Electrical conductivity and charge density wave formation in 4H$_b$ TaS$_2$ under pressure

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Abstract. The two charge density wave (CDW) transitions in 4H$_b$ TaS$_2$ have been followed under pressure. The two transition temperatures were lowered when pressure was applied; the 315 K atmospheric pressure transition associated with CDW formation in the octahedral layers was suppressed by 35 kbar, the 22 K transition associated with CDW formation in the trigonal prismatic layers was suppressed at 8.5 kbar. The fall in the 22 K transition correlates with the rise in superconducting transition temperature. The behaviour of the resistivity at the CDW transitions is discussed and charge transfer from the octahedral layers to the trigonal prismatic layers is proposed. The effect of pressure on CDW formation in trigonal prismatic material is related to its superconducting behaviour under pressure through the microscopic CDW theory of Chan and Heine. It is found that the CDW transition temperature is most sensitive to band structure changes through the density of states at the Fermi level.

1. Introduction

The formation of charge density waves in the metallic layered transition metal dichalcogenides has been established recently by electron and neutron diffraction experiments and measurements of transport properties (Scruby and Williams 1975, Wilson et al 1975, Moncton et al 1975). The two-dimensional character of the Fermi surface of these materials leads to good nesting over large areas of Fermi surface and to a Kohn anomaly in the phonon spectrum which below a critical temperature condenses into a static distortion with a wavevector corresponding to a spanning of the Fermi surface.

We present measurements of the pressure dependence of the charge density wave (CDW) transitions in the mixed polytype 4H$_b$ TaS$_2$. It consists of alternating layers of trigonal prismatic coordination and octahedral coordination TaS$_2$, and its properties are to a large extent the composite of those of the pure octahedral (1T) and the pure trigonal prismatic (2H) materials. 4H$_b$ TaS$_2$ shows two transitions in its transport properties, one at 315 K, the other at 22 K (Wattamaniuk et al 1975, Di Salvo et al 1973). Electron diffraction experiments (Wilson et al 1975, Tatlock 1976) suggest that the higher transition at which two $\sqrt{3}$a rotated superlattices appear is associated with CDW formation in the octahedral layers, and that at the lower transition, where an incommen-
surate $3 \times 3$ superlattice forms, there is CDW formation in the trigonal prismatic layers. In §4 we discuss the effect of pressure on CDW formation in relation to the effect of pressure on the superconducting transition temperature $T_c$ in the 2H materials.

2. Experimental

The crystals used were taken from the same batch as those used by Wattamaniuk et al (1975). The CDW transitions cause sharp changes in the electrical conductivity which was monitored with a four-terminal measurement using a low-frequency AC (70 Hz) phase-lock technique. The transitions were followed at hydrostatic pressures up to 30 kbar and in the temperature range 3–300 K using a high pressure intensifying cell described elsewhere (Delaplace et al 1976). Pressure was applied at room temperature where the isopentane–isoamyl alcohol high-pressure fluid is liquid.

The upper transition $T_d$ falls very quickly with pressure (see figure 1) and would be completely suppressed for pressures greater than 35 kbar (see figure 2). Temperature hysteresis was about 2 K at all pressures. At slow cooling rates of about 3 min/deg we see a sharp drop in resistivity just before the rise to the lower temperature phase. This effect is not seen on warming.

The low-temperature transition $T_o$, again falls fast with increasing pressure (see figure 3). For the 8.5 kbar curve, the CDW transition is below 4 K.

The temperature at which a resistive transition to a superconducting state appears rises rapidly and tends to level off with pressure (figure 4). At the same time the transition width decreases dramatically, as shown in table 1. At atmospheric pressure there is a sluggish transition of width 3 K centred at 2 K but no specific heat anomaly (W A Phillips 1976, private communication).
Charge density waves in $4H_TaS_2$ under pressure

Figure 2. Pressure dependence of the upper transition, $T_u$ in $4H_TaS_2$, measured for decreasing temperature.

