

It is remarkable that the d-wave-like dispersion is inherent also to the high-energy pseudogap in the insulating quasi-2D $Ca_2CuO_2Cl_2$ which is closely related to high-T_c superconductors [591]. Moreover, these photoemission experiments show the remnants of the FS in the non-conducting state. Thus, the pseudogap may be of the nesting-driven particle–hole origin [592], renewing the idea of the excitonic nature of small-band-gap semiconductors [45, 83]. Alternatively, the findings of [591] may also be explained [593] in the framework of projected SO(5) symmetry (a generalization of the SO(5) approach [452]).

3. Underlying theoretical considerations

The experimental data discussed in the preceding section can be understood in the framework of the theoretical pictures of two main types of the distorted, partially-gapped, but *still metallic*, low-T states of the parent unstable high-T phase, which are driven by electron–phonon and Coulomb interactions, respectively.

The 1D Peierls insulator is the archetypical representative of the electron–phonon type [1, 2, 6, 9, 15, 17, 477]. It results from the periodic displacements with the wavevector $\boldsymbol{Q}$ ($|\boldsymbol{Q}| = 2k_F$) appearing in the ion chain. Here k_F is the Fermi momentum of the 1D band above T_d. The emerging periodic potential gives rise to the dielectric gap and all filled electronic states are pushed down, leading to the energy gain greater than the extra elastic energy cost. The situation is analogous to the textbook problem of the quasi-free electron gas in an external periodical potential where electron spectrum branches are split at the Brillouin zone edges (see, e.g., [594]). The phenomenon discussed is possible because FS sections (Fermi planes separated by $2k_F$ in the 3D representation) are often congruent (nesting). Then the electron gas response to the external static charge is described by the polarization operator (response function) [477, 595]

$$\Pi_{1D}(\boldsymbol{q}, 0) = 2N_{1D}(0)\frac{k_F}{k_\perp}\ln\left|\frac{k_\perp + 2k_F}{k_\perp - 2k_F}\right| \qquad (4)$$

where $\boldsymbol{q}$ is the momentum transferred, $\boldsymbol{q}^2 = \boldsymbol{k}_\parallel^2 + \boldsymbol{k}_\perp^2$, $\boldsymbol{k}_\parallel$ and $\boldsymbol{k}_\perp$ are the $\boldsymbol{q}$-components normal and parallel to the FS and $N_{1D}(0)$ is the background density of states per spin direction for the 1D electron gas. It is precisely the logarithmic singularity of $\Pi_{1D}(\boldsymbol{q}, 0)$ that drives the spontaneous ion chain distortion—Peierls transition.

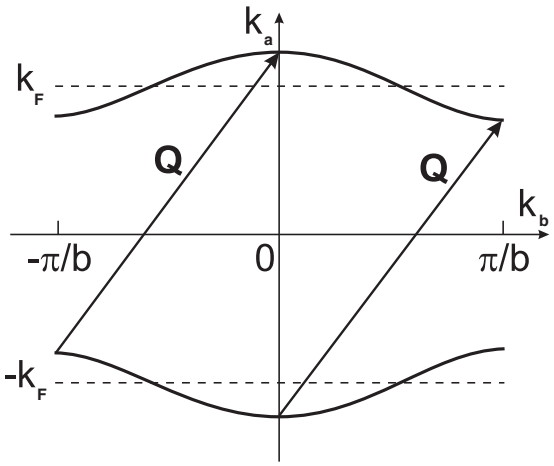

Figure 10. 2D view of the open FS for a typical $(TMTSF)_2X$ compound. The broken lines represent the planar 1D FS when the interchain hopping rate is zero. The degree of 'warping' of the FS is directly related to the electron hopping rate along the b crystal direction. (Reproduced by permission from [598]).

This singularity leads to the manifestation of a sharp FS edge in the standing electron wave diffraction. Of course, the same phenomenon survives for higher dimensions but in a substantially weaker form, because the nested FS planes spanned by the chosen wavevector are now reduced (again in the 3D representation) to two lines for 2D and a pair of points for 3D degenerate electron gases [258–260, 595].

