PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Charge Density Waves: Sliding and Related Phenomena in NbSe $_{3}$ and Other Transition-Metal Chalcogenides

J. A. Wilson

Phil. Trans. R. Soc. Lond. A 1985 **314**, 159-177
doi: 10.1098/rsta.1985.0016

Phil. Trans. R. Soc. Lond. A **314**, 159–177 (1985) [159]
Printed in Great Britain

Charge density waves: sliding and related phenomena in $NbSe_3$ and other transition-metal chalcogenides

By J. A. Wilson

H. H. Wills Physics Laboratory, University of Bristol,
Tyndall Avenue, Bristol BS8 1TL, U.K.

The establishment of charge density waves (c.d.ws) in $NbSe_3$ and the phenomena associated with their sliding are examined against the background of behaviour presented for a variety of other stranded transition metal chalcogenides. The work has been set in terms of discommensuration arrays, but with these not so highly defined as in the author's previous work, where the discommensuration array was used as a generator of regular soliton shot noise. The a.c. noise signal is now related rather to creation and destruction of the spatial modulation of the c.d.w. itself, occurring in close proximity to the contacts, with the characteristic length as $\frac{1}{2}\lambda$. The discommensuration array governs the depinning processes from lattice and impurities.

The differences between $NbSe_3$ and *m*- and *o*-TaS_3 have been examined, and related results on $[Ta(Se_4)]_2I$ and other seleno-halides are discussed in conjunction with results from $TaTe_4$, $ZrTe_3$, $ZrTe_5$, etc. to provide an overview of the materials aspect of the field. Suggestions are made for further experiments.

1. Introduction

The understanding of the electronic behaviour of a complex material like $NbSe_3$ requires first a detailed comprehension of its crystal structure, and secondly, the way this feeds through into its band structure. I have discussed the situation for $NbSe_3$ and family at some length in Wilson (1979, 1982). I shall briefly restate the position holding in $NbSe_3$.

The material contains trigonal prismatic chains but these are cross-linked by expanded coordination into slabs to produce a stranded layer compound. The unit cell contains six chains of three different types. Differentiating the types is the width of the back wall of the trigonal prism. The terminology 'yellow' (2.37 Å†), 'orange' (2.49 Å) and 'red' (2.91 Å) identifies the intensity of the Se–Se pairings responsible. Only the first two are sufficiently strong to eject the corresponding anti-bonding p-band above the Fermi level. However, quadrivalence in these $M(X_2)X$ chains is denied by the need to provide further electrons to complete the valence band of the red chain. The residual electron count on the yellow and orange chains in the d_{z^2} conduction band is approximately $\frac{1}{2}$e per Nb. The d_{z^2} band in the red chain is effectively empty. A detailed analysis by Bullett (1982) has affirmed this description.

The yellow and orange chains are not structurally equivalent and further electron transfer arises from the yellow to the orange chain. The high-temperature c.d.w. ($T_0 = 144$ K) is seen as arising in the yellow chains, which lie in continuous planes in the structure. The weaker low-temperature c.d.w. ($T_0 = 59$ K) independently arises on the orange chains, which occur in more isolated duos. N.m.r. results have borne out this interpretation (Devreux 1982).

The wavevectors of the two c.d.ws are temperature independent, very precisely defined, lie on either side of $\frac{1}{4}$, and come very close to adding to $\frac{1}{2}$ (see Fleming *et al.* (1983) for most recent

---

† $1\ \text{Å} = 10^{-10}\ \text{m} = 0.1\ \text{nm}$.

values). It seems best to interpret the situation not in terms of Fermi surface nesting, which is not so well defined, but in direct space terms of electron counting into the available d_{z^2} wavefunctions. The likely phasing of the c.d.ws in the latter, for the approximate electron count of $\frac{1}{2}$, is alternate-pair pairing.

The observed wavevectors indicate that following the yellow to orange interchain electron transfer, charged faults or discommensurations appear in the chain wavefunctions. These occur with closely determined average spacings of 28 atoms in the yellow chain and 24 atoms in the orange chain. Each discommensuration is associated with a charge of $|\frac{1}{2}e|$. What the width of the discommensuration might be is addressed in the main text.

The discommensurations are sufficiently ill-defined as to be readily depinned from the lattice, especially for the orange chain, and then to carry the Peierls sliding mode current. In the best samples electric fields of less than 10 mV cm^{-1} are sufficient to exceed the pinning threshold. As discovered by Fleming & Grimes (1979), there then appears a strongly structured a.c. component to the net current registered in the external circuit.

The following paper is worked throughout in terms of discommensurations (and their dynamic counterpart, solitons) in keeping with our direct observation of the central role these play in the incommensurate states of layered 2H–$TaSe_2$ (Fung *et al.* 1981; McKernan *et al.* 1982). Discommensurations are more likely in the present structure than in 2H–$TaSe_2$ on all counts. It should be remembered that the ease with which their presence was detected in 2 H–$TaSe_2$ was due largely to the areal contrast in the electron microscope images that arises from the broken hexagonal symmetry and the alternation in orientation of the orthorhombic axes across the discommensurations.

A useful collection of recent papers on $NbSe_3$ and similar material is available in *J. Phys., Paris* C-3 (part 2), **44** (1983) which came from the C.N.R.S. meeting in December 1982 at Les Arcs. Also very worth obtaining are the *Proceedings of the International Symposium on Nonlinear Transport and related Phenomena in Inorganic Quasi One-dimensional Conductors, University of Hokkaido, Sapporo, October* 1983. Attention is also drawn to the proceedings to be published from the Budapest conference on c.d.w. sliding (September 1984). The material is to appear in the Springer Verlag series *Lecture Notes in Physics*.

The structures of the materials discussed in the present paper are summarized in table 1.

2. INTERPRETATION OF THE C.D.W. TRANSPORT PHENOMENA IN $NbSe_3$

From the vast amount of work on sliding in $NbSe_3$ can a satisfactory picture of the microsopics be extracted? I would like to suggest the following path.

(a) *The strength of discommensurations and pinning*

At low temperatures there occurs the formation of two arrays of weakly defined discommensurations (d.cs). The d.c. densities are determined by the interchain electron transfer as outlined earlier (Wilson 1979, 1982). The d.cs are denied strong definition because the electron counts in the active chains are too far removed from $\frac{1}{2}$e per Nb, making the d.c. separations too low (Rice 1982); moreover, alternate-pair pairing is a configuration that possesses only weak commensurability energy (Kotani & Harada 1980).

Because the d.cs are not strongly defined they are not themselves strongly pinned by point defects or iso-electronic impurities. It is likely that the laterally cohering d.cs show a comparable

TABLE 1. SUMMARY OF STRUCTURES

300 K	spacegroup	Z	chains per cell	chain axis	in-slab axis	between-slabs axis	T_0/K	approx. λ in M–M	structural reference
$ZrTe_3$	$P2_1/m$	2	2	b	a	c	63	?	Furuseth *et al.* (1975)
$NbS_3(I)$ (1)	$P\bar{1}$	4	2	b	a	c	> 500	2	Rijnsdorp & Jellinek (1978)
$NbSe_3$	$P2_1/m$	6	6	b	c	a	144, 59	4	Hodeau *et al.* (1981)
m-TaS_3	$P2_1/m$ (2)	6	6	b	c	a	240, 160	4	Meerschaut *et al.* (1981)
o-TaS_3	$C222_1$ (2)	24	24	c	b	a	215 (lock in 140, 50)	4	Tsutsumi *et al.* (1978)
$TaSe_3$	$P2_1/m$	4	4	b	c and a diagonal		pre-super-cond. at 2 K?	—	Bjerkelund *et al.* (1966)
VS_4	$C2/c$	8	2	c	—	—	> 300	2	Allmann *et al.* (1964)
$TaTe_4$	$P4/mcc$ (subcell)	2	1	c	—	—	> 800	3	Selte & Kjekshus (1964)
$[TaSe_4]_2I$	I422	4	2	c	—	—	263	2	Gressier *et al.* (1982)
$[NbSe_4]_3I$	$P4/mnc$	4	2	c	—	—	> 300	3	Meerschaut *et al.* (1977)
$[NbSe_4]_{10}I_3$	$P4/mcc$	2	2	c	—	—	285	$2\frac{1}{2}$	Meerschaut *et al.* (1984)
$ZrTe_5$	Cmcm	4	4	a	c	b	84 (ρ peak 140K)	?	Furuseth *et al.* (1973)

(1) Type III NbS_3 shows broad transitions around 240 and 160 K.

(2) Presently being revised by M. Tanaka as B2/m and $Pn2_1m$ respectively, with the monoclinic cell of the former embracing 12 chains.

degree of lattice self-pinning. Being associated with a $d_{z^2}^2$ electron configuration, as discussed earlier, each d.c. plane will be associated with some elongation in local cell geometry (larger b/c; compare c/a in d^2 $MoSe_2$ against d^1NbSe_2 (Wilson & Yoffe 1969)).

