# LAYER COMPOUNDS. CHARGE DENSITY WAVES IN TRANSITIONS METAL COMPOUNDS.ELECTRONIC PROPERTIES OF TRANSITION METAL DICHALCOGENIDES : CONNECTION BETWEEN STRUCTURAL INSTABILITIES AND SUPERCONDUCTIVITY

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# ELECTRONIC PROPERTIES OF TRANSITION METAL DICHALCOGENIDES : CONNECTION BETWEEN STRUCTURAL INSTABILITIES AND SUPERCONDUCTIVITY (≠)

D. JÉROME (*), C. BERTHIER (†), P. MOLINIÉ (**) and J. ROUXEL (**)

**Résumé.** — Nous examinons les propriétés électroniques des dichalcogénures en couche des métaux de transition qui ont la particularité de présenter des transitions de phase accompagnées par l'apparition d'ondes de densité de charge (ODC). La stabilité d'un état avec ODC pour les composés $TX_2$(T = Nb, Ta, X = S, Se) est favorisée par la forme cylindrique de la surface de Fermi et par l'existence dans la structure de bande de singularités de Van-Hove proches du niveau de Fermi. L'anisotropie des composés lamellaires est reliée aux propriétés physiques telles que : compressibilité, conductivité électrique et propriétés supraconductrices. Dans les polytypes à environnement prismatique trigonal, 2H-$NbSe_2$, $TaSe_2$, $TaS_2$ l'apparition de l'ODC est caractérisée par une légère anomalie de la résistivité ; alors que pour les polytypes à environnement octaédrique 1T-$TaS_2$, la formation de l'ODC s'accompagne d'une transition métal-isolant. Nous présenterons une étude RMN de l'état avec ODC dans 2H-$NbSe_2$. Au-dessous de la température d'apparition la redistribution des électrons de conduction crée un élargissement inhomogène des satellites quadrupolaires de $^{93}$Nb.

De l'interprétation de la forme des raies de RMN nous avons pu en déduire l'existence de trois ondes de densité de charge incommensurables dans 2 H-$NbSe_2$ au-dessous de 33 K. L'amplitude de l'ODC mesurée par RMN est proportionnelle à la température d'apparition, en accord avec une théorie de champ moyen. Les effets prétransitionnels observés au-dessus de la transition ont été reliés aux perturbations statiques de la distribution électronique créées par les impuretés chargées. Nous avons observé au-dessus de 33 K une contribution à la relaxation nucléaire spin réseau de $^{93}$Nb due aux fluctuations critiques dynamiques. Les états avec ODC ont été étudiés par résistivité dans 2H-$TaSe_2$ où un ancrage de l'ODC incommensurable s'établit par une transition du premier ordre entre 87 et 93 K et dans le polytype mixte 4 $HbTaS_2$ avec un ancrage dans les feuillets 1T à 320 K et une apparition de l'ODC dans les feuillets 2H à 22 K. Une étude sous haute pression démontre l'existence d'une relation entre l'augmentation de $T_c$ et l'existence d'une transition structurale à $T_0 > T_c$. La transition de phase avec ODC sera examinée dans le cadre de la théorie phénoménologique de McMillan. A ce propos le cas de 4 $HbTaS_2$ présente un intérêt particulier puisque l'apparition de l'ODC se produit par une transition du premier ordre, ce qui suggère un couplage plus faible entre feuillets 2H des composés mixtes qu'entre ceux des polytypes 2H purs.