Figure 3. Low-temperature resistivity of $4H_TaS_2$ at high pressure showing the lower CDW transition (absent for $p \geq 8.5\text{kbar}$), and the superconducting transition. The order of runs was 6 kbar, 15 kbar, 28 kbar, 8.5 kbar and 1 bar.
Figure 4. Correlation between $T_{\text{CDW}}$, the onset transition, the $T_c$ the superconducting transition in 2H and 4H, TaS$_2$ under pressure. Data for 2H is from Delaplace et al (1976) and Smith et al (1975).

Table 1. Superconducting transition temperature and transition width for 4H, TaS$_2$ under pressure.

<table>
<thead>
<tr>
<th>$p$ (kbar)</th>
<th>$T_c$ (K)</th>
<th>$\Delta T$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>3.8</td>
<td>0.3</td>
</tr>
<tr>
<td>8.5</td>
<td>4.0</td>
<td>0.2</td>
</tr>
<tr>
<td>15</td>
<td>4.3</td>
<td>0.15</td>
</tr>
<tr>
<td>28</td>
<td>4.35</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The difference in the values of residual resistivity between the runs in figure 3 is most likely due to crystal and contact condition. The atmospheric pressure run was performed last and the 22 K transition was observed to be as sharp as in crystals that had not been pressure-cycled.

3. Discussion

3.1. Charge transfer

It is remarkable the extent to which the individual properties of the two types of layer resemble those of their respective pure, single coordination materials. Nevertheless there will be some interaction and charge transfer to even the Fermi levels. Some estimate of this transfer can be made from the magnitude of the wavevector seen in electron and neutron diffraction in the régime where the CDW is incommensurate with the lattice.
and its length is a reflection of the size of the Fermi surface. Values of this wavevector are collected in table 2 for the 2H, 1T and 4H₆ polytypes of TaS₂ and TaSe₂.

Table 2. Magnitude of superlattice wavevectors in TaS₂ and TaSe₂.

<table>
<thead>
<tr>
<th></th>
<th>TaS₂</th>
<th>TaSe₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2H 4H₆ 1T</td>
<td>2H 4H₆ 1T</td>
</tr>
<tr>
<td>Tₐ (K)</td>
<td>315† 350†</td>
<td>410</td>
</tr>
<tr>
<td>q'/a* T &gt; Tₐ</td>
<td>0.263† 0.288†</td>
<td>0.265</td>
</tr>
<tr>
<td>% incommensurate</td>
<td>−5.2 3.8</td>
<td>−4.3 2.6</td>
</tr>
<tr>
<td>Tₐ (K)</td>
<td>75† 22†</td>
<td>122</td>
</tr>
<tr>
<td>% incommensurate</td>
<td>small‡</td>
<td>-2.5</td>
</tr>
<tr>
<td>at T₀</td>
<td>+7°</td>
<td>0°</td>
</tr>
<tr>
<td>at 10 K</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


3.1.1. Octahedral layers. The commensurate superlattice is the rotated 3 × 1, √13 a cell with q'/a* = 0.277 (Wilson et al 1975), where a is the in-the-layer lattice vector, q' the superlattice wavevector and a* the in-the-layer reciprocal lattice vector. Both 1T polytypes have q'/a* larger than 0.277 and both 4H₆ polytypes have q'/a* smaller.