(*b*) *The materials aspect.* $NbSe_3$ *in relation to o- and m-*TaS_3

In the orange chain in $NbSe_3$ the d.cs are only 6λ or 80 Å apart, while in the yellow chain they are 7λ or 93 Å apart†. Also the yellow chains lie in continuous planes parallel to 'a_0'. Accordingly there is better definition of the yellow d.cs, stronger pinning and a higher characteristic depinning energy. In *o*-TaS_3 the d.cs are yet further apart (180 Å at onset), and also the lattice is more easily deformed and polarized because of the greater mass cation and more ionic anion (cf. $TaSe_2$ against NbS_2 and $NbSe_2$ (Wilson *et al.* 1975)). Hence depinning does not occur so readily. In correspondence with 1T–TaS_2 (Inada *et al.* 1983; Furukawa *et al.* 1984), and with disordered 1T-(Ta/Fe)S_2 (DiSalvo *et al.* 1976) and $FeNb_3Se_{10}$ (Hillenius & Coleman 1982), the residual carriers in *o*-TaS_3 become localized on further cooling because of the now quite strongly perturbed lattice coming with the c.d.w.–p.s.d. and the Fermi surface gapping process (Ido *et al.* 1979; Mihaly *et al.* 1984).

In regard to *o*-TaS_3 note should also be taken here that q does *not* lock-in along the chain at 140 K as is so often presumed. Even Wang *et al.* (1983) propagate this misconception, despite it being clear from their own data that it is lateral lock-in to $\frac{1}{8}a_0^*$ that occurs at this temperature. Longitudinal lock-in does not occur until *ca.* 60 K. Each event is accompanied by a rise in resistivity resulting from the enhanced gapping coming with commensurability (Higgs & Gill 1983).

A further very relevant observation is of the situation in *m*-TaS_3. Here the orange and yellow chains are structurally much more similar than in $NbSe_3$ (Meerschaut *et al.* 1981). This will mean less charge transfer between them. Indeed both q are closer to $\frac{1}{2}b_0^*$ (Wang *et al.* 1983). It should be noted, however, that the q dispositions are interchanged relative to $NbSe_3$, as now it is the yellow chain (with the higher T_0) where $q > \frac{1}{4}b_0^*$. Also, appropriate to the heavier lattice, the c.d.w. onset temperatures, again as in *o*-TaS_3, are higher in *m*-TaS_3 than in $NbSe_3$. For like reasons to those given for *o*-TaS_3, sliding in *m*-TaS_3 is more difficult to attain than it is in $NbSe_3$ (actually even more so than in *o*-TaS_3: E_T is *ca.* 1 V cm^{-1}) (Maeda *et al.* 1983).

That the wavevector should move to commensurability in *o*-TaS_3, yet not in *m*-TaS_3 (or $NbSe_3$) is an important feature. For 2H–$TaSe_2$ we have observed and reported on the ejection of well-defined d.cs in the drive toward $3a_0$ commensurability (Fung *et al.* 1981). For all these three materials q at onset has a very comparable incommensurability parameter $\delta \approx 2\%$. Maybe the still unrefined structure of *o*-TaS_3 contains only one active chain type (like $FeNb_3Se_{10}$, where q also moves towards $\frac{1}{4}$). Recall that $NbSe_3$ and *m*-TaS_3 undergo inevitable interchain charge transfer, with a resultant non-rational fractional electron count per cation in their orange and yellow chains; destroying the charged d.cs that then ensue is more difficult than otherwise. Even for the relatively uncharged d.cs in 2H–$TaSe_2$, d.c. elimination is retarded and does not proceed according to classical Landau theory predictions (Fleming *et al.* 1980).

---

† These numbers come from the revised q-vectors given by Fleming *et al.* (1983) (treated as in Wilson (1982), but for non-paired d.cs).

(*c*) *What might happen at depinning in* $NbSe_3$

Depinning of the d.cs, and consequently the c.d.w. from the lattice and its faults (point, line and planar, including the crystal bounds and contacts) can never, in its initial stages, be laterally coherent across the *ca.* 50 μm width of the sample (Matsukawa & Takayama 1984). The orange chains in particular are very weakly coupled. However, along the chains there is every indication that it is correct to expect rather little faulting of the c.d.w.–p.s.d. superstructure. The charge in the c.d.w. and its d.cs secures this order and internal rigidity.

The c.d.w. must depin first in those places where its amplitude is least; namely in close proximity to the contacts, for it is clear that the c.d.w. (i.e. its spatial charge modulation) cannot be supported by the material of the contacts. Moreover, where the current is injected into the sample is where the local field strength is likely to be greatest.

As various preliminary depinnings occur the d.cs will move towards enhanced regularization of the array, using their stored energy of elastic distortion. Anyone who has seen the video of d.c. motion during array growth and decay in 2H–$TaSe_2$, obtained by S. McKernan (shown at EPS Condensed Matter Division Second Annual General Conference (c.d.w. satellite), March 1982; see McKernan *et al.* 1982) will have seen how even in that system the whole array of d.cs is intercoupled. There is considerable 'shake-up' in each depinning event. For $NbSe_3$ with its charged d.cs the coupling should be stronger.

It is also feasible that in the propagation of a d.c. as a soliton the balance between its electronic and structural aspects will alter. While moving, the lattice response around the d.c. is likely to be less. The static 'friction' is greater than the dynamic 'friction'. If tunnelling were to occur it is probably from the weakly defined lattice-bound d.c. state to the dynamic soliton state. The lattice cooperatively reacts, and the impurities then play a secondary role. The latter of course do provide a prime source of the white noise peak generated beyond the depinning threshold (Zettl & Gruner 1983). The depinning barrier is clearly of such a magnitude as to be within the range of thermal energies *ca.* 30 K or 3 meV. This is the sort of energy associated with the phason and amplitudon modes of a weakly defined incommensurate c.d.w. (Fenton 1981) plus distortions thereof (Giuliani & Overhauser 1982).

(*d*) *Do discommensurations exist in* $NbSe_3$?

I have earlier been drawn, though not without some reservation, to extend the alternate-pair pairing model to the level of defining a strong d.c. lattice in $NbSe_3$ (Wilson 1979, 1982). The construct was employed in accounting for the highly coherent a.c. signal observed during sliding as regular soliton shot noise. However, I now believe that the weak d.c. array discussed above provide a correct description of the phenomena. It is very unlikely that a strongly defined array could avoid pinning irregularities from impurities to the level now demanded by the data. The d.c. lattice was originally introduced to account for the high-definition temperature-independent q-values appearing in high-intensity X-ray measurements (Fleming *et al.* 1978, 1983). Note that the construct implies that the commensurate patch sets the d.cs, rather than that the charged d.cs anchor the patch. As the situation has evolved it now seems preferable to regard the ultra-high degree of order apparent as being gained through regularization induced in the weakly pinned array by the X-ray beam itself. This would still account for the q-vectors being found to be independent of temperature (i.e. c.d.w. amplitude) and field (even into sliding), while at the same time permitting stronger high 'harmonics' not to be observed (specifically $3q$): regularity in the array is achieved without dramatic perturbation of the waveform.

The same regularization of the array is likely to ensue from electron bombardment in electron microscopy experiments (Fung & Steeds 1980; Steeds *et al.* 1983; Chen & Fleming 1983). It is, however, possible that continued irradiation and pumping may cause the chemical condition of the sample to deteriorate (Chen & Fleming 1984). Any deterioration in quality of the sample, and hence in the fault-free character of the phasing of the c.d.w., is a contributory factor to the twinkling and coarse fringes observed in dark-field imaging. If the d.c. array itself is at all evident in these experiments it is the very faint array of fine fringes that should be considered (Wilson 1982).

For less excited conditions even an array of weak discommensurations must inevitably take on a somewhat irregular aspect while sliding through a crystal from the action around the impurities, macro-faults, etc. Higgs & Gill (1983) have expressed their more recent pulse transport work on *o*-TaS_3 (memory effects, etc.) in the appropriate terms of individual d.cs being draped around and forced through the effective obstacles. In a similar way to such observations for 2H–$TaSe_2$, the specific heat anomalies and latent heats (Tomic *et al.* 1981) and the lossy Young modulus changes (Brill 1982) all signal collapse in the d.c. array order.

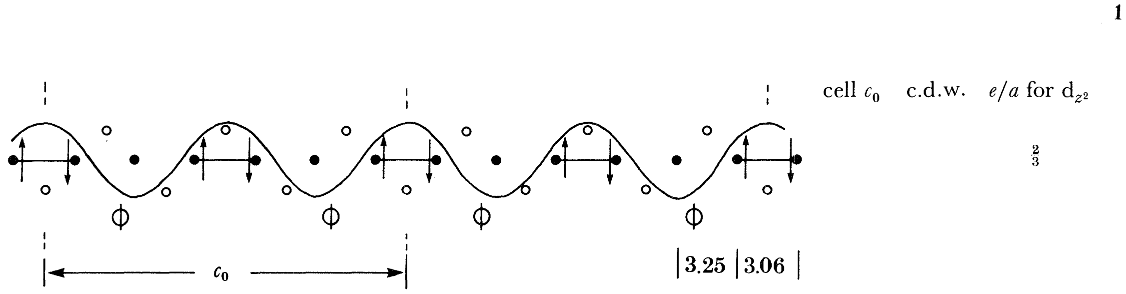
(*e*) *How does the condition in* $NbSe_3$ *match that in the tetra-seleno-halides?*

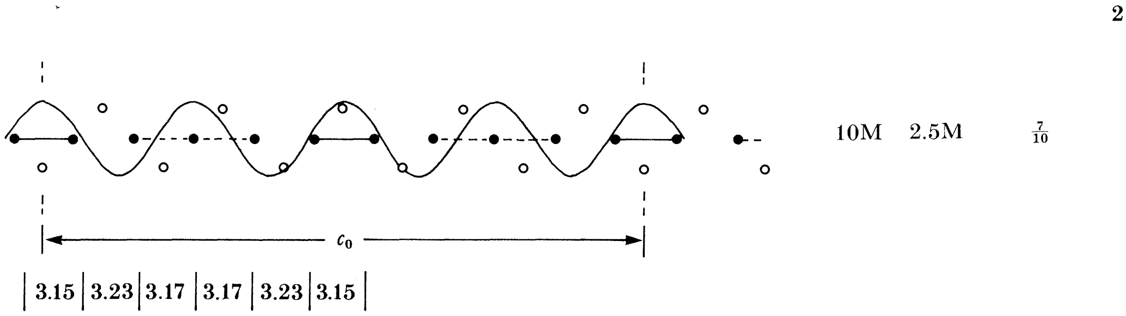
Although the chains of $[Ta(Se_2)_2]_2I$ hold the same electron count per cation as the yellow and orange chains in $NbSe_3$ (namely $\frac{1}{2}$), it does not form as suitable a starting point as other members in this family like $[Nb(Se_2)_2]_3I$ and $[Nb(Se_2)_2]_{10}I_3$ (Gressier *et al.* 1984; Meerschaut 1983). The distortion in the Ta compound that occurs at 263 K is not one standing in self-evident sympathy with M–M bonding for its given supply of d_{z^2} electrons.