Hence, in the 2D case we have [595]

$$\Pi_{2D}(\boldsymbol{q}, 0) = N_{2D}(0)\,\mathrm{Re}\left\{1 - \left[1 - \left(\frac{2k_F}{k_\perp}\right)^2\right]^{1/2}\right\} \qquad (5)$$

where $N_{2D}(0)$ is the 2D starting electronic density of states per spin direction. Here the square root singularity shows up only in the first derivative of $\Pi_{2D}(\boldsymbol{q}, 0)$. In three dimensions, the polarization operator $\Pi_{3D}(\boldsymbol{q}, 0)$ has the well known Lindhard form [594], and the logarithmic singularity appears only in the derivative $[\mathrm{d}\Pi_{3D}(\boldsymbol{q}, 0)/\mathrm{d}q]_{q\to 2k_F}$, being the origin of the electron density Friedel oscillations and the Kohn anomaly of the phonon dispersion relations. The nesting-driven transitions, therefore, seem to be appropriate only to 1D solids.

In reality all substances where the Peierls instability takes place are only quasi one dimensional ones, although strongly anisotropic [8, 143–146, 148, 152, 153, 258–261, 267, 268, 477, 596, 597]. Then the nesting Fermi planes are warped similarly to that shown in figure 10 for the particular case of the $(TMTSF)_2X$ compounds [598]. Thus, simple band-structure calculations show that the electronically-driven instability is fairly robust and adjusts itself by changing the DW vector $\boldsymbol{Q}$ which still spans a finite area of the FS, as can be inferred from figure 10.

Another example, where CDW emergence becomes possible is in quasi-2D materials, in the case when the nesting is *imperfect*, as demonstrated by ARPES for $SmTe_3$ [599].

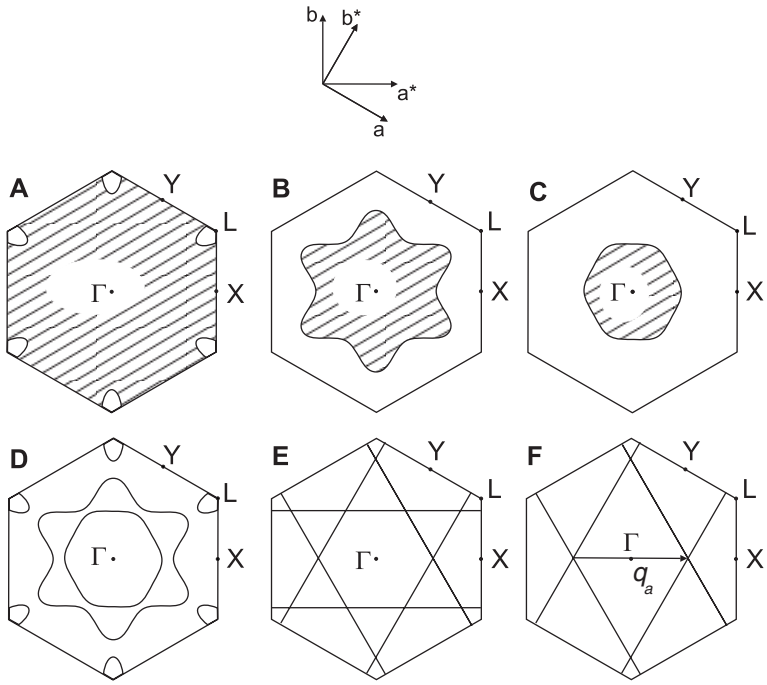

Figure 11. Hidden nesting in the purple bronze KMo_6O_{17}. The calculated FSs for the three partially filled d-block bands are shown in (A), (B) and (C), the combined FSs in (D) and the hidden 1D surfaces are nested by a common vector q_a in (F). (Reproduced by permission from [596]).

Here anomalously strong incommensurate CDW correlations persist up to the melting temperature $T < T_d$ and the measured dielectric gap is 200 meV. However, the most interesting observed feature is the inconstancy of the nesting wavevector $\boldsymbol{Q}_{nest}$ over the nested FS sections. Therefore, although $\boldsymbol{Q}_{nest}$ no longer coincides with the actual CDW vector $\boldsymbol{Q}$, the system can still reduce its energy below T_d!