Figure 5(a) shows the wavevector spanning the Fermi surface that corresponds to q'

![Figure 5(a)](image)

for 1T TaS₂, and it can be seen that the electron surfaces must shrink to accommodate q' for 4H₆ TaS₂. This indicates charge transfer out of the octahedral layers. Wilson et al (1975) find that q' falls on substitutional doping of Ti for Ta in 1T TaS₂ as each Ti takes one electron out of the conduction band, and find that 12% Ti is necessary to reduce q'/a* to 0.263, the value in 4H₆ TaS₂, suggesting a transfer of 0.12 electrons. Optical transmission experiments on the similar mixed coordination polytype 6R TaS₂ (A R Beal and W Y Liang 1976, private communication) in which the optical properties of 6R are regarded as the average of those of 1T and 2H TaS₂ also indicate charge transfer of this sort of magnitude from the octahedral to the trigonal prismatic layers. Preliminary band-structure calculations, however, point to a smaller value (Woolley A M and Doran N J 1976, private communication) so the position is not entirely clear at present. The transfer in 4H₆ TaSe₂ would be a little smaller than in the sulphide (see table 2).
3.1.2. Trigonal prismatic layers. The commensurate superlattice in this case is $3 \times 3$, although so far only 2H TaSe$_2$ has been seen to lock in. The superlattice wavevector in the incommensurate state is larger in the 4H$_b$ than in the 2H polytypes. As we know that there is charge transfer into the layers this allows us to distinguish which of the possible nestings for the more complicated 2H Fermi surface is strongest. In figure 5(b) $q_1$ and $q_2$ span the hole pockets at $\Gamma$ and $K$, but as the band is filled these wavevectors will shrink. The vector $q_3$ suggested by Wilson et al (1975) will grow, so it seems that it is this nesting that is dominant. Rice and Scott (1975) have proposed a model for 2H materials with the Fermi energy at the saddle points in the band structure. A condition for temperature-dependent peaking in $\chi_q$ is that the Fermi energy should be less than $kT$ away from the saddle points. It is difficult to see how this condition can hold for the 12% increase in band occupation going from 2H to 4H$_b$ TaS$_2$.

3.2. Upper transition

The shape of the resistivity anomaly at the upper transition is consistent with the formation of the commensurate $\sqrt{13}a$ superlattice in the octahedral layers. Pure octahedral materials (1T) show a large increase in resistivity at the corresponding transition, so below the transition in 4H$_b$, current will mainly flow in the trigonal prismatic layers. It can be seen in figure 1 that above the transition $\rho^{-1}d\rho/dp|_T$ is negative and equal to $-7.7 \times 10^{-3}$ kbar$^{-1}$, characteristic of 1T materials, see Di Salvo et al (1974) for 1T TaSe$_2$ and 1T TaS$_2$. Below the transition $\rho^{-1}d\rho/dp|_T$ is small—characteristic of 2H material, such as 2H NbSe$_2$ where there is a 10% change in 30 kbar (Frindt et al 1972). The value for $dT_d/dp$ at room temperature is measured to be $-5.3$ K/kbar in good agreement with the room-temperature high-pressure work of Di Salvo et al (1973), who find a value of $-5.5$ K/kbar and it seems generally true that $dT_d/dp$ is larger the lower the transition temperature, both for 2H and 1T materials.

The sharp decrease in resistivity seen at the upper transition for slow cooling rates (figure 1) has not previously been reported. However we have seen the same phenomenon at the 1T$_1$–1T$_2$ (190 K) transition in 1T TaS$_2$ where the quasicommensurate state locks into the fully commensurate superlattice; when cooling slowly enough we see sharp decreases in resistivity by as large as a factor of two just before the resistivity rises and the material goes to its semiconducting state. The size of the jump depends on the previous thermal history of the sample.

