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CHARGE DENSITY WAVES IN THE LAYERED TRANSITION METAL DICHALCOGENIDES

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Résumé. — Les dichalcogénides de métaux de transition de groupe Vₐ présentent une surface de Fermi robuste aux instabilités structurales. Dans des corps tels que IT-TaS₂, ces effets apparaissent clairement dans les propriétés électromagnétiques qui sont anomales. Le but de l'article est de présenter des preuves expérimentales, en particulier par la diffraction des électrons et les rayons X, pour l'adoption d'un état fondamental CDW couple à une distorsion périodique de réseau. Nous montrons comment cet état fondamental peut être perturbé en intercalant des métaux alcalins ou des terres rares.

Abstract. — The metallic layered transition metal dichalcogenides of group Vₐ exhibit Fermi surface linked structural instabilities. In materials such as IT-TaS₂, these effects readily manifest themselves in the electromagnetic properties, hitherto regarded as anomalous. The primary aim of the present paper is to present the diffraction evidence from electron and X-ray observations, for the adoption of a charge density wave ground state coupled to a periodic lattice distortion, and to show how this ground state may be perturbed by alkali metal and rare earth intercalation.

1. Introduction. — Recent recognition [1, 2] that certain properties of the group Vₐ transition metal dichalcogenides (TMD), hitherto regarded as anomalous, might be interpreted in terms of an electronic instability, has stimulated considerable interest in these layered metals. Nominally of simple structure, related either to that of CdCl₂ (P 3m) or MoS₂ (P 6₃/mmc), the earliest indications of such anomalous behaviour were reported in electron diffraction studies by Wilson and Yoffe (1968). For the octahedral polytype of TaS₂ (hereafter denoted 1 T-TaS₂), these authors found extra reflexions in (hk.0) projection diffraction patterns which were not anticipated for the space group P 3m; explanations in terms of either a shear structure or an excitonic insulator phase were offered at that time. Later, Thompson et al. [4] in studies of temperature dependence of the electrical conductivity of the same material found evidence of two first order phase transitions between states characterized most readily by their anomalously high resistivities. Their data for 1 T-TaS₂ is summarised in figure 1 together with that for 1 T-TaSe₂, and for the trigonal prismatically coordinated polytypes of the same materials (denoted 2 H-TaS₂ and 2 H-TaSe₂), as reviewed recently by Wilson et al. [2]. Over no range of temperature in figure 1 can the resistivity behaviour of 1 T-TaS₂ be classified as metallic even though simple charge transfer arguments (Wilson and Yoffe [3]) suggest metallic properties for all the group Vₐ TMD's. Indeed, detailed band structure calculations (Mattheiss [7]) and photoemission measurements (Shepherd and Williams [8]; Smith et al. [31]) both show narrow « d » bands which contain one electron per formula unit for group Vₐ 1 T and 2 H polytypes. Further evidence for departures from simple metallic behaviour has been observed for most of the group Vₐ TMD's, as reviewed by Wilson et al. [2].

With reference again to 1 T-TaS₂, the behaviour in figure 1, particularly within the temperature range 190-350 K, is in fact more reminiscent of a semiconductor than a metal, as first pointed out by Thompson et al. [4] ; comparison with materials such as SnS, however, where f-d hybridization may result in the opening of an energy gap at the Fermi level, are clearly inappropriate in the present case. A closer analogue may be found in recent work on so called one-dimensional metals such as KCP (Comes et al. [9]) where the structures have been recognized for some time as inherently unstable below an appropriate temperature with respect to a Peierls Transition.
Against the above background, electron diffraction observations in particular, of the superlattices and diffuse scattering observed as a function of temperature in the octahedral dichalcogenides of Tantalum led to the suggestion that these structural effects might themselves be driven by a giant Kohn-like anomaly, leading to a charge density wave ground state for the metallic layer TMD's (Williams et al. [1]; Wilson et al. [2]). Since then, numerous structural and electromagnetic studies of these and related layer TMD's have been reported. Theoretical and electronic considerations of these phenomena are dealt with in detail elsewhere in the present proceedings. In the present paper, we will therefore confine ourselves to a detailed consideration of the structural aspects of the problem, particularly with reference to 1 T-TaS$_2$. This material may be regarded as both archetypal of this class of CDW/PLD ground state metals and, in certain respects, exceptional, in its exhibition of two incommensurate CDW phases. The following sections, then, will present the diffraction data for this and other TMD's. The consequences of doping and intercalation on the ground state structure will also be reviewed. Finally, we will attempt to indicate how these observations might be interpreted in terms of the currently accepted models for the electronic structure of these materials.