By contrast there does appear along each of the two chains per unit cell in $[Nb(Se_2)_2]_3I$ at room temperature a p.s.d. appropriate to the d_{z^2} electron count (figure 1). The $\frac{2}{3}$e per Nb left in the d_{z^2} bands is sufficient to pair $\frac{2}{3}$ of the Nb as shown. The alternation of one long (3.25 Å) and two short (3.06 Å) distances is so marked that a semiconducting gap of 0.2 eV arises in the d_{z^2} manifold. The material then shows no sliding, and is akin to $Nb(S_2)S$ [type 1] (Rijnsdorp & Jellinek 1978) wherein there is full pairing under an e/a count of 1 (as for rutile-type VO_2).

Following the above, the more exotic stoichiometry of $[Nb(Se_2)_2]_{10}I_3$ leads to a p.s.d. showing three different Nb–Nb lengths (figure 2). This p.s.d. apparently undergoes some subsidiary distortion below 285 K, where a resistivity anomaly is found. Since sliding then occurs quite easily ($E_T^{\min} \approx 1\ \mathrm{V\ cm^{-1}}$) this final condition is likely not to be commensurate (as *o*-TaS_3 emerged not to be commensurate in its sliding régime (Wang *et al.* 1983)).

Finally, for $[Ta(Se_2)_2]I$ the basic structure is, unlike the other two compounds, found not to be distorted at 300 K, despite an e/a count of $\frac{1}{2}$. A uniform chain is reported, free from any bond-centred c.d.w. (figure 3). The benefit of an alternate-pair paired c.d.w.–p.s.d. phasing (as postulated for $NbSe_3$ at low temperatures) is negated by the anion arrangement in the seleno-iodide. The basic cell has itself, unlike in $NbSe_3$, a repeat length of four metal atoms. The metal chain in this iodide shows then at 300 K a uniform M–M spacing of 3.206 Å. This does not mean $[Ta(Se_2)_2]_2I$ is simply a one-dimensional metal with a quarter-filled band, even at room temperature. Note that the material is always diamagnetic, which we return to in §3. Moreover, as with the 10/3 compound, just below room temperature it goes into an incommensurate condition showing sliding and noise phenomena ($T_0 = 263$ K and





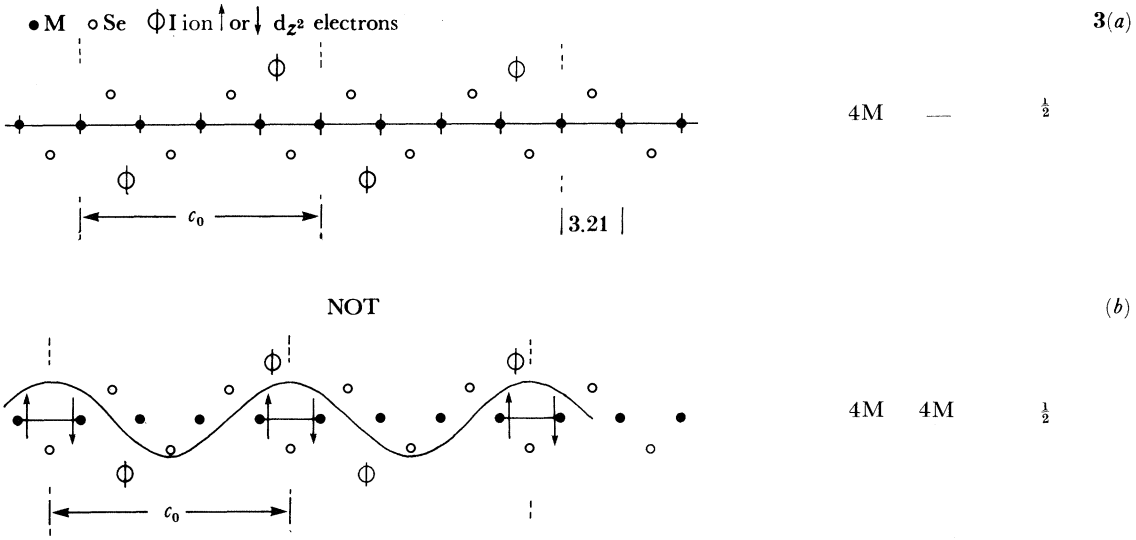


Figure 1. C.d.w. in $(NbSe_4)_3I$ at 300 K.

Figure 2. C.d.w. in $(NbSe_4)_{10}I_3$ at 300 K.

Figure 3. (*a*) Uniform state in $(TaSe_4)_2I$ at 300 K. (*b*) The unfavourable alternate-pair paired state.

$E_T^{\min} \approx 1$ V cm^{-1}). In both compounds the resistance rises monotonically on cooling. Also, the a.c. noise is not as well-structured as in $NbSe_3$. Both features are undoubtedly a reflection of the weaker interchain coupling in these seleno-halides. The lateral cation–cation distance is $\frac{1}{4} \times 6\frac{3}{4}$ Å. The fact that coherent noise is seen at all in such circumstances is a result that must be borne in mind.

Easy sliding in $[Ta(Se_2)_2]_2I$ was as perplexing as it was in *o*-TaS_3 until it was shown that the material below 263 K is not commensurate. How this incommensurateness can arise from a semi-metallic band structure will be outlined in §3*b*.

Anything to be said about sliding and noise in $NbSe_3$ will have to be appropriate to the results from these materials too (and others like $K_{0.3}MoO_3$). Of the c.d.w.-p.s.ds that have shown sliding so far, the orange c.d.w. in $NbSe_3$ remains by far the easiest to depin. This arises because (1) the material is the least ionic, (2) the structure has a sink for impurities (the red chain), (3) the chains of the material are strongly cross-linked into pairs and then into slabs aiding cooperative action, (4) the system is crystallographically and chemically well-formed.

(*f*) *What is the mechanism for the generation of the a.c. signal on sliding?*

In the best samples the a.c. 'noise' signal is a very appreciable part of the total c.d.w. current just beyond threshold, and is well defined in terms of frequency (Oda & Ido 1983, fig. 7). It is clearly the product of a coherent process, but what? Impurities and crystal faults break the rather fragile lateral coherence, but it is evident that longitudinally the process remains robust. Many domains simply cause heavily scrambled signals contributing to the accompanying white noise (Mutka *et al.* 1984), which tails off with frequency in a similar way to the harmonics of the well-structured signal (Richard *et al.* 1982; Weger *et al.* 1982). The heavy harmonic content to the signal implies a pulse rather than a smoothly varying generator. This was one of the original attractions of regular soliton shot noise.

Ong & Verma (1983 *a*, *b*) have confirmed, through a permutation of the roles and arrangement of current and voltage contacts, that the a.c. noise signal is indeed occurring to a great extent in some contact-sited process. However, as indicated earlier, it is rather unlikely that the necessary level of coherence will be maintained in the d.c. array to provide the action in question. We have seen that the same effects manage to survive for *o*-TaS_3, where pinning and E_T are quite strong (Zettl & Gruner 1983). However, what is feasible is that the lateral wave profile, however contorted, will advance systematically as a single coherent domain under the influence of the longitudinal rigidity of the c.d.w. and the elastic cross-coupling of the d.cs (Matsukawa & Takayama 1984). At each step the equilibriated d.c. array is corporately strained about the active pinning features to the point of cooperative release. The passage of a d.c. passed each point advances the whole c.d.w. by one lattice spacing. The c.d.w. accordingly presents itself at the contact, whatever detailed shape it may have, in a pulsed succession of segments with the length of one atom spacing (b_0 in $NbSe_3$).

Now at the contacts the spatial modulation of the c.d.w. has to disappear; it cannot be supported by the material of the contact. The detected a.c. current is, of course, uniform in space, although periodic in time. I believe now that the temporal modulation of the externally monitored voltage or current arises simply from the act of annihilation (creation) of the spatial modulation component to the total current at entry into (departure from) the contact material. The c.d.w. advances atom length by atom length along each strand. The requisite annihilation span, is however, in intervals of two c.d.w. quadrants, as indicated in figure 4.

The fact that the creation of the c.d.w.–p.s.d. at input and its destruction at output are likely to be lossy processes with respect to the lattice means that there will be a net energy imbalance capable of being made up from the external voltage when the current is constant. The most accurate assessment of the gradient $I_{\text{c.d.w.}}/f = n_c eAl$ made by Monceau *et al.* (1983) indeed suggests that the relevant length l is not b_0 or $\lambda = 4b_0$, but $\frac{1}{2}\lambda$.