McMillan (1976) has proposed a new description of the incommensurate state in 2H materials, where the charge density wave is for the most part commensurate with the lattice but has regions of quickly changing phase which he calls discommensurations. At the commensurate–incommensurate transition the density of discommensurations falls to zero, and the proposed mechanism for this is that of charge density wave dislocations (McMillan 1975) moving through the crystal interacting with the discommensurations and adjusting their density. A similar mechanism might be expected in the 4H$_b$ and 1T materials—there is evidence from photoemission from the Ta 4f core levels that the charge density wave in the ‘incommensurate’ 1T$_2$ phase of 1T TaS$_2$ is for the most part commensurate with the lattice (Hughes and Pollak 1976). It seems plausible that the sharp conductivity spike in 4H$_b$ TaS$_2$ and at the lock in transition in 1T TaS$_2$ may be due to current being carried by dislocations in the CDW. Dislocations can be either positively or negatively charged, and it would be expected that their mobility could rise fast as the density of discommensurations falls to zero at the transition, and could give a significant contribution to the conductivity.
It should be noted that this is not the so-called Fröhlich mode proposed for onedimensional (1D) systems where the charge density wave is supposed unpinned to the lattice (Fröhlich 1955) such that it can carry current without resistance. The proposed mechanism is essentially restricted to two dimensions though it has similarities with the nonlinear current-carrying excitation proposed by M J Rice et al (1976).

3.3. Lower transition

The shape of the lower resistivity anomaly differs from that in pure trigonal prismatic (2H) material in that there is temperature hysteresis of about one degree, and the resistivity drops very abruptly.

The temperature hysteresis (also seen in susceptibility) indicates a first-order transition, whereas the onset transition in 2H material is either second-order or more likely weakly first-order. McMillan (1976) in his latest, most exact, treatment of CDW transitions requires a Coulomb interaction between neighbouring layers to make the onset transition second order. In 4Hb material the trigonal prismatic layers are separated from one another by octahedral layers. The similar system of 4Hb TaSe2 has been investigated by neutron diffraction (Di Salvo et al 1976) and there is found to be no correlation between the CDW in one trigonal prismatic layer and the next. For these compounds the single-layer approximation in McMillan's earlier paper (McMillan 1975) should hold, where the transition is predicted to be first-order.

The behaviour of the resistivity at the 22K transition is at first sight very different from the much weaker transitions seen in the pure 2H materials, see figure 6. However in 4Hb the transition occurs at a lower temperature and it is this that can account for the difference. We picture the following situation:

Figure 6. Effective resistivity $\rho'$ for trigonal prismatic coordination TaS$_2$ in the 2H, 4Hb, and 6R polytypes. Since octahedral layers in 4Hb and 6R are effectively insulating below 300 K, $\rho'$ is defined as $\rho' = (\rho - \rho_{4Hb})$ for 2H and $\rho' = \frac{1}{2}(\rho - \rho_{4Hb})$ for 4Hb and 6R.

Figure 7. Schematic illustration for resistivity in trigonal prismatic coordination TaS$_2$, $\rho'$, showing ordinary metallic behaviour for an undistorted metal and additional resistivity due to enhanced impurity scattering or reduced area of Fermi surface. High- (T2) and low (T1) temperature transitions are shown, where $\rho'$ rises and falls respectively.
3.3.1. Above the onset temperature $T_0$. There will be enhanced electron–phonon scattering resulting from the softened phonon which will very effectively scatter electrons across the Fermi surface. Rice and Scott (1975) consider this mechanism for their model of the Fermi energy at saddle points of the energy band, although it will be the case for conventional ‘nesting’ of Fermi surfaces as well. Moncton et al (1975) find from inelastic neutron scattering that the longitudinal phonon mode does not soften completely at $T_0$, and for 2H TaSe$_2$ at 130 K, just above $T_0$, $\hbar \omega \sim 5 \text{ meV}$; so this scattering mode will be quenched below about 50 K. There will also be enhanced impurity scattering, as with decreasing temperature the increasingly unstable electron gas screens impurities in the lattice less effectively. Berthier (1976b) has seen pretransitional NMR line-broadening in 2H NbSe$_2$ and has found (Jérôme et al 1976) that most of the fluctuations in the electron density are static and pinned to the lattice. Real-space electron microscopy supports this observation (P M Williams and C D Scruby 1976, private communication).

This is to say that each impurity is surrounded by a region of charge density wave. Whilst there is no long-range coherence the contribution to the resistivity will be that of enhanced impurity scattering, and this will be effective at low temperatures.