2. Diffraction observations. — The octahedral, 1 T polytypes related to the CdI$_2$ structure (P 3m) are most common amongst the 3d$^3$ and 5d$^1$ dichalcogenides of vanadium and tantalum, although DiSalvo and co-workers (1975) have reported the growth of 1 T crystals of NbSe$_2$ substitutionally doped with Ti. Here we will consider in detail the case of 1 T-TaS$_2$ as outlined above. This data will be contrasted with effects observed in the 2 H, trigonal prismatic polytypes of TaSe$_2$ and NbSe$_2$ (P 6$_3$/mmc) where the CDW/PLD ground state appears to adopt a different form. The contrast between 2 H and 1 T polytypes is further highlighted in observations of 4 H$_2$-TaS$_2$ where octahedral and trigonal prismatic layers alternate; it will be shown that these layers apparently behave independently and conform to their parent (1 T or 2 H) lattice type. Controlled perturbation of the CDW/PLD ground state in the 1 T-polytypes will be demonstrated following electron transfer on doping or intercalation.

2.1 1 T-TaS$_2$. — Since the earliest report of superlattice effects in high energy electron diffraction patterns of 1 T-TaS$_2$ (Wilson and Yoffe [3]), extensive studies have been carried out by many groups using electrons and X rays (Wilson et al. [2]; Williams et al. [1], [15]). Although there have been certain differences over the interpretation of results, there is an almost precise reproducibility between the diffraction patterns recorded over a wide range of temperatures for materials prepared in different laboratories. We reproduce in figure 2 the results of Scruby et al. [1] showing (hk,0) transmission electron diffraction

![Figure 1](image_url)
Fig. 2. — Selected area diffraction patterns for 1T-TaS$_2$ with incident electron beam parallel to c$^*$ (a) the 1T$_1$ phase at 340 K showing strong triangular groupings $\{S_{10.1}\}$; (b) 1T$_2$ at 290 K; (c) 1T$_3$ at 150 K.
patterns for 1T-TaS$_2$ recorded at the temperatures indicated (using either heated or liquid nitrogen cooled stages in a JEM 7A electron microscope operating at 100 keV). The three phases are denoted 1T$_1$, 1T$_2$, and 1T$_3$ (after Williams et al. [1]) to indicate regions in the $\rho \rightarrow T$ relationship of figure 1 above the first transition, between first and second transitions, and below the second transition in temperature respectively.

The transformation temperature of the 1T$_3$ phase we will denote T$_3$ (after Wilson et al.) that from 1T$_1$, T$_2$, T$_4$. Figure 3 reproduces single crystal X-ray oscillation photographs (Scruby et al. [2]) again for the three regimes 1T, 1T$_2$, 1T$_3$. With both X-ray and electron diffraction, the extra periodicities referred to above, which are not consistent with the simple CdI$_2$ structure, are clearly noted, the X-ray observations confirming that these periodicities seen perhaps most readily in selected area diffraction are characteristic of bulk single crystals and not of localized defects. For convenience, we summarise this data schematically in figure 4; thus the matrix CdI$_2$ structure reflexions, \{M\}, are surrounded by groups of extra reflexions, \{SM\}, disposed with three or six fold symmetry about each parent in \{M\}. If vectors Q_{in} (where $i$ refers to a set of 3 symmetry related PLD's and 1 T$_n$ for $n = 1, 2$ or 3) the region of the $\rho \rightarrow T$ curve, Fig. 1) define the disposition of the \{SM\} about each \{M\} as shown then the following may be deduced for the three phases.

a) In both 1T$_1$ and 1T$_2$ the magnitude of vectors Q$_{in}$ \leq |Q$_{in}$|, defining the first order reflexions in \{SM\}, is an irrational fraction of the reciprocal lattice parameter of matrix structure, $|a^*|$. Only in 1T$_3$ do Q$_{13}$ and $a^*$ become commensurate (i.e. they are related on a rational coincidence mesh), the \{SM\} defining in the (hk.0) plane a perfect $\sqrt{13} \times \sqrt{13}$ superlattice mesh.

b) The vector Q$_{13}$ in 1T$_3$ is parallel to $a^*$ but rotates by 110° 6' away from $a^*$ at the transition to 1T$_2$. Q$_{13}$ then rotates gradually, as the temperature is lowered, to $\sim 14^\circ$ at the transition to 1T$_3$ to form the perfect $\sqrt{13} \times \sqrt{13}$ superlattice. At the same time $|Q_{12}|$ varies in magnitude with temperature, decreasing from 0.286 $a^*$ at T$_4$ to 0.277 $a^*$ at T$_6$.