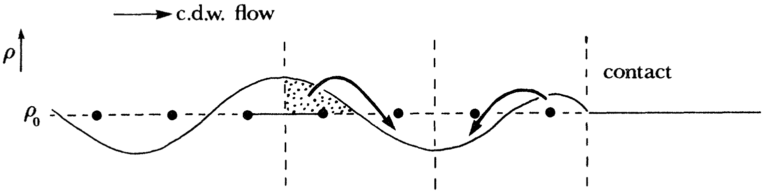


FIGURE 4. Origin of characteristic length of $\frac{1}{2}\lambda$ in a.c. noise signal. Annihilation (and creation) of c.d.w. occurs by pairs of quadrants when leaving (entering) $NbSe_3$.

$J_{\text{c.d.w.}}/f$ itself directly varies as n_c, which is approximately proportional to the amplitude of the c.d.w., following the structural order parameter (see figure 3 in Oda & Ido (1982) and figures 8 and 9 in Zettl (1983)). The Hall (Kawabata *et al.* 1981; Tessema & Ong 1981), and more recently the Seebeck results (Stokes *et al.* 1984), also certify that the whole process is related to c.d.w. transport. The Seebeck results reveal that phonon drag is significant at low temperatures. It is during cooling to low temperatures, of course, that E_0, the characteristic field in the phenomenological formulae of sliding, rises along with E_T. This stronger effective pinning is reflected in normalized plots of the extra conductivity against field strength by their deviation at low field strengths from a universal curve (see figure 2 in Oda & Ido 1982).

For r.f. induced sliding (Gruner *et al.* 1980) the natural interpretation would seem to be that synchronization is effected in the attempt rate toward corporate breakdown of pinning and permits the c.d.w. *in toto* to advance unit cell by unit cell. To achieve sustained sliding the impressed frequency has to be greater than the 'washboard' frequency, the reciprocal of the time spent in passage through each cell. The likely consequence of a cooperative attempt at passage is the reduction in *size* of the effective barrier. This is distinct from the notion of photon-assisted tunnelling (Seeger *et al.* 1984). Pulse work has shown there is a short induction time (*ca.* 10^{-7} sec) before achieving sliding (see figure 6 in Oda & Ido 1983).

If the above notion of how the a.c. noise is generated is right it may well be possible to arrange matters so that the noise can be eliminated in a favourable crystal. Possibly the c.d.w.–p.s.d. creation and annihilation can be made less severe by using $NbSe_3$ as its own contact material. This might be attempted by thinning the centre section of a fibre so that there $E > E_T$, while towards the ends $E < E_T$. Alternatively only the centre section of a crystal might be cooled below T_0. The weighting in the total current between c.d.w. and normal components can then transfer over a considerable length of crystal.

(*g*) *Summary of c.d.w. transport phenomena in* $NbSe_3$

(i) Charged d.cs are present because of interchain charge transfer and the drive towards commensurability.

(ii) The d.c. arrays are weakly defined, and so weakly pinned; impurities and probably the discreteness of the lattice effect the pinning.

(iii) The static d.c. arrays can be regularized by excitation.

(iv) The entry into sliding is cooperative and is probably precipitated through shake-up in the d.c. arrays.

(v) The sliding is stepped, with a considerable dwell time of *ca.* 1 μs (which is proportionately longer at low sliding rates).

(vi) Applied a.c. of period less than the dwell time coordinates the jump attempts across the sample and promotes sliding at lower applied fields.

(vii) During dynamic sliding conditions the array is inevitably irregular and can not provide the source of the a.c. signal.

(viii) The noise signal is generated at the contacts as the amplitude of the c.d.w. is forced to zero for transit to and from the external circuit.

(ix) Breakdown of lateral coherence in the advance rate of the c.d.w. by 'domain' formation leads to a multiplicity of signal frequencies and ultimately to white noise.

(x) Sliding is easy to attain in $NbSe_3$ because it is highly covalent, not truly one-dimensional, and has a means of keeping impurities out of the chains. It also shows good stoichiometry.

(xi) Note that discommensurations, contact processes, impurities and the bulk c.d.w. all play a role in the above description of the sliding phenomena.

3. $TaSe_3$, $ZrTe_3$, $ZrTe_5$, $NbTe_4$. More as before, or something new?

(*a*) $TaSe_3$

This has only 'orange' and 'red' chains (see Wilson 1979). The result is that both tantalum atoms behave pentavalently. Were it not for a slight overlap between the antibonding p-states from the red chain at the top of the valence band with the bottom of the d_{z^2} conduction band, we would have a semiconductive compound. Band structure calculation (Bullett 1979) showed a very minor indirect overlap, but Shubnikov–de Haas experiments (Fleming *et al.* 1978) reveal a content to the Fermi sea that implies greater p–d overlap than for the calculated bands. This is typical of most calculations done in the framework of the local density approximation. Typically these overestimate the p–d band separation by *ca.* 0.25 eV for such compounds (cf. $TiSe_2$ in Boehm & Isomaki (1982)). $TaSe_3$ is only just diamagnetic (DiSalvo *et al.* 1980). The carrier content clearly is somewhat greater than in $TiSe_2$, and supports superconductivity. Unlike $TiSe_2$, where the overlap is indirect, there is no positive evidence of any e–h driven instability with accompanying lattice distortion. The only exotic behaviour reported for $TaSe_3$ is a large resistivity hump in a few samples examined by Tajima *et al.* (1983, 1984) just before they became superconducting. With one-dimensional excitonic mediation just a possibility (since T_s is 2 K while the number of carriers is quite small) we tried to duplicate this result but without success (W. G. Herrenden Harker and N. Tothill, unpublished work (1984)).

(*b*) $[Ta(Se_2)_2]_2I$

As noted above the electron count left over to enter the d_{z^2} bands in this material is $\frac{1}{2}$e per Ta atom. Note there are two equivalent chains per unit cell and 4 Ta in each are encompassed by the unit cell (Gressier *et al.* 1982). The resistivity at 300 K is rather high (*ca.* $10^{-3}\ \Omega$ cm (Maki *et al.* 1983, Wang *et al.* 1983)), but the material has a net diamagnetism comparable to that of $TaSe_3$ (Kikkawa *et al.* 1983) and so the free carrier count cannot be too low. As discussed above an important feature of this material is that at 300 K the chain is uniform (Gressier *et al.* 1982). However, what again has attracted attention to the material is that below $T_0 = 263$ K it displays a c.d.w. and sliding phenomena (Maki *et al.* 1983; Wang *et al.* 1983). In this state the wavevector becomes slightly displaced from the commensurate condition along all three axes (0.05, 0.05, 0.085 (Fujishita *et al.* 1984)). Reference to figure 5 shows how the projected band structure might lend itself to energy gain from a p.s.d. wavevector close to the

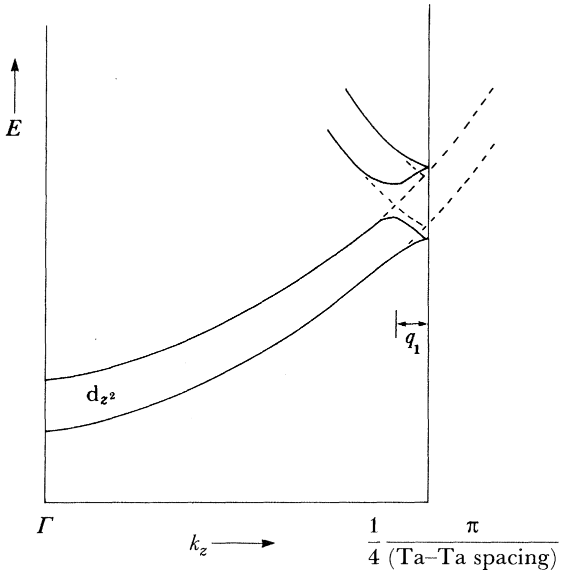


FIGURE 5. Possible source of small-q i.c.d.w. in $(TaSe_4)_2I$. The two closely spaced d_{z^2} bands come from the two widely spaced chains per unit cell.

fundamental wavevectors of the basic cell of 8 Ta atoms. As figure 5 indicates the effect is perceived to stem from the fact that there are two chains per unit cell. In this case, since there is very weak interaction between the two chains, the two d_{z^2} bands ($\psi_A \pm \psi_B$ combinations) will be rather close in energy by contrast with the situation in $NbSe_3$. The 4 electrons available are sufficient to fill two bands to the zone boundary defined by the chain repeat length of 4 atoms. However, with the two bands a metallic situation will still result if, as seems likely in the high symmetry of the parent structure, the two bands in question have symmetries belonging to different representations (i.e. they can cross without interaction). Time reversal symmetry enforces degeneracy on the face of the Brillouin zone. Away from the high symmetry point, however, the subsidiary periodicity is able to spring the non-interacting bands apart and we have an electronic energy gain. Experimentally it is found that ρ rises rapidly below the transition temperature with an activation energy of *ca.* 0.25 eV, implying strong disorder localization of whatever F.s. might have remained ungapped by the p.s.d., as in *o*-TaS_3.

The incommensurate periodicity above probably primarily involves lateral rather than longitudinal shifts of the Ta atoms, since even in the basic structure the Ta atoms do not sit at the centre of the $Ta(Se_2)_2$ rectangles. The wavevector of the distortion is reported to be temperature independent, which may be due at 8.5% to its being farther from lock-in than for any c.d.w. reported to date.