3.3.2. Below the onset temperature, $T_0$. The scattering processes will now be different. The CDW is now coherent over larger distances and the Fermi surface must be reconstructed into the new Brillouin zone with the superlattice periodicity. The enhancement of impurity scattering will be absent, and scattering will be by electron–phonon processes, though the resistivity will be higher than for the undisturbed, normal metal (figure 7) as the projected area of Fermi surface is reduced by the gaps opened up by the CDW at the Fermi level.

As is shown schematically in figure 7, if the transition is at a high temperature, $T_2$, $\rho$ may rise, but at low temperature, $T_1$, $\rho$ will fall as the electron–phonon scattering in the CDW state will be quenched out. Figure 6, which shows effective resistivity in trigonal prismatic layers in the 2H, 4H$_b$ and 6R polytypes of TaS$_2$, indicates how the scheme in figure 7 works in practice. What is surprising perhaps is that in 4H$_b$ TaS$_2$ at pressures of 8.5 kbar and above, where the CDW state is not stable, $\rho$ is still falling fast at helium temperatures (figure 3). This may reflect changes in the strength and coherence length of the screening around impurities, or electron–electron scattering, which will be enhanced as the Coulomb interaction between electrons will be poorly screened by the almost unstable electron gas.

The transition at 22K in 4H$_b$ falls very fast with pressure and fits the general observation that the lower the transition the faster it falls. A relation of the form $dT_0/d\rho \propto 1/T_0$ is quite well obeyed for the trigonal prismatic materials, see table 3. We discuss this further in §4.

Table 3. CDW onset temperature and rate of fall with pressure for trigonal prismatic coordination compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_0$ (K)</th>
<th>$dT_0/d\rho$ (K kbar$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H TaS$_2$</td>
<td>75</td>
<td>-0.17</td>
</tr>
<tr>
<td>2H NbSe$_2$</td>
<td>33</td>
<td>-0.36</td>
</tr>
<tr>
<td>4H$_b$ TaS$_2$</td>
<td>22</td>
<td>-0.8</td>
</tr>
</tbody>
</table>

3.4. Superconductivity

Superconductivity is found in all the purely trigonal prismatic coordination sulphides
and selenides (2H and 3R) of Nb and Ta so far investigated. It has not been found in the semimetallic or semiconducting octahedral coordination materials.

4H$_2$ TaS$_2$ does not become a bulk superconductor above 1·1 K (Meyer et al 1975) at atmospheric pressure, although nearly all crystals show sluggish resistive transitions with widths of several degrees between 1K and 4K. We consider that the strong correlation between the falling CDW transition and the rising $T_c$, and the narrowing of the transition, to be a strong indication that the transition seen under pressure is a bulk effect and associated with the trigonal prismatic layers. The correlation between the fall in CDW transition temperature and rise in $T_c$ with increasing pressure shown in figure 4 has now been firmly established in 2H TaS$_2$ (Delaplace et al 1976) and 2H NbSe$_2$ (Berthier et al 1976a) and it seems clear that the weakening of the CDW with pressure restores areas of the Fermi surface lost by the creation of gaps at the Fermi level, thereby increasing the density of states at the Fermi level and hence the superconducting transition temperature. That $T_c$ remains almost constant between 15 and 28 kbar confirms the suggestion by Friedel (1975) that the soft phonon mode is not responsible for the behaviour of $T_c$ but rather the density of states at the Fermi level, $N(E_F)$.

Smith et al (1975) have investigated the pressure dependence of $T_c$ for TaS$_{2-x}$Se$_x$ compounds, and find for 4H$_b$ TaS$_{1.8}$Se$_{0.2}$ that $T_c$ is almost pressure independent, rising at $2.3 \times 10^{-2}$ K kbar$^{-1}$ to 3.1 K at 22 kbar. Anion disorder will suppress the CDW transition, so $N(E_F)$ will not be lowered, and pressure will have relatively little effect.