**Abstract.** — We discuss the electronic properties of the transition metal dichalcogenide layer compounds which have been investigated in detail because they undergo phase transitions accompanied by the occurence of charge density waves (CDW). The CDW state is favoured by the cylindrical nature of the Fermi surface and also by the possible existence of Van-Hove singularities in the band structure close to the Fermi level of the compounds $TX_2$(T = Nb, Ta, X = S, Se). The anisotropy of the layer compounds is related to physical properties such as : compressibility, electrical conductivity and the superconducting properties. In the trigonal prismatic polytypes 2H-$NbSe_2$, $TaSe_2$, $TaS_2$ the onset of a CDW is characterized by a weak anomaly in the resistivity ; whereas in the octahedral coordinated polytypes (1T-$TaS_2$), the formation of a CDW induces a metal-insulator transition. A detailed study of the CDW state by NMR on 2H-$NbSe_2$ will be presented. Below the onset temperature, a redistribution of the conduction electrons causes an inhomogeneous broadening of the $^{93}$Nb quadrupolar satellites. From the interpretation of the line shape of the NMR lines we have deduced the existence of 3 incommensurate CDW in 2H-$NbSe_2$ below 33 K. The amplitude of the CDW measured by NMR is proportional to the onset temperature as expected in a mean field theory. The pretransitional effects observed above the transition are related to static perturbations of the electron distribution induced by the charged impurities. A contribution of dynamical critical fluctuations above 33 K to the $^{93}$Nb spin-lattice relaxation rate has also been observed. The CDW states have been studied by resistivity measurements in other systems such as 2H-$TaSe_2$ where a lock-in of the ICDW occurs through a 1st order phase transition between 87 and 93 K, or in the mixed polytype 4 $HbTaS_2$ with a lock-in in 1T layers at 320 K and an onset in the 2H layers at 22 K. A pressure investigation shows a connection between the enhancement of $T_c$ and the existence of a structural phase transition at $T_0 > T_c$. The CDW phase transition will be discussed in terms of the phenomenological theory of McMillan. In this respect 4 $HbTaS_2$ is of particular interest since the onset of CDW's occurs through a 1st order transition and therefore suggests that the coupling between the trigonal prismatic layers is relatively weaker in the mixed polytypes than in the pure 2H polytypes.

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1. **Introduction.** — Transition metal layer compounds dichalcogenides have been the subject of intensive work for the last decade. At the beginning the metallic layer compounds were studied for their superconductivity properties related to the strong anisotropy of the crystalline structure. More recently, structural instabilities have been discovered in these compounds the origin of which is connected with the two dimensional character of the electronic structure. It is only during the last few years that a tight connection between structural instabilities and superconductivity has become evident.

After a short presentation of the anisotropic properties of layer dichalcogenides, this paper intends to offer a complete reexamination of their electronic structure based on the more recent experimental results. We plan to present in this article :

(i) A microscopic experimental investigation of structural instabilities in the trigonal prismatic compounds by NMR.

(ii) An experimental study of structural instabilities and superconductivity under high pressure.

(iii) A review of the theoretical approaches to the distorted phases.

(iv) The connection between the existence of distorted phases and superconductivity : some models.

For a review of the physical properties of layer dichalcogenides the reader can be refered to several exhaustive articles written on the subject [1, 2, 3, 4].

We shall concentrate in this article more particularly on the compounds with formula $TX_2$ (T = Nb, Ta, X = S, Se) with the following structure : the basic element is a $TX_2$ layer built with a hexagonal compact metal ion arrangement sandwiched between two chalcogen ion arrangements. The anisotropy of the crystals comes from covalent bonding within every layer and weaker Van der Waals forces from one layer to its neighbours. This latter bonding is weak enough however to allow intercalation between layers of metal ions or of Lewis base organic molecules.

A peculiarity of the layer compounds is the diversity of possible stacking of the layers leading to different polytypes. They are characterized by the environnement of the transition metal ions.

*a*) An octahedral environnement corresponds to the 1T polytypes with one molecule per unit cell along the *c* axis (stacking axis) and a stacking sequence, AbC, AbC, etc...

*b*) A trigonal prismatic environnement corresponds to the 2H polytypes with two molecules per unit cell along *c* and a stacking sequence AbA, CbC, AbA, etc...

*c*) There exist also mixed-coordination polytypes called 4 Hb corresponding to the stacking sequence AbA, CbA, CbC, AbC, ... These polytypes have alternating trigonal prismatic and octahedral layers.

1T polytypes include the IVb group of cations (Ti, Zr, Hf) which are semiconducting compounds because of the absence of any d electrons in the conduction band. 2H polytypes are characteristics of the VIb group for which the band formed by the overlapping of mainly $dz^2$ atomic orbitals is completely filled with the two d electrons. The $dz^2$ band appears to be well separated from the upper d bands, as shown by optical and energy loss experiments [5]. The few eV energy gap between the full $dz^2$ band and the upper bands was attributed to the intralayer hybridization between wavefunctions $dz^2$ and $dxy$ or $dx^2$-$y^2$ in the trigonal prismatic environnement [6].