At room temperature there is no evidence from Ta 4f X.p.s. (Kikkawa *et al.* 1983) that the Ta sites are other than equivalent, in terms of valence, and this feature may well continue to be true below T_0. A reduced Ta periodicity via the mixed valence sequence

$$\vdots\,\mathrm{Ta}^{5+}\text{–}\mathrm{Ta}^{4+}\,\vdots\,\mathrm{Ta}^{5+}\text{–}\mathrm{Ta}^{4+}\,\vdots$$

does not match the basic structure, while tendency to establish the sequence

$$\vdots\,\mathrm{Ta}^{5+}\text{–}\mathrm{Ta}^{5+}\text{–}\mathrm{Ta}^{4+}\text{–}\mathrm{Ta}^{4+}\,\vdots$$

(as suggested for $NbSe_3$) is not advantageous, since the structure already holds this periodicity.

Given the scheme suggested for $[Ta(Se_2)_2]_2I$ it is not difficult to see why d.c. and a.c. induced c.d.w. sliding occur fairly easily ($E_0 \approx 2$ V cm^{-1}). The highly one-dimensional crystal structure means though that there is greater fragmentation into domains than for $NbSe_3$, and so the a.c. noise signal is much less clean (Maki *et al.* 1983; Wang *et al.* 1983).

(*c*) $Ta(Te_2)_2$

From this formulation, appropriate to the tetratelluride structure (Selte & Kjekshus 1964), we see that the d_{z^2} electron count is 1 per Ta site. Contrary to the previous compound the Te_2 units (2.87 Å) now are located so as to bind the Nb chains together. Actually, because of the stoichiometry the Nb chains still are rather far apart (Nb–Nb$\parallel c$, 3.42 Å, as against $\perp c$, 6.50 Å), so that, with regard to the d_{z^2} band, a one-dimensional band structure is still to be expected.

Because of the square antiprism coordination the chain axis repeat of the basic structure is two coordination units. This has the effect of making M–M pairing under the d^1 count less attractive than in NbS_3 or VO_2 with a repeat of one. (But note that $V(S_2)_2$ manages to pair (Allmann *et al.* 1964).) Bullett (1984*a*, *b*) has presented a Nb-paired band structure, and it is apparent that for the prevailing tetragonal structure there is no clean dropping away of a full bonding sub-band. Strong overlap occurs along the vertical edges of the Brillouin zone. The two d_{z^2} bands (i.e. bonding and antibonding) are mixed both with each other and with the main valence band. The latter circumstance is difficult to avoid with a telluride, where the state involved is the extensive 5p.

In fact it is found that the favourable option for distortion in $TaTe_4$ is to adopt a $2a_0 \times 2a_0 \times 3c_0$ supercell containing 24 Ta atoms (Boswell *et al.* 1983). This 6-atom chain-axis repeat is similar to that present in $[Nb(Se_2)_2]_3I$ (see figure 1). In $NbTe_4$, however, the electron count does not suit a distortion like the latter, unless p–d overlap were to boost the d_{z^2} electron count to $\frac{4}{3}$. Then, however, the accompanying generation of p-band holes is most unpromising since it would lead to quite isotropic conductivity in the dense Te sublattice, and this is not found (Gill, unpublished work (1983)).

The alternative is to allow the Ta atoms to generate the superlattice by moving away from the coordination unit centres not along the chains but laterally, as postulated for $[Ta(Se_2)_2]_2I$. Note that even VO_2 does this to its 'pairs' (especially if it is Cr-doped). It is known that the square antiprism is susceptible to such distortion (Kepert 1972). It then would become possible to generate the 2 × 2 geometry perpendicular to the chains by displacing the cations towards the soft untethered edge of the coordination unit in the pattern shown in figure 6*a* in keeping with the observed retention of the crystal tetrad axis. The arrangement has the benefit of keeping all chains equivalent. It avoids the supercell geometry suggested by Boswell *et al.* (1983), which for a primitive space group must have three crystallographically if not chemically inequivalent chains, in the awkward population ratio 1:1:2 (figure 6*b*).

There remains the question of the *c*-axis geometry with its threefold superperiod. First it should be noted that the distortion does not succeed in producing an insulating situation as did $[Nb(Se_2)_2]_3I$. The material is an excellent conductor (comparable to 2H–$TaSe_2$). As was stated above this conductivity is probably not due to p-band holes since it is very anisotropic. Because we never find $TaTe_4$ in its undistorted condition we cannot exclude the possibility that one pocket of electrons has served to 'nest out' the p-band holes ($\frac{1}{3}h + \frac{1}{3}e$) to leave the original unit electron count per cation. However, in the ditelluride $TaTe_2$ the p-band appeared not to reach the Fermi level, and in the tetratelluride $TaTe_4$ the occupied p states are stabilized further through Te–Te bonding.

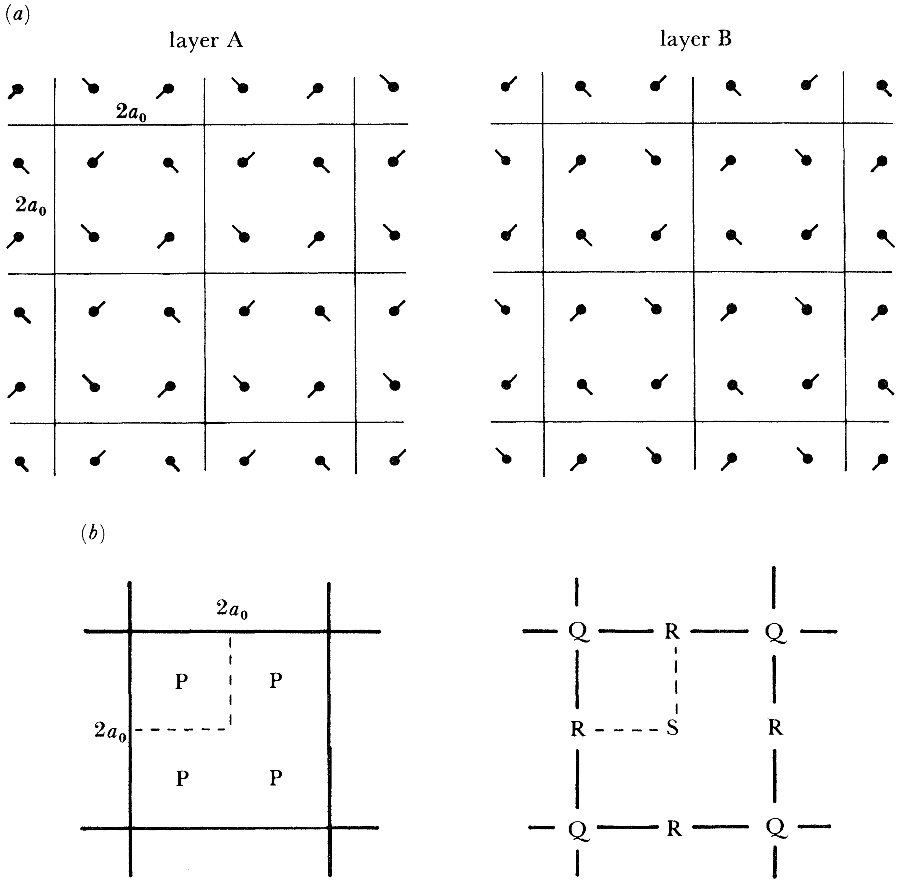


FIGURE 6. (*a*) Lateral displacements of Ta atoms postulated to gain $2a_0 \times 2a_0 \times 3c_0$ supercell of $TaTe_4$. The *c*-axis in six layer sequence AOBBOA. Layer A shown on left, layer B to right, layer O undisturbed. (*b*) Two settings of basal plane supercell. To left, as postulated in (*a*) with all chains physically equivalent P. To right, the earlier favoured register of the cell on the lattice, with its three kinds of chain. (R:S:Q, 2:1:1).

On the other hand, we may proceed from Bullett's (1984*a*, *b*) calculation for the simple M–M paired state to nest out hole and electron pockets in the d-bands (about 000 and 110 respectively) by vectors 110. Then, auxilliary to this, the *c*-axis periodicity of 3 (i.e. 6 Ta) leads to further gapping of these pockets in that direction also. The residual carriers yielding the observed conductivity should then be from the d-band hole pocket about 111. The *c*-axis pairs A–A and B–B in the interlayer sequence A/AOBBOA/A will be in phase between chains as in $(NbSe_4)_3I$.

Under pressure $TaTe_4$ collapses to a structure with only 72% the volume of the normal structure (Bjerkelund *et al.* 1968) The action is not unlike that in ReO_3, eliminating the large voids in the structure.

The Te–Te distance that bound the chains together (2.87 Å) into the original open square network is comparable to that in $MnTe_2$(2.75 Å), or in $ZrTe_3$(2.76 Å) discussed below (Furuseth *et al.* 1975).

(*d*) $Nb(Te_2)_2$

Unlike $TaTe_4$, $NbTe_4$ is strongly incommensurate up the chain at room temperature, only becoming like $TaTe_4$ below *ca.* 50 K (Boswell *et al.* 1983). There is a linear and apparently continuous change in wavevector (and hence discommensuration spacing) through the system (Nb/Ta)Te_4, with commensurateness seemingly reached a little before $TaTe_4$. $NbTe_4$ is 3% incommensurate, making the d.cs 60 coordination units apart on average. D. Eaglesham of this department has seemingly resolved the d.c. arrays, and will report on this system in due course.