Finally, one more reason for the instability to survive in non-1D systems is the occurrence of hidden nesting. This concept was first applied to the purple bronzes AMo_6O_{17} (A = K, Na) undergoing a CDW phase transition [596]. In these oxides the three lowest lying filled d-block bands make up three 2D non-nested FSs. However, when combined together and with no regard for avoided crossing the total FS can be decomposed into three sets of nested 1D FSs (see figure 11). One can see (figure 11(F)) that the wavevector $\boldsymbol{q}_a$, *deviating* from the chain directions, unites two chosen sets of the nested FS sections. Of course, two other nesting wavevectors are also possible [258–261, 267, 268, 596]. The corresponding superlattice spots in the x-ray patterns as well as evidence in ARPES spectra, resistive, Hall effect and thermoelectric power anomalies, supporting the hidden-nesting concept, were observed for AMo_6O_{17} [596, 597, 600–603], Magneli phases Mo_4O_{11} [267, 268, 601, 602] and monophosphate tungsten bronzes $(PO_2)_4(WO_3)_{2m}$ [258–260, 601, 602, 604].

Hidden nesting is also inherent to the layered dichalcogenide family [258–260, 267, 268, 597] which also includes CDW superconductors (see table 1). Here, however, a cooperative (band) Jahn–Teller effect [411] can be the driving force for structural modulations [267, 268]. Although the microscopical origin of the Jahn–Teller effect may have nothing to do with the polarization operator (4) divergence, the loss of the initial symmetry through lattice distortions, appropriate both to the Jahn–Teller low-T state and the Peierls insulator, makes their description quite similar at the mean-field and the phenomenological Ginzburg-Landau levels [93, 186, 267, 268, 302–304, 547, 597, 605]. On the other hand, the dynamic band Jahn–Teller effect may be responsible [606], for example, for the phase separation in $La_{2-x}Sr_xCuO_4$ [186, 394, 395] with mobile walls between LTO and LTT domains.

In 2D systems the Jahn–Teller effect can lead to the splitting of two degenerate Van Hove singularities [186, 606]. In this connection it is necessary to mention the Van Hove picture of quasi-2D superconductors, which in particular, popular for high-T_c cuprates [186, 547, 564, 607]. The logarithmic singularity of $\Pi_{2D}(\boldsymbol{q}, 0)$ in the Van Hove scenario, as was indicated in [187] when studying layered chalcogenides, stems not from the FS nesting but from the logarithmic divergence of the primordial electronic density of states in the case of the disruption or creation of a FS neck [608]. This singularity survives the momentum space integration when calculating the polarization operator $\Pi_{2D}(\boldsymbol{q}, 0)$ for $\boldsymbol{q} = \boldsymbol{Q}_0$, the latter being the wavevector connecting two Van Hove saddle points, so that [187]

$$\Pi_{2D}(\boldsymbol{Q}_0, 0) \simeq N_{Q_0} \ln\left(\frac{\epsilon_0}{|\mu|}\right). \tag{6}$$

Here ϵ_0 is the cut-off energy and μ is the chemical potential, reckoned from the saddle point. The divergence (6) deduced for the 2D electron gas is of the same type as (4), obtained either for the 1D case or for the congruent electron and hole pockets (see below). On the other hand, the nature and the magnitude of the resulting CDW vector is quite different, as can be seen from figure 12 [186, 609] drawn in agreement with the calculations made for cuprates [610]. Figure 12 demonstrates