In the Wilson and Yoffe [1] model the splitting between the $dz^2$ band and the rest of the d bands was attributed to crystal field effects. Both 1T and 2H polytypes exist for the group Vb(Nb, Ta). In the absence of strong correlation effects the half filled conduction band leads to rather good metals, becoming superconductors when the metallic phase is stable down to low temperature (2H and 4 Hb polytypes). The anisotropy can be viewed through the transport properties. For example the ratio of the resistivity parallel to *c* to the resistivity perpendicular to *c* is $\rho \,//\, c/\rho \,//\, c \approx 30$ in 2 H-$NbSe_2$ at room temperatures [7, 8].

The $Hc_2$ critical fields are strongly anisotropic whether the magnetic field is $//\, c$ or $\perp c$ for single crystal samples, $Hc_2 \perp c/Hc_2 \,//\, c = \varepsilon \approx 3 - 4$ in 2H-$NbS_2$ or 2H-$NbSe_2$ [9].

The strong anisotropy of electrical and optical properties have stimulated a superconductivity study under pressure. The first results obtained on 2H-$NbSe_2$ have shown a strong (though slightly overestimated) positive pressure coefficient for $T_c$ between 0 and 15 kbar [10]. Several additional contributions showed that the fast increase of $T_c$ stops around 36 kbar [11, 12, 13]. Beyond that pressure up to 150 kbar the coefficient becomes at least one order of magnitude smaller [14].

A description of superconductivity in these layer compounds in terms of an interlayer Josephson coupling has been proposed by Lawrence and Doniach [15] Kats [16] and Tsusuki [17]. A similar model has been used to explain the pressure enhancement of $T_c$ [18]. However, pressure experiments on 2H-$NbS_2$ [9] have revealed a behaviour of $T_c$ for that compound strikingly different from that observed in 2H-$NbSe_2$, whereas the band structures and the analogies between $H_{c2}$ anisotropies would indicate the existence of similar enhancement mechanisms of $T_c$ for both compounds. These results led Molinié *et al.* [9] to reject the Josephson model for the pure 2H layer compounds. It appears however that the Josephson picture is valid as long as the jump frequency of carriers between layers remains small compared with the energy gap of superconductivity [19]. Only intercalated dichalcogenides for which $\rho \,//\, c/\rho \perp c > 10^5$ [20] can be described by the Josephson model up to the immediate vicinity of $T_c$ [21].

The pure compounds 2H-$NbSe_2$ and 2H-$TaS_2$ are anisotropic type II superconductors and can be described by a Landau-Ginzburg anisotropic model [22]. In such case the effective mass anisotropy $m \perp c/m \parallel c$ is equal to $\varepsilon^2$. Experimental value for $m \perp c/m \parallel c$ varies from 10 to 6.2 in 2H-$NbSe_2$ according to the various authors and is equal to 8.4 in 2H-$NbS_2$ [9]. A connection between the enhancement of $T_c$ and the existence of a distorted phase for 2H-$NbSe_2$ was suggested by Molinié *et al.* [9].

2. **A microscopic experimental investigation of structural instabilities in trigonal prismatic compounds by NMR.** — A renewed interest in the study of layer dichalcogenides was triggered by the finding of satellites around Bragg diffractions in electron and X-ray diffraction patterns. The first observations of Bragg satellites were made for the 1T polytypes of the Vb group [23, 24]. They are extensively reviewed by Wilson *et al.* [3] and Williams [4]. The existence of superlattice or periodic lattice distortion (PLD) accompanied by charge density waves (CDW) was subsequently found in all 1T polytypes.

More recently similar observations have been reported by neutron and electron diffraction in 2H-$NbSe_2$ [25, 26] and the mixed polytypes 4 $HbTaSe_2$ [27] and 4 $HbTaS_2$ [28].

The occurrence of superlattices is accompanied by either metal-insulator transition (1st order M-I transition at 352 K in 1T-$TaS_2$) or by metal-semimetal transition (1st order M-SM transition at 473 K in 1T-$TaSe_2$).

As far as the 2H polytypes are concerned, less intense effects have been observed at lower temperatures, leading to metal-metal transitions. The formation of a superlattice is accompanied by peaks in the Pauli susceptibility at 120 and 77 K for 2H-$TaSe_2$ and 2H-$TaS_2$ respectively [29], together with slight resistivity anomalies at the same temperatures [30]. In 2H-$TaSe_2$, a second transition (1st order) occurs at lower temperature $\approx$ 90 K, which was discovered by neutron diffraction [5]. In 2H-$NbSe_2$ a resistivity anomaly is observed at 33 K [31, 32]. All these resistivity anomalies, signatures of the phase transformations, have made possible the various pressure investigations discussed in this article.