The absence of sliding indicates a well-defined, well-pinned d.c. array, owing to the larger d.c. spacing and greater electron count than in the materials above. However, given what occurs for $HfTe_5$ (see below) it would be surprising if sliding is not attained under higher fields and frequencies.

(*e*) $Zr(Te)_2Te$

$ZrTe_3$ with the same stoichiometry and basic structure as $ZrSe_3$ is quadrivalent. The latter has a semiconducting gap somewhat larger than in $ZrSe_2$. Following the evidence in the absorption spectra of $ZrSe_3$ reported by Kurita *et al.* (1981) there is a minimum indirect gap of 1.5 eV, while in $ZrSe_2$ E_g^{ind} is 0.9 eV (Greenaway & Nitsche 1965). The strong excitonic feature in the reflectivity of $ZrTe_3$ (Bayliss & Liang 1981), upon comparison with that in $ZrSe_3$, points to a typical reduction in p–d energy separations of about 0.5 eV from triselenide to tritelluride. This approach thus leads to an estimate for the indirect gap in $ZrTe_3 \approx 1.0$ eV.

However, in conflict with this conclusion electrical measurements (Takahashi *et al.* 1983, 1984) indicate a very considerable number of carriers in $ZrTe_3$, its room temperature resistivity ρ (chain) being only $2 \times 10^{-4}\ \Omega$ cm, with decrease to low temperatures. Any semiconductive band structure must then be associated with a very high level of non-stoichiometry or defecting, comparable to TiS_2 (Wilson 1978). The negative sign of the Hall coefficient R_H may indicate a defective Te content; tellurides are often Te-poor (cf. $ZrTe_2$).

However, this simple scenario looks suspect because the magnitude of R_H corresponds on a single carrier basis to 3.5×10^{21} cm^{-3}! One is encouraged then to reappraise the situation, especially in the light of the interesting transition that occurs at 63 K.

At this point let us note that something looks amiss in the band calculation presented by Myron *et al.* (1981) for $ZrSe_3$. The fault may possibly lie in an incorrect definition of the k-space vectors. The calculation presents the lowest conduction band (c.b.) states as being the anti-bonding p-states of the Se–Se pair, far too low for these. One should note, aided by the adoption of the B-variant of the $ZrSe_3$ structure (see figure 3 in Wilson 1979), that the Te–Te distance in $ZrTe_3$ is almost as short as in $MnTe_2$.

With the B variant the coordination number drops from 8 to 7, and the effect is to couple up pairs of Zr chains. This should have the effect of making the lowest of the two d_{z^2} bands $(\psi_A + \psi_B)$ drop away more sharply from the bottom of the c.b. than in the A-variant materials. In view of what Bullett (1982, 1984*b*) found for the $NbSe_3$ chain pairs, for $ZrTe_3$ there could arise splittings in excess of 0.5 eV.

It may just be possible then to envisage some slight p–d overlap being gained in $ZrTe_3$, probably between a band maximum away from Γ and a single minimum at Γ (see $NbSe_3$). However, the Drude edge we find in the vicinity of 2 μm (Maule 1984) would imply an electron–hole concentration *ca.* 5×10^{20} cm^{-3}. This would call for overlap of *ca.* 0.25 eV, comparable with that present in $TiSe_2$ (Wilson *et al.* 1978). One might hope to resolve this extrinsic–intrinsic question by Hall measurements under pressure, as was done for TiS_2 and $TiSe_2$ (Friend *et al.* 1982).

The reason that the matter is of some current interest is the transition uncovered at 63 K. This is interesting in that strong anomalies show up in only the lateral conductivities. The threefold increase in R_H is reminiscent of a c.d.w. transition, but the dip and rise in Young modulus is much larger than in $NbSe_3$. One possibility is a variant conversion occurring in martensitic fashion. The transition is marked by a small though definite contraction in the chain direction (W. G. Herrenden Harker, unpublished work 1984) and two series of extra spots appear in electron diffraction (Eaglesham *et al.* 1984). A band structure clearly must be produced for the B-variant before one is in a position to consider the alternative interpretation of electron–hole coupling, as in $TiSe_2$ (Wilson & Mahajan 1977). How such coupling might proceed by employing defect states has not been considered.

(*f*) $ZrTe_5$ *and* $HfTe_5$

I have left a system even more perplexing than the above until last, which incorporates many elements of their behaviour in its own special way.

$ZrTe_5$ like $ZrTe_3$ has slabs containing quadrivalent $Zr(Te_2)Te$ trigonal prismatic chains, but these are now spaced within the slab by tellurium chains (Furuseth *et al.* 1973). Te–Te bonding in the latter is slightly weaker (2.91 Å) than in elemental tellurium, which results in the compound being semimetallic. The carrier concentration is clearly not very high at 300 K, since the Seebeck coefficient is *ca.* 100 μV K^{-1} (Jones *et al.* 1982). High-field Hall data is in keeping with *ca.* 10^{18} carriers per cubic centimetre (Izumi *et al.* 1982). However, the two-band nature of the situation becomes plainly apparent in the rather sharp reversal of sign in both Hall and Seebeck coefficients from positive to negative upon cooling. Actually, at He temperatures, de Haas–Shubnikov measurements (Izumi *et al.* 1983) show there remains only a single very small and highly anisotropic pocket of carriers. For $HfTe_5$ this corresponds to just 4×10^{16} electrons per cubic centimetre; amazingly small, even as a defect concentration. This figure means that the majority of the carriers present at room temperature have been lost. For a simple semimetal this can occur on cooling via two processes: (*a*) thermally induced band uncrossing; (*b*) reduced generation of carriers by thermal excitation. Indeed, upon cooling the pentatellurides from room temperature the susceptibility becomes more negative (Okada *et al.* 1982) while the resistivity rises, in keeping with a diminution in the number of carriers. A concensus value for ρ(300 K) is about 5×10^{-4} Ω cm, a value rather higher than in semimetallic $TiSe_2$.

On cooling from the intrinsic into the extrinsic régime some improvement in conductivity may be expected, following from improvement in carrier mobility as electron–hole scattering falls away. The very large resistivity humps appearing in the pentatellurides are probably the product of such behaviour. Note they are found at 140 K in $ZrTe_5$ but at only 75 K in $HfTe_5$, which is the reverse of what would be expected if deriving from soft-phonon mode condensation in a c.d.w.–p.s.d. (DiSalvo *et al.* 1981). Furthermore, since the hump cancels completely from the anisotropic resistivity ratio (Okada *et al.* 1982) we are once more encouraged to consider the semimetallic loss of carriers and not Fermi surface nesting.

Below the resistivity hump the number of carriers is so few that the residual resistance becomes very dependent on sample quality. The transverse magneto-resistance also becomes independent of temperature in this régime (Izumi *et al.* 1982). Band structural work suggests that these electrons of high mobility reside in the tellurium chain antibonding orbitals. With the loss of the major carriers all the phonon modes are observed to stiffen (Taguchi *et al.* 1983). The fact that the size of the resistivity hump is found to be strongly enhanced under pressure (Fuller *et al.* 1983) may follow from the increased dispersion in the bands, i.e. more difficult carrier excitation. Light Ta doping eliminates the hump (DiSalvo *et al.* 1981).

All the above phenomena are compatible with a semimetallic condition, and Bullett's (1983, 1984*b*,*c*) band structural work is in support of this view. The calculated band overlap occurs in ΓB, and involves the interchange between the conduction band and valence band of two Te-based bands. It is unlikely from past experience that the separation of the p and d-bands is understated, and thus in contrast with $ZrTe_3$ semimetallic overlap of some degree is not unexpected.

The above, however, does not complete the matter, for we have yet to confront the following additional data in which there are clear structural complications. First, DiSalvo *et al.* (1981) reported that at room temperature it seemed the structure was distorting into the superlattice (0.5, 0.5, 0). Okada *et al.* (1982) were unable to detect such superspots, but our results indicate some complexities (McKernan 1984, unpublished work). What has been shown is a breakdown in the symmetry-forbidden character of spots $(00l)$ where l is odd; this in-slab diffraction is found to peak just below the temperatures at which the resistivity maxima occur (Skelton *et al.* 1982). The susceptibility component $\chi(H \perp \text{slabs})$ also has a strong minimum here (i.e. is most diamagnetic), though $\chi(H \parallel \text{chains})$ is virtually temperature independent (and of course numerically much smaller) (Okada *et al.* 1982; Izumi *et al.* 1983). It may be that the tellurium chain cant angles are being adjusted to diminish the Te–Te distance, causing the $ZrTe_3$ chains to twist. Finally, at 84 K in $ZrTe_5$ (where the behaviour of $\chi_\perp$ changes again), there is now a report of a definite slight transition. Brill & Sambongi (1984) reveal a very small sharp decrease in Young modulus by using the vibrating reed technique. Also, in the Seebeck data (Fuller 1983) there is indication of something happening at this point in $ZrTe_5$. The latter data now suggest that investigation should be made of $HfTe_5$ at *ca.* 110 K.