It is interesting to note that if the $T_c$ versus pressure data of Smith et al (1975) for 2H TaS$_2$ is extrapolated to 43 kbar where the CDW will have been driven out (Delaplace et al 1976), $T_c$ will have risen to 4.5 K—a value surprisingly close to the 4.35 K seen in 4H$_b$TaS$_2$ at high pressure. Both these values are similar to the higher values of $T_c$ found for crystals of 2H and 4H$_b$TaS$_2$ intercalated with hydrogen and organic bases (Meyer et al 1975, Murphy et al 1975). The CDW transport property anomalies are suppressed in these intercalated crystals, and the high pressure results certainly give strength to the view that the rise in $T_c$ in these compounds when intercalated is to some extent due to the weakening of the charge density waves in them.

The broad superconducting transitions seen between 1 K and 4 K in 4H$_b$ TaS$_2$ at atmospheric pressure, and 2H TaS$_2$, where crystal samples gave $T_c$ between 1·8 K and 4 K with $\Delta T$ 1-2K (Di Salvo 1971), which are picked up in measurements of susceptibility or conductivity may be due to trigonal prismatic coordination material which either through stacking faults or other crystal defects has a weakened CDW and hence an enhanced $T_c$. The effect of pressure is to drive the bulk transition through this ambient-pressure transition, leading to much sharper transition widths at high pressure.

4. Effect of pressure on CDW formation

It is not immediately clear by what mechanism pressure decreases CDW transition temperatures, though this is the case for all the onset transitions in trigonal prismatic material and lock-in transitions in octahedral material so far investigated. However in the closely related quasi one-dimensional metallic systems that undergo Peierls distortions, the distortion temperature does not always fall with pressure. It does fall in the mixed-valence planar platinum complex $K_3$ Pt(CN)$_9$Br$_{0.3}$H$_2$O (Thierlemans et al 1976) but in the organic charge-transfer salt TTF–TCNQ the upper transition which is associated with formation of the charge density wave state in each chain rises at 0.7 ± 0.3 K/kbar (Cooper et al 1975). For the layer compounds, however, Delaplace et al
(1976) suggest that with pressure the increasing interlayer interaction will lead to a more three-dimensional Fermi surface, reducing the Fermi surface nesting and the corresponding Kohn anomaly. Doran et al (1976) have suggested that the degree of nesting is not so important and that the strength of the electron–phonon interactions is a more crucial factor. In this case the stiffening of the lattice with pressure will be significant. It is possible to relate the CDW transition temperatures of the trigonal prismatic 2H polytypes to their superconducting transition temperatures through the microscopic CDW theory of Chan and Heine (1973) and the theory for strongly coupled superconductors of McMillan (1968).

The criterion for a charge density wave coupled to a periodic lattice distortion is

\[ 2I^2/M\omega^2 - (2\bar{U} - \bar{V}) \geq 1/\chi_q, \]  

(1)

where \( I \) is the electron–phonon matrix element at wavevector \( q \), \( \omega \) is the bare phonon frequency at \( q \), \( \bar{U} \) and \( \bar{V} \) are the Coulomb and exchange energies at \( q \), and \( \chi_q \), the wavevector-dependent susceptibility, is defined as

\[ \chi_q = \sum_k \frac{f_k - f_{k+q}}{\delta_{k+q} - \delta_k} \]

where \( f_k \) is the Fermi function.