c) Second order reflexions of the type $Q_{12} \pm Q_{22}$ are observed in both 1T$_1$ and 1T$_2$ (and of course in the perfect superlattice mesh of 1T$_3$), being most noticeable in 1T$_2$ (Fig. 2). Following the notation of Scruby et al., we will adopt a system of coordinates local to each \{M\} to describe the association \{SM\}; thus the first order reflexions we will denote SM(10.1) the second SM(11.1). This notation will be used throughout the text in the descriptions of all the materials.

d) Within the 1T$_1$ phase, in addition to the \{SM\}, there is a diffuse background in the form of streaks passing through the SM(10.1) apparently in the form of circles or bicycle chains (Wilson et al. [2]). The intensity in these streaks increases with temperature until the irreversible 1T-2H inter-polotypic transition occurs near 450 K; figure 5 shows a typical higher-temperature transmission electron diffraction pattern accentuating this streaking; the precise interpretation of this effect is the subject of some controversy, as we shall see later.

These results for 1T-TaS$_2$ establish the basic characteristics of the observations, many of which are common to other layer materials within the group. In particular, 1T-TaSe$_2$ exhibits similar diffraction effects, with the exception that the intermediate, 1T$_2$ phase is absent. Thus we shall see that in many respects, the incommensurate nature of the Q$_{11}$, at high temperature (>$T_3$) is the signature of the charge density wave in the electron gas, being related to the geometry of the Fermi surface and not of the lattice. The diffracted intensities derive, however, not from the scattering

![Figure 3](image-url)  
**Fig. 3.** Oscillation X-ray photographs with incident beam in similar orientation to figure 2 for (a) 1T, at 390 K (b) 1T$_2$ at 290 K (c) 1T$_3$ at 80 K confirming the reciprocal space geometry given by electron diffraction. Distortion amplitude is too small in 1T$_1$ for SM(11.1) to be observed.

![Figure 4](image-url)  
**Fig. 4.** Reciprocal cells for each distorted 1T-TaS$_2$ phase, where Q$_{11}$, Q$_{13}$, Q$_{23}$ are distortion wave vectors. In (a) 1T$_1$ and (b) 1T$_2$ the unit cell is that of the matrix with $\pm$ \{SM\} reflexions in (h0k) plane of \{M\}; -- \{SM\} reflexions at $\pm i e^*$. In (c) 1T$_3$, the commensurate distortions define a reduced $\sqrt{13} \times \sqrt{13}$ reciprocal cell, shown in projection.
graph with the X-ray beam incident perpendicular to c*, the intensities in the \( S_M \) \((10.1) \) (rows arrowed) increase dramatically as we pass from \( M(00.1), (0.1), \) through \( M(10.1), (11.1), \) to \( M(20.1), (21.1). \) This intensity variation, as has been pointed out by Comes [9] and others in the related case of the one dimensional metals, is very specifically the signature of a periodic modulation of the lattice and cannot be explained in terms of defect ordering or shear structures, as originally proposed. This X-ray observation is thus, along with the neutron data for the 2 H polytypes (Monckton et al. [15]), the single most conclusive piece of evidence for CDW/PLD behavior in these materials. The intensities in the electron observations again show similar increases for \( S_M \) \((10.1) \) with increasing \( M(hk.0) \), but in this case, curvature of the Ewald sphere in reciprocal space precludes too literal an interpretation of the variations. Again with reference to figure 6, careful study shows the reflexions \( S_M \) \((10.1) \) to be located out of the \((hk.l) \) planes at positions \( = \pm c^*/3 \), forming an octahedron of reflexions about each \( \{ M \} \), of local symmetry \( \bar{3} \) (a fact which may also be deduced from careful electron microscope observations by tilting flat areas of sample). This observation is true for both 1 \( T_1 \) and 1 \( T_2 \) phases and implies strong correlation between PLD's in neighbouring layers; the situation in 1 \( T_2 \) is more complex and is discussed fully below. Finally, with reference to TaS\(_2\), we note that in both the 1 \( T_1 \) and 1 \( T_2 \) phases, the matrix appears to remain strictly hexagonal; in 1 \( T_2 \), there is some indication that this is no longer true, the structure being triclinic with a stacking repeat of 13 \( c^0 \) as opposed to 3 \( c^0 \) in 1 \( T_1 \) and 1 \( T_2 \).