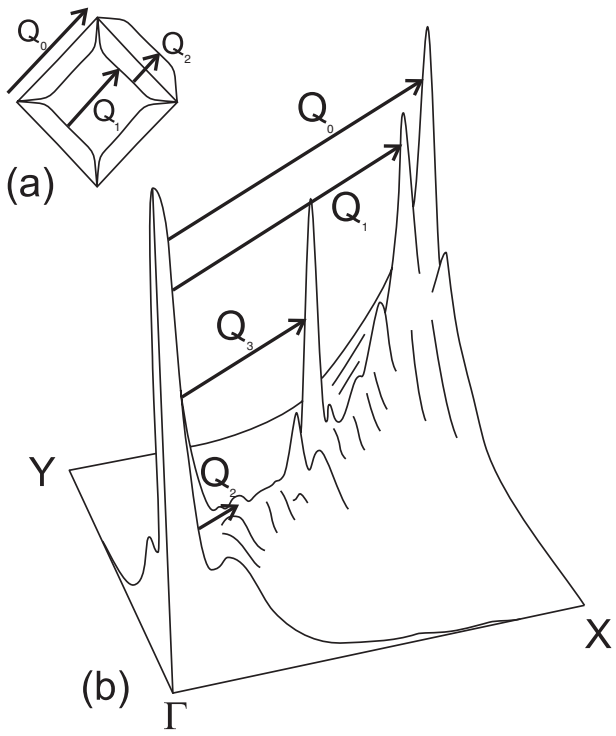

Figure 12. (*a*) Schematic FS of $La_{1.85}Sr_{0.15}CuO_4$, illustrating both nesting wavevectors ($\boldsymbol{Q}_1$, $\boldsymbol{Q}_2$) and the Van Hove singularity-connecting wavevector ($\boldsymbol{Q}_0$). (*b*) Peaks in the joint density of states for this material, showing various associated wavevectors. (Reprinted from *Physica* C **217** Markiewicz R S The van Hove singularity in the cuprate superconductors. A reassessment 381. Copyright (1993) with permission from Elsevier [609] and *Science* [610] with permission from the American Association for the Advancement of Science).

that the vector $\boldsymbol{Q}_0$ connecting two Van Hove singularities for the real substance $La_{2-x}Sr_xCuO_4$ does not coincide with the wavevectors $\boldsymbol{Q}_1$ or $\boldsymbol{Q}_2$ spanning nesting FS sections for the same compound.

As was stressed in [187], nesting leads to the *additional* logarithmic divergence of the factor N_{Q_0}. In the general Van Hove singularity scenario, SDWs, CDWs and maybe even flux phases compete with each other and with superconductivity for the gapping of the Fermi surface [489, 533–536, 611].

Thus, it is possible to distinguish between two instability scenarios. For cuprates the proper identification is still not clear, unlike the case of $2H$-$NbSe_2$ [277] (see section 2.1). One should note that the extended Van Hove saddle point case can also be included in the Van Hove singularity picture [612–614] (when the divergence of the density of states becomes the square root one similar to (5), and is often used to explain high T_c's of oxides [186, 607, 612, 615–617].

So far we have envisaged the Peierls instability for only the restricted case of noninteracting charge carriers. Of course, the effects of electron–electron interaction should also be taken into account properly, which is a very hard job for the case of low-dimensional metals on the verge of instability [8, 91, 186, 194, 489, 605, 618, 619]. One of the main consequences of the incorporation of many-body effects is a strong screening of the bare Coulomb potentials and the failure of the Fröhlich Hamiltonian to give quantitative predictions both for normal and superconducting metal properties [91, 618–622]. Nevertheless, these difficulties are not dangerous for our mean-field treatment, taking for granted the existence of the high-T metal–low-T metal phase transition (inferred from the experiment!) and not trying to calculate the transition temperatures T_d, T_N or T_c directly from first principles. In any case, the self-consistent theory of elastic waves and electrostatic fields shows that the Peierls transition survives while making allowance for long-range charge screening [619, 623, 624].

Summing up the terminology concerning various reconstructed states discussed above, it should be pointed out that the notion 'CDW' incorporates both nesting- and Van-Hove-singularity-driven states. Peierls and excitonic insulators as well as various combined phases in low-dimensional substances represent different realizations of CDW solids.

The SDW state of low-dimensional metals is treated in substantially the same manner as the CDW Peierls metal but with $\Pi_{1D}(\boldsymbol{q}, 0)$ substituted by the magnetic susceptibility and the electron–phonon interaction replaced by the electron–electron repulsion. Usually the approach is simplified and the latter is described by the simplest possible contact Hubbard Hamiltonian [75, 77]. In the mean-field approximation the subsequent mathematics is formally the same. The only (but essential!) distinction is the spin-triplet structure of the dielectric order parameter matrix.