The superconducting coupling constant is

\[ \lambda = N(E_F) \langle I^2 \rangle / M \langle \omega^2 \rangle \]

(3)

where \( \langle I^2 \rangle \) is the Fermi surface average of the matrix element, and \( \langle \omega^2 \rangle \) is an average of phonon frequencies, renormalized by the Kohn anomaly. In spite of \( I \) and \( \omega \) being averaged differently in equations (1) and (3) we expect them to scale with pressure and take

\[ \lambda = \frac{1}{2} N(E_F) \left( \frac{2I^2}{M\omega^2} \right). \]

(4)

First we see how \( \lambda \) varies with pressure for the system 2H NbS\(_2\) which does not show a CDW transition. The superconducting transition temperature, \( T_c \), is almost constant with pressure, \( |dT_c/dp| < 2 \times 10^{-3} \text{ K/kbar} \) (Molinié et al 1974). We note that \( T_c \) is also relatively pressure-independent in 2H NbSe\(_2\) at pressures greater than 36 kbar (Smith et al 1972) where the CDW state is no longer stable (Berthier et al 1976a), \( dT_c/dp = +2 \times 10^{-3} \text{ K/kbar} \). Using the McMillan formula for \( T_c \),

\[ T_c = \frac{\theta_D}{1.45} \exp \left[ \frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right], \]

(5)

where \( \theta_D \) is the Debye temperature and \( \mu^* \) the Coulomb pseudopotential, Hopfield (1971) obtained

\[ \frac{d\ln T_c}{dp} = \frac{1}{B} \left[ \gamma_G + \left( \frac{1.04\lambda}{\lambda - \mu^*(1 + 0.62\lambda)} - \frac{1.04(1 + \lambda)(1 - 0.62\mu^*)}{[\lambda - \mu^*(1 + 0.62\lambda)]^2} \right) \right. \]

\[ \left. \times \left( 2\gamma_G + \frac{d\ln(N(E_F)I^2)}{d\ln V} \right) \right], \]

(6)

where \( B \) is the bulk modulus, \( \gamma_G \) the Gruneisen constant defined as \( -d\ln\theta_D/d\ln V \) and \( \theta_D/1.45 \) has been replaced by \( \omega_{\text{average}} \). This assumes that \( \mu^* \) is constant with pressure.

A value of \( \lambda \) for 2H NbS\(_2\) can be obtained by using the specific heat data in table 6.
of Wilson et al (1975) in McMillan's formula
\[ \lambda = \frac{1.04 + \mu^* \ln(\theta_D / 1.45 T_c)}{(1 - 0.62 \mu^*) \ln(\theta_D / 1.45 T_c) - 1.04}. \] (7)

Taking \( T_c = 6.3 \text{ K} \), \( \theta_D = 200 \text{ K} \) and \( \mu^* = 0.13 \), the average value for d-band metals, gives \( \lambda = 0.79 \). Setting \( d\ln T_c / dp = 0 \) gives
\[ \frac{d\ln(N(E_F)I^2)}{d\ln V} = -1.59 \gamma_G \text{ and } \frac{d\ln \lambda}{d\ln V} = 2\gamma_G + \frac{d\ln(N(E_F)I^2)}{d\ln V} = 0.41 \gamma_G. \]

Taking \( \gamma_G = 1.5 \) than gives \( \frac{d\ln(N(E_F)I^2)}{d\ln V} = -1.13 \).

Now to the CDW criterion, and the electron–phonon term in equation (1)
\[ \frac{d\ln(2I^2/M\omega^2)}{d\ln V} = \frac{d\ln \lambda}{d\ln V} - \frac{d\ln N(E_F)}{d\ln V}. \] (10)

For tight binding, the bandwidth is proportional to the overlap integral between neighbouring atoms which goes as \( e^{-aq} \). Taking \( N(E_F) \) inversely proportional to the bandwidth we have
\[ \frac{d\ln N(E_F)}{d\ln V} = +\frac{1}{2}aq_0, \] (11)

so in (10)
\[ \frac{d\ln(2I^2/M\omega^2)}{d\ln V} \approx 0.26 - 1.13 = -0.52. \]

This is probably an overestimate; we took \( d\ln T_c / dp = 0 \), in fact it is slightly positive, making \( d\ln \lambda/d\ln V \) smaller. This is to say that \( 2I^2/M\omega^2 \) will increase with pressure making the CDW more stable, which is contrary to experimental findings. The increase in lattice frequency with pressure is more than compensated by the increase in electron–phonon matrix element. In the tight-binding theory of Barisić et al (1970) this matrix element is proportional to the width of the d band and the overlap integral, which will increase with pressure. We must look therefore for changes in the band structure which will decrease \( \chi_q \) in equation (1) at high pressure.