### 2.2 The 2 H Polytypes: NbSe\(_2\) and TaSe\(_2\)

Figure 1 presents much less dramatic evidence, in the form of weak shoulders in the T data, for electronic anomalies in the 2 H polytypes of the metallic layered TMD's, although examination of the same temperature region with other forms of physical measurement (e.g. magnetic susceptibility, Wilson et al. [2]; elasticity, Barmatz et al. [16]) does reveal anomalous discontinuities. Equally, early structural studies at room temperature (Wilson and Yoffe [3]) using electron diffraction revealed no extra scattered intensity, but low temperature magnetic resonance studies NbSe\(_2\) (Ehrenfreund et al. [17]) suggested Niobium site inequivalencies, and low temperature X-ray diffraction (Marek et al. 1972) again demonstrated the possibilities of some weak distortion. More recently, direct evidence of a low temperature structural distortion in the 2 H polytypes has been obtained from both electron (Williams et al. [15]) and neutron (Monckton et al. [15]) diffraction and from n.m.r. data (Valic et al. [18], Berthier et al. [18]). The electron data is reproduced in figure 7 which shows \((hk.0) \) diffraction patterns recorded at 40 K for TaSe\(_2\) and 17 K for NbSe\(_2\). In neither case could any reflexions other than

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**FIG. 5.** — Selected area electron diffraction pattern for 1 \( T_1 \)-TaS\(_2\) at 420 K showing diffuse streaking which images the Fermi surface. All six \( \{ S_M(10.1) \} \) reflexions are visible because of crystal buckling.

**FIG. 6.** — Oscillation X-ray photograph of 1 \( T_1 \)-TaS\(_2\) with incident beam perpendicular to c*, and recorded with a cylindrical camera. There is an increase in intensity of \( \{ S_M \} \) reflexions (indicated by arrows) relative to the adjacent matrix reflexions with increase in the component of scattering vector normal to c* \((M(0k.l) \) to \( M(1k.l) \) to \( M(2k.l) \)).
2.3 Mixed Polytypes: 4 H$_x$-TaS$_2$. — The above contrast in behaviour between 1 T and 2 H polytypes raises interesting questions regarding the behaviour to be expected for mixed polytypes such as 4 H$_x$-TaS$_2$. This material comprises alternating layers with octahedral and trigonal prismatic coordination of the Ta by S. As such, effects related to both classes of phenomena considered above might be anticipated. Both resistivity (Wattamaniuk et al. [20]) and susceptibility data (Wilson et al. [21]) reveal evidence for first order transitions near 315 K and 20 K, and it has long been conjectured that the upper of these derives from CDW/PLD behaviour in the octahedral layers, the lower one from the trigonal prismatically coordinated layers. This is in contrast to the case of 1 T-TaS$_2$ where both upper and lower transitions (T$_d$ and T$_a$) must clearly be associated with octahedral layers only. Once more, recent evidence from both neutron (Di Salvo et al. [21]) and electron (Tatlock [22]) diffraction provides an answer. Figure 8 shows an (hk.0) trans-
in 1 T$_2$-TaS$_2$. The third contribution, consisting of weaker reflexions close to, but not coincident with $\pm a^*/3$, may readily be compared with the data of figure 7 for the 2 H polytypes; this third set of reflexions \{S$_{cdw}$\} remains incommensurate down to 10 K. No absolute support may as yet be derived from accurate structure factor fits to the measured intensities in either neutron or electron studies, but nevertheless, the inescapable conclusion in the present case is that the $\sqrt{13} \times \sqrt{13}$ superlattice is located only within the octahedral layers, the incommensurate distortion only within those with trigonal prismatic coordination. This is perhaps the most striking example of two dimensionality in these layered solids, the two types of layers behaving effectively independently. Such is their apparent independence that Wattamaniuk \textit{et al.} [20] have suggested that the transport properties $\sigma$ for this material may be considered in terms of tunnelling between metallic (trigonal prismatic) layers separated by insulating (octahedral) layers.

2.4 Diffraction Studies of Intercalated Materials. — The effects described above in the pure, stoichiometric materials will be discussed in section 3 in terms of charge density wave instabilities. For the present, we suggest only that these structural anomalies are related in some way to the Fermi surface in these materials; their behaviour following controlled changes in the size of shape of the surface should therefore be regarded as one of the most significant tests of this hypothesis. Within the layered compounds, such changes may readily be accomplished in one of two ways. Substitutional doping of the cation enables continuous variation in electron density to be produced, provided that it is possible to grow single phase crystals of such mixed compounds. Alternatively, the layered compounds offer a unique means of controlling the intralamellar electron density via intercalation, that is the insertion between lamellae of dopant species such as alkali metals and organic compounds, notably the amines. Wilson, Di Salvo, and co-workers have extensively investigated the electronic properties and structures of doped group $V_a$ TMD's, as considered elsewhere in the present proceedings (Di Salvo). For the present we note only that whilst it is relatively easy to control the overall electron density and hence the size of the Fermi surface in 1 T-TaS$_2$, for example, by the substitution of Ti, the random cation potentials so introduced tend to scatter the charge density wave and hence introduce disorder into the PLD effects observed in diffraction. Such scattering favours the adoption of an incommensurate CDW/PLD ground state, as pointed out by McMillan [23], thereby preventing the controlled study of new commensurate superlattice structures (Wilson \textit{et al.} [2]).