That these anomalies bear on $NbSe_3$ can be realized from the report by Jackson *et al.* (1983) that for $HfTe_5$ ($ZrTe_5$), starting from 110 K (280 K), the resistivity hump is found to be eliminated by gigahertz r.f. fields just as for c.d.w. sliding. In apparent conflict with this, Okada *et al.* (1982), working on $ZrTe_5$, found no diminution in ρ there under direct current fields up to 30 V cm^{-1} for all temperatures covered by the ρ hump. However, one should note that there was no measurement made below the 84 K anomaly. Clearly the direct current experiment should be repeated for $HfTe_5$. If there is a c.d.w. transition present in addition to the ρ hump in $HfTe_5$, one expects its onset to higher temperatures. Note that 84 and 110 K are in the ratio of the square roots of the masses for the two compounds.

In these materials it will be worth seeking some form of excitonic insulator behaviour as the

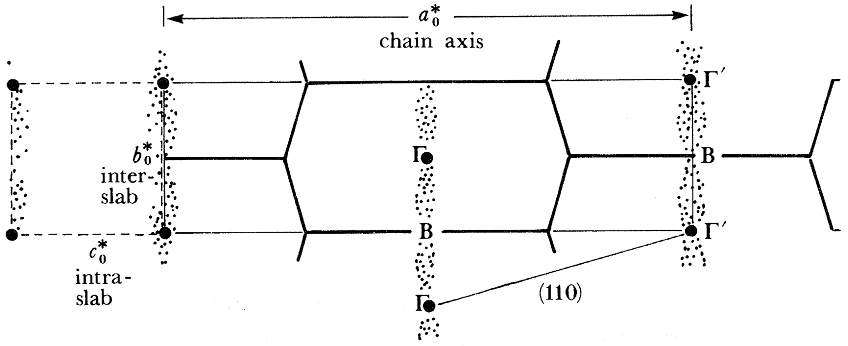


FIGURE 7. Reciprocal space for C-centred orthorhombic $HfTe_5$. Shading indicates the extent of the Fermi sea likely from Bullett's (1984*b*,*c*) calculation. Electron–hole coupling is possible under vector $\frac{1}{2}(010)$, leading to a new reciprocal lattice incorporating $\frac{1}{2}(110)$.

bands uncross. Figure 7 shows the reciprocal space for the C-centred orthorhombic pentatelluride structure, with an indication of how the Fermi sea is disposed given Bullett's (1984*b*, *c*) calculation. Note that the lozenge-shaped section of the zone relates to the chain direction and to the interslab direction (b_0). The anomaly indicated by the room temperature diffraction work with wavevector $(\frac{1}{2}, \frac{1}{2}, 0)$ lies in this plane. It may emanate from interaction under $(0, \frac{1}{2}, 0)$ between the two semimetallic band crossing points in axis ΓBΓ. The along-chain component to the suggested *q*-vector preserves the C-centred geometry and may come from in-chain phasing shifts for the lateral distortions.

4. Conclusion

It is hoped that this paper has helped to consolidate and coordinate some of the fascinating information now emerging on low-dimensional transition-metal chalcogenides. The number of new members in this category of c.d.w.-distorted compounds is growing fast. I have not discussed Nb_3Te_4 (Ishihara *et al.* 1984) or Mo_2S_3 (Rashid *et al.* 1982) since there is no report of sliding in these yet, a consequence presumably of their more three-dimensional structures. Nevertheless, these materials are of interest in that like $NbSe_3$ there is more than one chain type and correspondingly more than one transition. This is also true for some of the complex one- and two-dimensional molybdenum oxides being studied by the Grenoble group (C. Schlenker, R. Buder, J. Dumas, C. Escribe-Fillipiné, H. Guyot, J. Marcus, J. Mercier *et al.*). Of these oxides the one-dimensional blue bronze $K_{0.3}MoO_3$ in fact does show sliding phenomena rather similar to *o*-TaS_3.

If one had a choice on what new data one would like to see emerge and what questions one would like to see answered, they would be, first, a determination of the structure of *o*-TaS_3 and the phasing of its c.c.d.w. Is there only one active chain? Secondly, is it indeed possible to eliminate a.c. noise from the sliding signal in $NbSe_3$, as proposed at the end of §2? Thirdly, is d.c.-induced sliding observable in $HfTe_5$, with 110 K as onset point? Fourthly, how does the structure change in $[Nb(Se_2)_2]_{10}I_3$ below 285 K? Fifthly, can high resolution Mössbauer studies on $TaTe_4$ and n.m.r. on $NbTe_4$ identify all chains as equivalent? Finally, will a band structure for B-variant $ZrTe_3$ offer any chance of the material being semimetallic. The Hall measurement under pressure will not be easy to make reliably.

I thank the Royal Society for funding my work in this area, and for sponsoring this symposium. I also acknowledge the many useful discussions with my colleagues at Bristol over the full range of c.d.w.-related problems. Finally, thanks are due to the Hokkaido group for sending a copy of the Sapporo Symposium book, and to Dr Bullett for a copy of his manuscript for Reidel Press. The typescript for this contribution to the report was submitted on 31 May 1984.

References

Allmann, R., Bauman, I., Kutoglu, A., Rosch, H. & Hellner, E. 1964 *Naturwissenschaften* **51**, 263.
Bayliss, S. C. & Liang, W. Y. 1981 *J. Phys.* C **14**, L803–L807.
Bjerkelund, E., Fermor, J. H. & Kjekshus, A. 1966 *Acta chem. scand.* **20**, 1836–1841.
Bjerkelund, E., Kjekshus, A., & Meisalo, V. 1968 *Acta chem. scand.* **22**, 3336–3338.
von Boehm, J. & Isomaki, H. M. 1982 *J. Phys.* C **15**, L733–L737.
Boswell, F. W. & Prodan, A. 1984 *Mater. Res. Bull.* **19**, 93–97.
Boswell, F. W., Prodan, A. & Brandon, J. K. 1983 *J. Phys.* C **16**, 1067–1076.

Brill, J. W. 1982 *Solid St. Commun.* **41**, 925–929.

Brill, J. W. & Sambongi, T. 1984 *J. phys. Soc. Japan* **53**, 20–23.

Bullett, D. W. 1978 *J. Phys.* C **12**, 277–281.

Bullett, D. W. 1982 *J. Phys.* C **15**, 3069–3077.

Bullett, D. W. 1984*a* *J. Phys.* C **17**, 253–256.

Bullett, D. W. 1984*b* *Physics & chemistry of materials with low-dimensional structures.* Dordrecht: Reidel. (In the press.)

Bullett, D. W. 1984*c* *Solid St. Commun.* **42**, 691–693.

Chen, C. H. & Fleming, R. M. 1983 *Solid St. Commun.* **48**, 777–779.

Chen, C. H. & Fleming, R. M. 1984 *Phys. Rev.* B **29**, 4811–4813.

Devreux, F. 1982 *J. Phys., Paris* **43**, 1489–1495.

DiSalvo, F. J., Fleming, R. M. & Waszczak, J. V. 1981 *Phys. Rev.* B **24**, 2935–2939.

DiSalvo, F. J., Waszczak, J. V. & Yamaya, K. 1980 *J. Phys. Chem. Solids* **41**, 1311–1313.

DiSalvo, F. J., Wilson, J. A. & Waszczak, J. V. 1976 *Phys. Rev. Lett.* **36**, 885–888.

Eaglesham, D. J., Steeds, J. W. & Wilson, J. A. 1984 *J. Phys.* C **17** L697–701.

Fenton, E. W. 1981 *J. Phys.* C **14**, 4217–4224.

Fleming, R. M., Chen, C. H. & Moncton, D. E. 1983 *J. Phys., Paris* **44**, C-3, 1651–1658.

Fleming, R. M. & Grimes C. C. 1979 *Phys. Rev. Lett.* **42**, 1423–1427.

Fleming, R. M., Moncton, D. E. & McWhan, D. B. 1978 *Phys. Rev.* B **19**, 5560–5563.

Fleming, R. M., Moncton, D. E., McWhan, D. B. & DiSalvo, F. J. 1980 *Phys. Rev. Lett.* **45**, 576–579.

Fleming, R. M., Polo, J. A. Jr. & Coleman, R. V. 1978 *Phys. Rev.* B **17**, 1634–1644.

Friend, R. H., Jérome, D. & Yoffe, A. D. 1982 *J. Phys.* C **15**, 2183–2192.

Fujishita, H., Sato, M. & Hoshino, S. 1984 *Solid St. Commun.* **49**, 313–316.

Fuller, W. W., Wolf, S. A., Wieting, T. J., Lacoe, R. C., Chaikin, P. M. & Huang, C. Y. 1983 *J. Phys., Paris* **44**, C-3, 1705–1712.

Fung, K. K., McKernan, S., Steeds, J. W. & Wilson, J. A. 1981 *J. Phys.* C **14**, 5417–5432.

Fung, K. K. & Steeds, J. W. 1980 *Phys. Rev. Lett.* **45**, 1696–1699.

Furukawa, A., Oda, Y., Nagano, H. & Onuki, Y. 1984 *J. phys. Soc. Japan* **53**, 30–34.

Furuseth, S., Brattås, L. & Kjekshus, A. 1973 *Acta chem. Scand.* A **27**, 2367–2374.

Furuseth, S., Brattås, L. & Kjekshus, A. 1975 *Acta chem. Scand.* A **29**, 623–631.

Giuliani, G. F. & Overhauser, A. W. 1982 *Phys. Rev.* B **26**, 1660–1668.

Greenaway, D. L. & Nitsche, R. 1965 *J. Phys. Chem. Solids* **26**, 1445–1458.

Gressier, P., Guemas, L. & Meerschaut, A. 1982 *Acta crystallogr.* B **38**, 2877–2879.

Gressier, P., Meerschaut, A., Guemas, L., Rouxel, J. & Monceau, P. 1984 *J. Solid St. Chem.* **51**, 141–151.