Band structure calculations have demonstrated the electronic nature of the structural instabilities [6, 33, 34, 35]. The conduction band is built with the hybridized $dz^2$ atomic orbitals. The filling of that band by a single d electron and the quasi 2 d nature of the materials lead to simple, nearly cylindrical, Fermi surfaces [36]. It has further been noticed that the special geometry of the Fermi surface reveals large portions which can be superimposed by the translation of a unique wave vector **Q** (nesting properties) [23, 25, 3]. However, the various mechanisms for the structural instabilities will be discussed in section 4.

Now, we shall see how NMR studies on $^{93}Nb$ can provide information on static as well as dynamic properties of the structural instabilities of 2H-$NbSe_2$ single crystals. In a total magnetic field $\mathbf{H}=\mathbf{H}_0+\mathbf{H}_{int}$ at an axial symmetry site the hamiltonian of a nuclear spin **I**, with quadrupolar moment $Q$, becomes [37]

$$\mathcal{H} = -\gamma_n \hbar \mathbf{I}.\mathbf{H} + \frac{e^2 qQ}{4I(2I-1)}(3I_z^2 - I(I+1)) \quad (1)$$

where $eq = V_{ZZ}$ is the component of the electric field gradient (EFG) along the principal axis $Z$ taken as the $c$ axis. For $^{93}Nb$ $I = 9/2$ and $\gamma_n$ is the nuclear gyromagnetic ratio. If the magnetic field is parallel to the $c$ axis, the 9 different frequencies of the Zeeman transitions are given by the relation :

$$\hbar\omega_{m\to m-1} = \gamma_n \hbar H_0(1 + K_{//}) + \hbar\omega_Q(m - 1/2) . \quad (2)$$

In (2), $K_{//}$ is the Knight shift given by the internal field $\mathbf{H}_{int}$ when $\mathbf{H}_0 \parallel c$, $\hbar\omega_Q = 3e^2 qQ/2I(2I-1)$ and $Q = 0.15 \times 10^{-24}$ cm$^2$ for $Nb^{93}$. We see immediately from (2) that a distribution of EFG at nuclear sites induces an inhomogeneous broadening of the quadrupolar satellites $m \neq 1/2$.

Although NMR is particularly well suited to the study of ICDW in 2H-$NbSe_2$, there have been few such experiments until now. Ehrenfreund *et al.* [38] interpreted their powder results as the occurrence, at low temperature, of a structural distortion with two distinct Nb sites ; an interpretation which as we shall later see is probably erroneous. More recently Valič *et al.* [39] reported a preliminary CW NMR study which is consistent with the results presented in our article [40]. All our results have been obtained with a pulsed NMR spectrometer. Figure 1 shows the evolution of the $(-3/2, -1/2)$ satellite line as a function of temperature. The linewidth remains nearly constant down to 77 K and then subsequently broadens on cooling down to 33 K. Below 33 K, a structure appears which extends over 300 G at 4.2 K. On the central line $(-1/2, 1/2)$ no broadening is observed down to 33 K. Below 33 K a structure occurs, Figure 2, the amplitude of which is proportional to the intensity of the magnetic field and which corresponds to a Knight shift distribution according to relation (2).

At 33 K, neutron diffraction has shown [25] the existence of a second order or very weakly first order transition. At lower temperatures a superlattice is characterized by the star of 3 wave vectors $\mathbf{K}_1$, $\mathbf{K}_2$, $\mathbf{K}_3$ with projections on the $\mathbf{a}_1^*$, $\mathbf{a}_2^*$ plane given by

$$\mathbf{K}_1' = \frac{\mathbf{a}_1^*}{3}(1-\delta), \qquad \mathbf{K}_2' = \frac{\mathbf{a}_2^*}{3}(1-\delta),$$

$\mathbf{K}_1' + \mathbf{K}_2' + \mathbf{K}_3' = 0$, where $\mathbf{a}_1^*$ and $\mathbf{a}_2^*$ are vectors of the planar hexagonal reciprocal lattice. The positive coefficient $\delta$, a few %, in 2H-$NbSe_2$ is a measure of the incommensurability of the periodic lattice distortion below 33 K. The PLD is accompanied by a CDW of similar symmetry. Taking the origin of the CDW