With regard to the individual lamellae on the other hand, intercalation can be considered as less disruptive. The intercalating or guest species often orders on some lattice array determined by, and hence commensurate with the host lattice. As such, although these species may be charged, no new Fourier components are introduced into the modified crystal potential with which the CDW interacts. Furthermore, the CDW, which may be regarded as having existence predominately within the layer, may be effectively screened from any new potentials introduced by the regular ionic array in the interlamellar space, thereby again minimising scattering. Since electron transfer to the host layer is thought to accompany intercalation (see, for example, Acrivos \textit{et al.} [24]) this method has many attractions as a controlled means of studying the consequences of Fermi surface expansion for the CDW/PLD ground state.

For 1 T-TaS$_2$, the alkali metals Li, Na, K and the rare earth Europium have all been successfully intercalated, either from solution in ammonia (Na, K, Eu) or, for Li, from n-butyl lithium (Clark \textit{et al.} [25]). Figure 9a shows the diffraction pattern which results at room temperature following saturation intercalation. In each case, a geometrically identical pattern is produced, independent of the metal used, strongly suggesting that the diffraction effects are associated with the TaS$_2$ layer and not with the intercalate (Lithium, for example, has insufficient scattering power for electrons or X-rays to account for the present observations). X-ray diffraction data yields similar results and figure 10 shows a crystal of Li$_x$1 T-TaS$_2$ recorded at room temperature (W. B. Clark, unpublished). The same cell as in figure 9a is observed confirming the bulk nature of these effects. This apparently complex pattern may in fact be interpreted in terms of two PLD's ($Q_x^1 = \pm a^*/3$; $Q_x^2 = \pm (2 a^* \sqrt{3})/9$) suggesting some competition on the Fermi surface for the optimum

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9}
\caption{(b) selected area electron diffraction patterns for (a) 1 T-TaS$_2$ intercalated with Na, 295 K and (b) the same, at 100 K. Pattern (a) was also obtained for Li, Li and Eu intercalates.}
\end{figure}
spanning vector. Lowering the temperature, however (Fig. 9b) produces an interesting transition to a state in which $Q_i^2$ is absent, the remaining reflections forming a perfect 3 $\times$ 3 superlattice. Detailed discussion of these effects is beyond the scope of the present paper. Here, we confine ourselves to noting that the wave vectors characterizing the PLD do expand on intercalation which change in size of the Fermi surface. Effects is beyond the scope of the present paper. Here, we confine ourselves to noting that the wave vectors characterizing the PLD do expand on intercalation relative to those in pristine 1 T-TaS$_2$ consistent with a change in size of the Fermi surface.

3. Discussion. — An interpretation of the above diffraction phenomena in terms of periodic lattice distortions and the origins of the latter in terms of charge density wave instabilities has been indicated where appropriate throughout the text. In this section, we will attempt to establish first the structural lines of this assertion and then to justify its further relationship to the electronic structures of these materials.

3.1 Diffraction by a Distorted Structure. — Readers are referred to standard texts for detailed consideration of the diffraction of electrons and X-rays (or neutrons) by periodically modulated structures. Here we will emphasize only the key features to be anticipated for such data. Assuming for the present, then, that distortion waves may be responsible, we note that for each of the hexagonal materials considered here, the trigonal (or hexagonal) disposition of the $\{ S_M \}$ about $\{ M \}$ implies the presence of three symmetry related distortions of wave vector $Q_i$ and amplitude $U_{Q_i}$, where $i = 1, 2, 3$. The layered structures of all the materials suggests that the distortion waves lie within each layer so that $Q_{in}.c^* = 0$. This restriction on the orientation of $Q_{in}$ implies that the Fourier transform of the distortion wave system within a single layer is a family of rods in reciprocal space, which are perpendicular to the layer and hence $\parallel c^*$. The relative phases of the distortion waves in adjacent layers modulates these rods so as to produce sharp extra reflections $\{ S_M \}$ where $\{ M = h a^* + k b^* + 2 c^* \}$ is the scattering vector of a single reflexion in $\{ M \}$ and $K = M + Q_{in}$ the scattering vector of any extra reflexion in $\{ S_M \}$.