Grüner, G., Tippie, L. C., Sanny, J., Clark, W. G. & Ong, N. P. 1980 *Phys. Rev. Lett.* **45**, 935–938.

Higgs, A. W. & Gill, J. C. 1983 *Solid St. Commun.* **47**, 737–742.

Hillenius, S. J. & Coleman, R. V. 1982 *Phys. Rev.* B **25**, 2191–2195.

Hodeau, J. L., Marezio, M., Roucau, C., Ayroles, R., Meerschaut, A., Rouxel, J. & Monceau, P. 1978 *J. Phys.* C **11**, 4117–4134.

Ido, M., Tsutsumi, K., Sambongi, T. & Mori, N. 1979 *Solid St. Commun.* **29**, 399–402.

Inada, R., Onuki, Y. & Tanuma, S. 1983 *J. phys. Soc. Japan* **52**, 3536–3543.

Ishihara, Y., Nakada, I., Suzuki, K. & Ichihara, M. 1984 *Solid St. Commun.* **50**, 657–659.

Izumi, M., Uchinokura, K., Matsuura, E. & Harada, S. 1982 *Solid St. Commun.* **42**, 773–778.

Izumi, M., Uchinokura, K., Yoshizaki, R., Harada, S., Nakayama, T., Yamada, A. & Matsuura, E. 1983 *J. Phys., Paris* **44**, C-3, 1705–1708.

Jackson, C. M., Zettl, A., Gruner, G. & DiSalvo, F. J. 1983 *Solid St. Commun.* **45**, 247–249.

Jones, T. E., Fuller, W. W., Wieting, T. J. & Levy, F. 1982 *Solid St. Commun.* **42**, 793–798.

Kawabata, K., Ido, M. & Sambongi, T. 1981 *J. Phys. Soc. Japan* **50**, 739–740.

Kepert, D. L. 1972 *The early transitions metals*, p. 18 ff. New York: Academic Press.

Kikkawa, S., Uenosono, S. & Koisumi, M. 1983 In *Proc. Int. Symp. Nonlinear Transport and Related Phenomena in Inorganic Quasi One-Dimensional Conductors, Hokkaido Univ., Sapporo, Japan*, pp. 245–255.

Kotani, A. & Harada, I. 1980 *J. phys. Soc. Japan* **49**, 535–544.

Kurita, S., Staehli, J. L., Guzzi, M. & Levy, F. 1981 *Physica* **105**B, 169–173.

Maeda, A., Naito, M. & Tanaka, S. 1983 *Solid St. Commun.* **47**, 1001–1005.

Maki, M., Kaiser, M., Zettl, A. & Gruner, G. 1983 *Solid St. Commun.* **46**, 497–499.

Matsukawa, H. & Takayama, H. 1984 *Solid St. Commun.* **50**, 283–286.

Maule, C. 1984 Ph.D. thesis, University of Bristol.

McKernan, S., Steeds, J. W. & Wilson, J. A. 1982 *Physica Scr.* **T1**, 74–77.

Meerschaut, A. 1983 In *Proc. Int. Symp. Nonlinear Transport and Related Phenomena in Inorganic Quasi One-Dimensional Conductors, Hokkaido Univ., Sapporo, Japan*, pp. 231–244.

Meerschaut, A., Gressier, P., Guemas, L. & Rouxel, J. 1984 *J. Solid St. Chem.* **51**, 304.

Meerschaut, A., Guemas, L. & Rouxel, J. 1981 *J. Solid St. Chem.* **36**, 118–123.

Meerschaut, A., Palvadeau, P. & Rouxel, J. 1977 *J. Solid St. Chem.* **20**, 21–27.

Mihaly, G., Mihaly, L. & Mutka, H. 1984 *Solid St. Commun.* **49**, 1009–1012.

Monceau, P., Renard, M., Richard, J., St. Lager, M. C., Salva, H. & Wang, Z. Z. 1983 *Phys. Rev.* B **28**, 1646–1648.

Mutka, H., Bouffard, S., Mihaly, G. & Mihaly, L. 1984 *J. Phys. Lett., Paris* **45**, L113–L119.

Myron, H. W., Harmon, B. N. & Khumalo, F. S. 1981 *J. Phys. Chem. Solids* **42**, 263–267.

Oda, M. & Ido, M. 1982 *Solid St. Commun.* **44**, 1535–1538.

Oda, M. & Ido, M. 1983 In *Proc. Int. Symp. Nonlinear Transport and Related Phenomena in Inorganic Quasi One-Dimensional Conductors, Hokkaido Univ., Sapporo, Japan*, pp. 161–178.

Okada, S., Sambongi, T., Ido, M., Tazuke, Y., Aoki, R. & Fujita, O. 1982 *J. phys. Soc. Japan* **51**, 460–467.

Ong, N. P. & Verma, P. 1983 *Phys. Rev.* B **27**, 4495–4498.

Ong, N. P. & Verma, P. 1983 In *Proc. Int. Symp. Nonlinear Transport and Related Phenomena in Inorganic Quasi One-Dimensional Conductors, Hokkaido Univ., Sapporo, Japan*, pp. 115–127.

Rashid, M. H., Sellmyer, D. J., Katkanant, V. & Kirby, R. P. 1982 *Solid St. Commun.* **43**, 675–678.

Rice, M. J. 1982 *Phys. Rev. Lett.* **48**, 1640.

Richard, J., Monceau, P., Papoular & Renard, M. 1982 *J. Phys.* C **15**, 7157–7164.

Rijnsdorp, J. & Jellinek, F. 1978 *J. Solid St. Chem.* **25**, 325–328.

Seeger, K., Philipp, A. & Mayr, W. 1984 *Solid St. Commun.* **50**, 223–227.

Selte, K. & Kjekshus, A. 1964 *Acta Chem. Scand.* **18**, 690–696.

Skelton, E. F., Wieting, T. J., Wolf, S. A., Fuller, W. W., Guber, D. U., Francavilla, T. L. & Levy, F. 1982 *Solid St. Commun.* **42**, 1–3.

Steeds, J. W., Fung, K. K. & McKernan, S. 1983 *J. Phys., Paris* **44**, C-3, 1623–1629.

Stokes, J. P., Bloch, A. N., Janossy, A. & Grüner, G. 1984 *Phys. Rev. Lett.* **52**, 372–375.

Taguchi, I., Grisel, A. & Levy, F. 1983 In *Proc. Int. Symp. Nonlinear Transport and Related Phenomena in Inorganic Quasi One-Dimensional Conductors, Hokkaido Univ., Sapporo, Japan*, pp. 263–273.

Tajima, Y. & Yamaya, K. 1984 *J. phys. Soc. Japan.*

Tajima, Y., Yamaya, K. & Abe, Y. 1983 In *Proc. Int. Symp. Nonlinear Transport and Related Phenomena in Inorganic Quasi One-Dimensional Conductors, Hokkaido Univ., Sapporo, Japan*, pp. 292–300.

Takahashi, S., Sambongi, T., Brill, J. W. & Roark, W. 1984 *Solid St. Commun.* **49**, 1031–1033.

Takahashi, S., Sambongi, T. & Okada, S. 1983 *J. Phys., Paris* **44**, C-3, 1733–1736.

Tessema, G. X. & Ong, N. P. 1981 *Phys. Rev.* B **23**, 5607–5610.

Tomic, S., Biljakovic, K., Djurek, D., Cooper, J. R., Monceau, P. & Meerschaut, A. 1981 *Solid St. Commun.* **38**, 109–112.

Tsutsumi, K., Sambongi, T., Kagoshima, S. & Ishiguro, T. 1978 *J. phys. Soc. Japan* **44**, 1735–1736.

Wang, Z. Z., Salva, H., Monceau, P., Renard, M., Roucau, C., Ayroles, R., Levy, F., Guemas, L. & Meerschaut, A. 1983 *J. Phys. Lett., Paris* **44**, L311–L319.

Wang, Z. Z., St. Lager, M. C., Monceau, P., Renard, M., Gressier, P., Meerschaut, A., Guesmas, L. & Rouxel, J. 1983 *Solid St. Commun.* **46**, 325–328.

Weger, M., Gruner, G. & Clark, W. G. 1982 *Solid St. Commun.* **44**, 1179–1182.

Wilson, J. A. 1978 *Physica Status Solidi* B **86**, 11–36.

Wilson, J. A. 1979 *Phys. Rev.* B **19**, 6456–6468.

Wilson, J. A. 1982 *J. Phys.* F **12**, 2469–2482.

Wilson, J. A., Barker, A. S., DiSalvo, F. J. & Ditzenberger, J. A. 1978 *Phys. Rev.* B **18**, 2866–2875.

Wilson, J. A., DiSalvo, F. J. & Mahajan, S. 1975 *Adv. Phys.* **24**, 117–201.

Wilson, J. A. & Mahajan, S. 1977 *Communs Phys.* **2**, 23–29.

Wilson, J. A. & Yoffe, A. D. 1969 *Adv. Phys.* **18**, 193–335.

Zettl, A. 1983 In *Proc. Int. Symp. Nonlinear Transport and Related Phenomena in Inorganic Quasi One-Dimensional Conductors, Hokkaido Univ., Sapporo, Japan*, pp. 41–76.

Zettl, A. & Gruner, G. 1983 *Solid St. Commun.* **46**, 29–32.

Zettl, A. & Gruner, G. 1983 *Phys. Rev.* B **28**, 2091–2103.