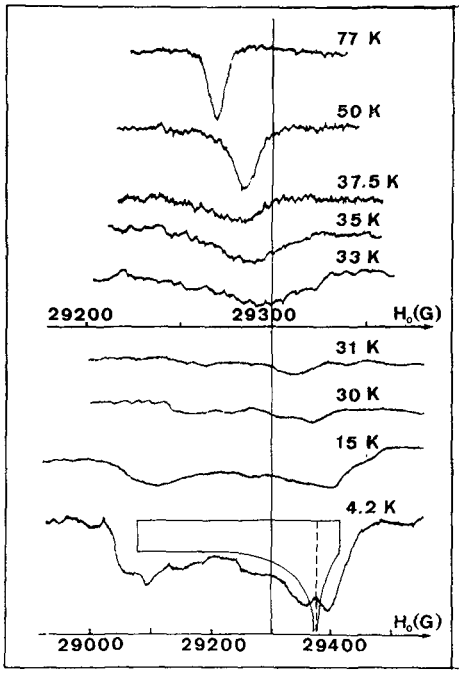


FIG. 1. — Evolution of the $(-\frac{1}{2}, -\frac{3}{2})$ transition as a function of temperature ($P = 1$ bar). The solid line represents the calculated lineshape for an EFG distribution associated to a triple ICDW. Recordings are obtained by Fourier transform of the free decay above 33 K and of spin echo below that temperature.

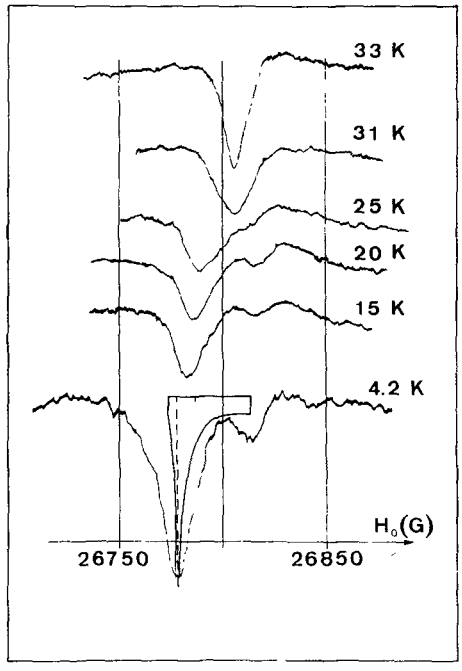


FIG. 2. — Lineshape of the central line $(\frac{1}{2}, -\frac{1}{2})$ below 33 K ($P = 1$ bar). The solid line is the calculated line shape corresponding to a Knight shift distribution associated to a triple incommensurate CDW (PLD).

on one of the cationic sites, the local change of the charge at **R** and temperature $T$ becomes

$$\Delta\rho(\mathbf{R}, T) = \Delta\rho(T) \times \times (\cos \mathbf{K}'_1.\mathbf{R} + \cos \mathbf{K}'_2.\mathbf{R} + \cos \mathbf{K}'_3.\mathbf{R}) . \quad (3)$$

In the tight binding approximation, the local change of EFG at a nuclear site $\mathbf{R}_i$, $\Delta q(\mathbf{R}_i)$, is proportional to the change of the average charge density in the atomic cell surrounding $\mathbf{R}_i$, $\Delta\rho(\mathbf{R}_i)$.

Therefore the shift of resonance frequencies are derived by a relation similar to 3 and leads to a resonance frequency distribution $g(\omega)\, d\omega$. This distribution shows an infinite singularity at $-\Delta\omega(T)$ and 2 step singularities at $3\,\Delta\omega(T)$ and $-1.5\,\Delta\omega(T)$. The overall width of the structure is taken as proportional to the order parameter of the PLD, in agreement with Mc Millan's theory [41], see figure 2.

Similar broadenings are observed on the central line and are attributed to a distribution of orbital Knight shift [42]. Comparing results at 0 and 21 kbar the onset temperature was found proportional to the amplitude of the CDW at low temperature as expected from mean field theory.

The strong pressure dependence of the Knight shift $K_{//}$ correlated with the weak pressure dependence of $T_1^{-1}$ between 0 and 21 kbar is in favour of an important orbital contribution rather than a dipolar one. This decrease of $K_{orb}$ under pressure is interpreted in terms of an increase of the interlayer splitting between the two $dz^2$ bands [6], which are believed to provide a significant contribution to $K_{orb}$ [42].