Theories of the scattering of X-rays, electrons, or neutrons from regular lattices to which a periodic modulation has been applied are to be found elsewhere (see, for example, James [26]; Overhauser [13]). Briefly, then, for the present case of three symmetry related distortions, the intensity of a matrix reflexion $M$ will be reduced by a factor

$$1 - \sum_i (\pi M . U_{Q_i})^2,$$

where $U_{Q_i}$ is the amplitude of the distortion mode $Q_i$. More readily noted are the six first order reflexions $S_M (10.2)$ with intensities proportional to

$$\frac{1}{2} | 2 \pi (M + Q_{in}) . U_{Q_{in}} |^2$$

at

$$M \pm (Q_{in} + n 2 c^*).$$

Strictly these expressions hold only when

$$(M + Q_{in}) . U_{Q_{in}} \ll 1/2 \pi,$$

being approximations of Bessel functions

$$J_0(2 \pi M . U_{Q_{in}})$$

and

$$J_1(2 \pi (M + Q_{in})).$$

$U_{Q_{in}}$ which give the true intensities for $\{ M \}$ and $\{ S_M \}$ respectively. Nevertheless, since the approximation is valid for a distortion amplitude small compared with the lattice spacing for the first few orders in $\{ M \}$, it is of use in considering the present results. Again, the above relates to a simple system with one atom per unit cell, but for TaS$_2$, where the scattering amplitude of the Ta atoms in the unit cell is considerably greater than that of the two sulphurs, we may apply the analysis directly. With the diperiodic like of Ta and Nb, the selenium now contributes significantly to the observed scattering, so we must now take into account the distortion waves in the chalcogen layers as well as in the cation sheets. However, this leads to extra information concerning the relative phases of these two sets of distortion waves, as seen in 2 H-NbSe$_2$, for example.

3.2 The 1 T Polytypes. — The distortion waves in 1 T-TaS$_2$ have been described in details by Scruby et al. [27]. For the present purposes, we will summarize their findings, noting firstly that for a given wave vector $Q_{in}$, there are three possible distortion modes within the TaS$_2$ layer:

i) Longitudinal (LA); $U_{Q_{in}} \parallel Q_{in}$ and $\perp c^*$.

ii) Transverse (TA); $U_{Q_{in}} \perp Q_{in}$ and $\perp c^*$.

iii) Transverse (TA); $U_{Q_{in}} \parallel Q_{in}$ and $\parallel c^*$. 

Fig. 10. — Oscillation X-ray photograph corresponding to figure 9, for Li intercalated 1 T-TaS$_2$, recorded at 295 K.
By virtue of the dot vector product in the intensity expressions above, we may readily deduce which mode contributes predominantly. The increase in intensity in figure 6 of the $\{ S_M \}$ surrounding each $M(hk.l)$ for increasing $h$, $k$ is expected for the increase in $M + Q_{in}$ and thus confirms the supposition of a periodic distortion. Furthermore, since the $\{ S_M \}$ increase in intensity with $h$, $k$ but not significantly with 2 for any fixed row in reciprocal space, it must be concluded that $U_{Q_{in}} e^* = 0$, the distortions lying predominantly within the layers, as assumed above. Since the $\{ S_M \}$ are also strongest for $Q_{in} \parallel M$ and weakest for $Q_{in} \perp M$, $U_{Q_{in}}$ must have a large component parallel to $Q_{in}$ so that the distortions are predominantly LA.

The amplitudes of the distortion wave in the $1T$-$TaS_2$ structure is sufficient ($\sim 0.1 \text{ Å}$) to produce considerable intensity in the $S_M (10.1)$ reflections; for this case, it is then possible in the electron microscope to form a dark field image of the distortion wave as is shown in figure 11 (Scruby [27]) where one of the three symmetry related wave vectors $Q_{in}$ and a matrix $M (20.0)$ reflexion have been used. This observation, apart from high lighting the physical reality of these effects, assumes great value in the absence of neutron diffraction data for this material. Although electron and X-ray diffraction are inherently incapable of distinguishing between static and dynamic effects, the micrograph of figure 11 (with an exposure time of over 60 s) retains phase information and conclusively demonstrates this mode in $1T$ to be soft; any fluctuations must be limited in amplitude to considerably less than the PLD wavelength, as any significant non zero frequency component would prelude its direct lattice imaging. The value of this result lies in its demonstration of the existence of long range static correlations in the incommensurate phase, since both diffraction data and the direct (averaged) measurement of PLD fringe spacing confirm the incommensurate nature of the mode. With regard to the differentiation between static and dynamic effects, it is also relevant here to point to the suggested dynamic origins of the diffuse streaking present in $1T$-$TaS_2$ (Scruby et al. [27]). For the present, we will not comment in detail on the appearance of this scattering except to identify (after Scruby et al.) the streaks as being predominantly transverse in character.