We can express \( \chi_q \) as \( \chi_q = N(E_F)\phi(T) \), where \( \phi(T) \) contains the temperature dependence of the ‘peaking’ of \( \chi_q \) at the nesting wavevector \( q \). For a one-dimensional system, where there is perfect nesting, \( \chi_q \) diverges logarithmically with \( T \) (Rice 1975). \( \phi(T) \) will reflect the amount of Fermi surface nesting, which will fall as, with increasing interlayer interaction, the Fermi surface becomes less two-dimensional. \( N(E_F) \) will depend on the width of the d sub-band where the Fermi level lies. We can most easily picture the structure of the d band in a ligand-field model (Mattheiss 1973). The d orbitals are split by an octahedral field into an upper doubly-degenerate \( e_g \) level and a lower triply-degenerate \( t_{2g} \) level. The trigonal prismatic field further splits the \( t_{2g} \) level into a singly-
degenerate $d_z^2$ lower level and a doubly-degenerate $d_{xy}$, $d_{x^2-y^2}$ upper level. Hybridization between these two levels results in a lower sub-band with mixed $d_{x^2-y^2}$ character split off from the rest of the $d$ band by about one electron volt. Pressure will increase the width of this sub-band where the Fermi level lies in two ways. First with increasing overlap between neighbouring $d$ states the $d$ band width will increase, as previously discussed. Secondly as the compounds are more compressible perpendicular to the layers rather than parallel, pressure will decrease the ratio of the lattice parameters, $c/a$, increase the trigonal prismatic ligand field, and increase the splitting between the $d_z^2$ and the $d_{xy}$, $d_{x^2-y^2}$ levels. This will reduce the amount of hybridization between them, thereby increasing the sub-band width, and decreasing the density of states.

Thompson (1975) has noted the correlation between $T_{CDW}$ and $c/a$ in the Group V dichalcogenides, successfully fitting in his scheme the absence of a CDW in 2H NbS$_2$. This is consistent with the dependence of the sub-band width on the strength of the trigonal prismatic ligand field. It is difficult to be quantitative in equation (1) as the relative values of the terms in the inequality are not well known, but it is possible to say that the increase in $2I^2/M\omega^2$ with pressure is more than compensated by a faster decrease in $\chi_q$. The decrease in $\chi_q$ is largely brought about by the increase in sub-band width, and it is not clear how important is the fall in Fermi surface nesting.

Jérôme et al (1976) have considered the case where $\phi(T) \sim \ln(T'/T)$. Putting this in (1) gives

$$T_0 = T' e^{-1/\Lambda},$$

where

$$\Lambda = N(E_F)[2I^2/M\omega^2 - (2U - V)]$$

and $T_0$ is the CDW transition temperature. So

$$\frac{d\ln T_0}{dp} = \frac{1}{\Lambda^2} \frac{d\Lambda}{dp}.$$  

If $d\Lambda/dp$ is approximately the same for the whole series of Group V dichalcogenides, and since $\Lambda$ will be small for compounds with a low $T_0$, we can expect $d\ln T_0/dp$ to be largest for systems where $T_0$ is small; this is seen to be the case in table 3.

In conclusion, we have compared the effect of pressure on CDW formation and superconductivity for trigonal prismatic materials. We suggest that the CDW transition temperature is more determined by band structure changes than by lattice stiffening, and that the band structure determines CDW formation both through the density of states at the Fermi level and the two-dimensionality of the Fermi surface. At present we cannot resolve the relative importance of these two effects.

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Charge density waves in 4H-TaS₂ under pressure

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