The significant results of the NMR study confirm the existence of 3 incommensurate waves and any explanation in terms of domains with a single wave vector must be rejected.

An interpretation with only two inequivalent sites [38] must be rejected as well : in that case one would observe two distinct lines of about 10 gauss wide.

The pretransitional broadening observed above 33 K on the satellite line, figure 1 can be attributed either to dynamic fluctuations as calculated by Bhatt and McMillan [43] or to static fluctuations driven by impurities [44]. The key has been given by a spin-spin $T_2$ measurement of the (1/2, − 3/2) satellite above $T_0$ [45] which showed that the broadening is static ($T_2 = 240$ μs at 40 K whereas the linewidth is $\approx 35$ G).

Some measurements performed at the *magic angle* $\theta = 56°$ from 33 to 150 K indicate a contribution of the CDW dynamic fluctuations to the relaxation rate $T_1^{-1} \sim 40\ s^{-1}$ at 33 K which would give a negligible effect on the linewidth. Therefore the $S(\mathbf{Q}, \omega)$ structure factor exhibits a strong $\delta$ contribution, due to impurities, and a central peak the width of which is estimated at 0.01-0.1 meV. This latter result is smaller than the energy resolution of neutron scattering experiments. We found $T_1\, T = 500 \pm 10$ msK for $H_0 \,//\, c$ throughout the temperature range 4.2-77 K. Hence we can say that any change in the density of states at the Fermi level due to the onset of the CDW (PLD) and (or) to pressure is smaller than 10 %.

3. **An experimental study of structural instabilities and superconductivity under high pressure.** — Since the first measurements of superconductivity, high pressure appeared to be a very valuable parameter. The chemical bonding of the layer compounds provides strongly anisotropic compressibilities, namely : $K_a = 4 \times 10^{-4}$ kbar$^{-1}$ and $K_c = 16 \times 10^{-4}$ kbar$^{-1}$ for 2H-$NbSe_2$ and $K_a = 1.6 \times 10^{-4}$ kbar$^{-1}$, $K_c = 11 \times 10^{-4}$ kbar$^{-1}$ for 3 R-$NbS_2$ [11]. The application therefore of a hydrostatic pressure produces a strenghtening of the interlayer coupling as well as an increase of intralayer interaction, which is similar to what is observed in normal transition metals.

Measurements under pressure have been performed on the 2H polytypes of $TaS_2$ [46], $NbSe_2$ [32] and $TaSe_2$ [47], and the onset of a PLD was detected through the anomaly of resistivity at $T_0$. The results are summarized on figures 3, 4, 5, 6 and table I.

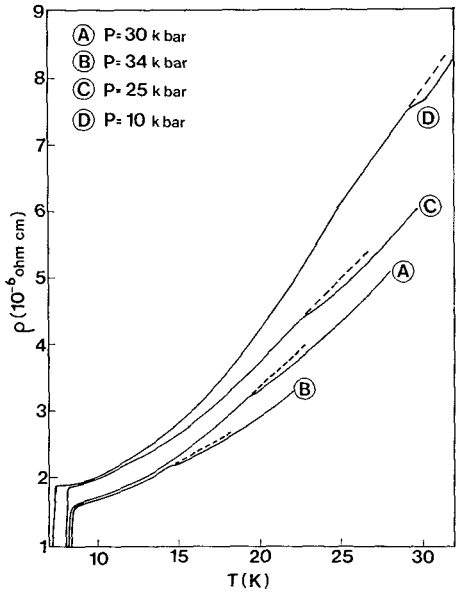


FIG. 3. — Temperature dependence of the resistivity of 2H-$NbSe_2$ showing the onset of CDW (PLD) states at different pressures.

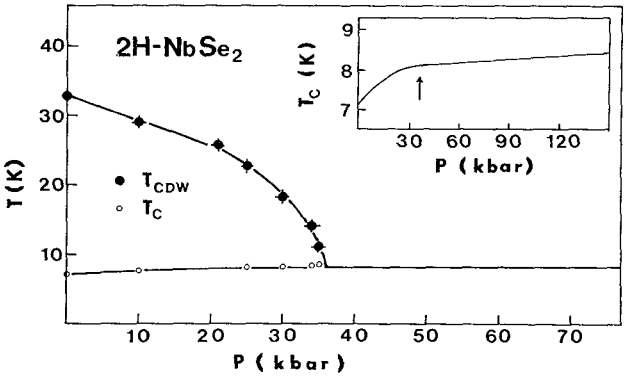


FIG. 4. — Phase diagram of the CDW (PLD) state and of the superconductivity state in 2H-$NbSe_2$. (Inset, pressure dependence of $T_c$ after reference [14].)