3.3 The 2H Polytotypes. — Qualitatively the behaviour, in terms of PLD/CDW, differs considerably in the 2H polytypes from that in the 1T forms above. The lower temperatures at which the effects manifest themselves coupled with the thermodynamic stability of the 2H trigonal prison coordinating unit, facilitates observation of the onset of the incommensurate phase in the undistorted metal; this contrasts with the 1T polytypes where irreversible transitions to the 2H phase usually set in before this can be observed ($T \sim 400$-$600$ K). The distortion wave amplitudes are considerably less in the 2H forms and in all cases, the observations indicate that the extra reflexions $\{ S_M \}$ are located with finite intensity within the zero layer in reciprocal space, suggesting the most likely interpretation in terms of a stacking repeat in phase with the matrix. Monckton et al. have shown in quantitative studies of $TaSe_2$ at 5 K that the static distortions in this material reveal opposite displacements of Ta and Se atoms. The electron observation of 2H-$NbSe_2$ reinforces this argument (Fig. 7) where for reflexions where scattering from the Nb and Se atoms in the all reinforce (for $h-k=3n$) leading to strong $\{ S_M \}$, the associated $\{ S_M \}$ are weak suggesting antiphase contributions from the PLD's in Nb and Se layers. For $TaSe_2$, $f(Ta) \sim f(Se)$ so that this effect is not as readily observed. The distortion modes responsible for the $\{ S_M \}$ are thus predominantly longitudinal in both 1T and 2H forms, although by and large, this is the only point of similarity between the two classes of polytypes.

3.4 Electronic Origins of the Lattice Distortions. — The reader is referred elsewhere for detailed considerations of the electronic origins of the above effects. Briefly, however, the response of a system of conduction electrons in a metal to an applied spatial perturbation of wave vector $q$ is determined by the form of the renormalised susceptibility, $\chi q$, derived from the bare unscreened $\chi^0 q$, where,

$$
\chi^0 q = \sum f_k \frac{f_{k+q}}{E_{k+q} - E_k}
$$

$f_k, f_{k+q}$ being Fermi distributions over $|k|, |k+q|$. For a free electron, gas Kohn (1959) pointed out that as a result of the form of the denominator in the above, a logarithmic divergence in the static susceptibility $\chi^0 q$ may occur when $q$ is close to spanning the Fermi surface i.e. $q \sim 2k_F$, giving rise to Kohn anomalies in the phonon spectra of metals. The magnitude of this effect is determined partly by the precise Geometric form of the Fermi surface;
and in particular Afanaseev et al. (1963) and later Fehlner and Loly [30] considered the increased contributions to the divergence in $\chi^0 q$ from cylindrical and nearly flat (i.e. parallel or nesting) pieces of Fermi surfaces, compared with the spherical surface discussed by Kohn.

If electron-electron as well as electron-phonon interactions are then taken into account, Overhauser [13] further postulated that below a suitable temperature, the divergence in $\chi^0 q$ may lead to the adoption of a CDW ground state in which the spatial fluctuations in electron density are determined by the $2k_f$ wave vector. The CDW ground state is then stabilized by coupling to a PLD, the ion core displacements essentially screening out the inhomogeneities in the electrostatic field of the CDW. The lowering in electrostatic energy in the conduction electrons is thus balanced by the increased elastic strain energy of distortions in the lattice.

Against this background, the adoption of a CDW/PLD ground state, particularly in the 1 T polytypes, becomes a credible proposition. Figure 12 reproduces the Fermi surfaces predicted for 2 H and 1 T-TaS$_2$ by Wilson et al. [2] from the calculations of Mattheiss [7]. Weak interlayer interactions, implying little band dispersion along $c^*$, result in large flat areas of Fermi surface, closely satisfying the criteria for good nesting. Empirically, figure 13 then compares the measured values (Scruby et al. [11]) of spanning vectors $Q_{12}$ with values of $k_f$ inferred from Mattheiss' calculations. The above proximity in points is reassuring, but sections $\Gamma K$ and $\Gamma M$ only were available in the calculations and no errors in either data are shown. As such, the detailed shape suggested by Scruby et al. [27] and later by Yamada et al. [28] requires examination as this departs from the simple ellipse proposed by Wilson et al. [2]. In fact, it is the form of the diffuse streaking in both electron and X-ray diffraction which suggests this shape. Assuming the critical $Q_{12}$ which produce strong reflexions $\{S_m\}$ are not unique scattering vectors, general perturbations $q_s$ (Fig. 12) might also be expected to give rise to divergent contributions in $\chi^0 q$ leading to a detectable phonon softening for certain modes. The diffuse streaking might therefore be interpreted as an image of the Fermi surface provided that $\chi^0 q$ (or more properly $\chi q$) peaks close to wave vectors characterising its undistorted geometry (Free- man et al. [29]; Fehlner and Loly [30]). This begs the question regarding the precise nature of the scattering which, as we have pointed out above, is predominantly transverse in character, and may, we conjecture, represent a dynamic effect.