The other low-T reconstructed state resulting from the primordial semimetallic (or semiconducting) phase is the excitonic insulator phase, caused by the electron–hole (Coulomb) interaction [36–40, 43, 45, 91]. The necessary condition for the gapping reads

$$\xi_1(\boldsymbol{p}) = -\xi_2(\boldsymbol{p} + \boldsymbol{Q}) \tag{7}$$

where the branch $\xi_{1(2)}$ corresponds to the electron (hole) band and $\boldsymbol{Q}$ is the DW vector. This is identical to the nesting (degeneracy) condition we have been talking about for the Peierls case, and which is automatically fulfilled for a single 1D self-congruent electronic band [1, 2, 6, 15, 17, 18, 477]. In the general case of an anisotropic metal it is assumed that condition (7) is valid for definite FS sections, the rest of the FS remaining intact and being described by the branch $\xi_3(\boldsymbol{p})$ [108]. All energies $\xi_i(\boldsymbol{p})$ are reckoned from the Fermi level. Accepting this picture, due to Bilbro and McMillan [108], and admitting an arbitrary interplay between the electron–phonon and the Coulomb interaction [45], we arrive at the general model [108, 109, 126–129] that is also valid for partially-gapped 'Peierls metals'. This model is capable of adequately describing the superconducting properties. The excitonic insulator concept allows electron spectrum gapping of either the CDW or SDW types [37, 39, 45, 77].

As for the excitonic insulator itself, its existence driven by pressure was proved not long ago for $TmSe_{1-x}Te_x$, $Sm_{0.75}La_{0.25}S$, YbO and YbS [625].

Another kind of the excitonic (electron–hole) transition has recently been considered for the 2D model with the appropriate Van Hove singularity and applied to high-T_c oxides [436, 533, 534, 611]. The DW vector $\boldsymbol{Q}$ in this case joins the electronic maximum at $\boldsymbol{k} = (\pi, 0)$ and the minimum at $\boldsymbol{k} = (0, \pi)$ of the 2D Brillouin zone.

We should stress once more that superconductivity coexisting with DWs, driven by the above-described instabilities, becomes possible only because the FS distortion is incomplete, i.e. the intermediate phase at $T_c < T < T_d$ or T_N remains metallic.

It seems that such a situation is best described by the Bilbro–McMillan model [108] initially applied to CDW superconductors and extended to SDW ones by Machida [126]. According to the model, the dielectric order parameter appears only on the distorted FS segments ($i = 1, 2$), whereas the superconducting order parameter spreads over the whole FS ($i = 1, 2, 3$). In the substances concerned the superconductivity is singlet. Due to gauge invariance [44] the spin-independent factor Δ of the superconducting order parameter can be taken as real and positive. On the other hand, the spin matrix of the dielectric order parameter may be either a singlet or a triplet. We shall consider DWs to be pinned, so that coherent sliding phenomena [9, 15, 18] are not taken into account. Thus, the phase of the spin-independent factor Σ of the dielectric order parameter is fixed [45, 626]. The quantity Σ can be real of either sign since its imaginary part would correspond to the yet unobserved states with current-density (spin-singlet) or spin-current-density (spin-triplet) waves [37, 45, 412, 626]. CDWs correspond to the singlet Σ while SDWs are described by the triplet Σ.

The theory of the partially-gapped DW superconductors using the ideas presented above has been developed in detail [73, 105–108, 558, 627, 628]. It has numerous consequences which we will discuss elsewhere.

4. Conclusions

The great body of information analysed in this review indicates the existence of common features for many different classes of superconducting substances. It is shown that they can be adequately described in the framework of the concept of partial electron spectrum gapping. It is interesting that many of the superconductors with the highest T_c values also possess DW instabilities. These are systems with large electron–phonon or electron–electron interactions, leading to many different types of instability of the Fermi surface, in addition to superconductivity. Here we have shown that the Cooper pairing and the various other instabilities compete for the FS and so the presence of DWs is likely to limit possible T_c's from above. This competition results in the appearance of the combined phases where DWs and Cooper pairing coexist and gives rise to a great many new and interesting phenomena regardless of the background microscopic instability mechanisms. The complexity of these competing instabilities leads to the wide diversity of non-trivial phenomena seen in many superconducting materials. Further theoretical and experimental investigations will definitely be required in order to clarify the understanding of these phenomena. Further experimental measurements are necessary to fully explore the occurrence of CDW and SDW phenomena in superconductors and to relate the DW behaviour to the observable experimental properties. More theoretical work is also needed to relate the fundamental DW concepts to the actual experimental results, and to make predictive calculations of phenomena such as T_c or the normal state pseudogap.

Acknowledgments

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