The inflected, dumb-bell shape is, furthermore, consistent with Wilson et al.; suggestions regarding nesting of this Fermi surface for the critical vector $Q_1$. As those authors correctly point out for the unphysical case of a parallel, flat sided Fermi surface (Fig. 14a), the $Q_1$ adopted, parallel to $M$ maximises nesting of all six segments of Fermi surface, whereas the other possibility, parallel to $\Gamma K$ (14b) couples only two segments effectively. Unfortunately, as is seen in figure 14c, an elliptical cross section, of any significant curvature close to the zone boundary, destroys much of the nesting of figure 14a. Only for the proposed dumb bell shape is effective nesting restored for $Q_1 \parallel \Gamma M$. We note further that such a geometry results in points of inflexion close to the critical, spanning $Q_2$, with, therefore, large local radius ($\rightarrow \infty$) again a situation favouring a divergent $\chi^0 q$. 

![Fig. 12. - Fermi surfaces for (a) 2 H-TaS$_2$ showing both lower and upper bands respectively, deduced from the calculations of Mattheiss (b) 1 T-TaS$_2$.](image1)

![Fig. 13. - Comparison of, x, measured vectors $Q_{11}$ for 1 T-TaS$_2$ with, y, $k_f$ values inferred from APW calculations, projected onto the $\Gamma M K$ ($k_x,0)$ plane. Solid lines indicate part of surface imaged in diffraction by phonons.](image2)
Electronically, the consequences of the foregoing, namely the adoption of a CDW/PLD ground state (in pristine or intercalated material), are the destruction of large areas of nested Fermi surface by energy gaps. In this context, we note (Scruby, 1976) that for both 1 T1 and 1 T3-TaS2, not only the Q1 for S1 (10.1) span the surface but also those for second order perturbations S0 (11.1). As such reflections are not to be regarded as simple second order satellites of the S0 (10.1), but in fact represent distinct soft modes of different character, they also may give rise to gaps at the Fermi surface. On adoption of the \( \sqrt{13} \) superlattice in 1 T3, therefore, much, if not all, of the surface might conceivably be destroyed, consistent with the resistivity data below 190 K. This does not explain the metallic decrease in resistivity for 1 T-TaSe2 (Wattamaniak et al. [20]).

Finally we note that the question of the relative phases of the symmetry related CDW’s within individual lamellae of the CDW/PLD ground state lattices has yet to be considered. This has been discussed in detail by Scruby et al. [1] and by Wilson et al. [2] and for the present purposes, we will confine ourselves to a brief review of the consequences of these phase relationships. Of initial interest are the relative phases of the CDW and PLD within individual layers. These may most logically be considered to be in phase, since this results in an overlap between regions of high ion core and conduction electron density, optimising screening of the potentials set up by the CDW. Having suggested that, however, it is the three dimensional elastic and coulomb interactions between neighbouring layers and between the symmetry related CDW/PLD’s in each individual layer which determine the final form of the structure. The adoption of the 3 c c rhombohedral repeat in the PLD stacking in the incommensurate 1 T and 1 T2 phases is an expression of this, the interlayer...
interactions being minimised, as discussed elsewhere (Scruby et al. [1]; Wilson et al. [2]). In real space however, it is the relative phases of the PLD's within the single layer which produce the result of most immediate physical significance. Thus, figure 14 illustrates a modulated matrix structure for the three phases of 1-TaS2 for an arbitrary distortion amplitude and for three waves whose nodes coincide. In the incommensurate case (1 T1, 1 T2), the choice of origin is arbitrary, but in the commensurate 1 T1 phase, this has been chosen to coincide with a metal atom site. For all three phases, particularly 1 T3, the clumping of metal atoms around the CDW/PLD Supercell corners is evident, resulting in a reduced metal-metal overlap in the regions between. The strong resemblance between this situation and the conditions required for a Mott — type metal — insulator transition deriving from reduced metallic overlap form a tempting speculation with which to conclude the present discussion.

4. Summary and acknowledgments. — Concise summary of the above is difficult. This purely structural discussion omits references to the wealth of physical consequences of these charge density wave driven transitions, such as are reviewed elsewhere in the present volume. Final judgement on the above effects is therefore left to the reader, and we will conclude by thanking our colleagues A.D. Yoffe and A.J. Grant for stimulating discussions.

References

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