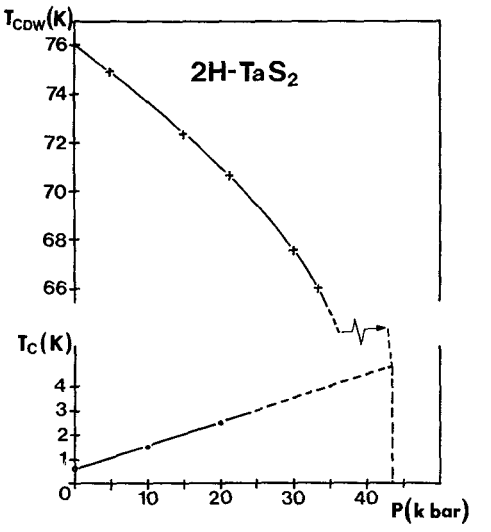


FIG. 5. — Phase diagram of the CDW (PLD) state and of the superconducting state in 2H-$TaS_2$, with extrapolation of $T_0$ to high pressure.

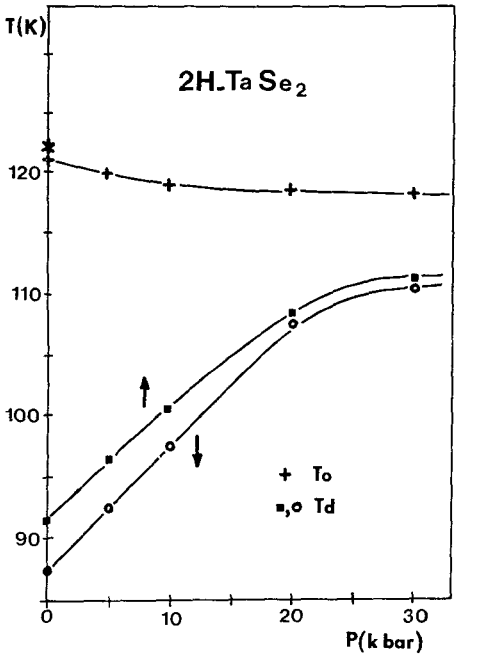


FIG. 6. — Phase diagram of $T_0$ and $T_d$ in 2H-$TaSe_2$ after reference [47]. The star at $T_0 = 122$ K is the value derived from neutron scattering experiments, reference [25]. Curves $T_{d\uparrow}$ and $T_{d\downarrow}$ correspond to the pressure dependence of the lock-in temperature warming and cooling the sample.

For all compounds, we found $dT_0/dP < 0$. In the case of 2H-$TaSe_2$, the PLD becomes commensurate with the $3\,a_0$ lattice at $T_d = 90$ K. This latter transition is first order, accompanied by a change of slope in $\rho(T)$ and the hysteresis found by resistivity agrees with the study of elastic constants [48]. Moreover figure 6 indicates $dT_d/dP > 0$ and a decrease of the first order character under pressure.

TABLE I

| | $T_0$ (K) | $\frac{\partial \ln T_0}{\partial P}$ (%) (kbar)$^{-1}$ | $T_c$(K) | $\frac{\partial \ln T_c}{\partial P}$ (%) (kbar)$^{-1}$ | $P^*$(kbar) |
|---|---|---|---|---|---|
| 2 H-$TaSe_2$ | 121 | — 0.15 | 0.15 ([a]) | ~ + 5 ([a]) | ⩾ 38 |
| 2 H-$TaS_2$ | 77 | — 0.3 | 0.65 ([c]) | + 10 ([c]) | ~ 43 |
| 2 H-$NbSe_2$ | 33.5 | — 1 | 7.2 | + 0.7 | 36 |
| 4 Hb-$TaS_2$ | 22 | — 3.6 | 2.5 ([b]) | + (10-20) | 10 |
| 2 H-$NbS_2$ | | | 6.3 | + 0.04 | |

([a]) From VAN MAAREN M. H. and SCHAEFFER G. M., *Phys. Lett.* **24** A (1967) 654 and reference [51].

([b]) There are some problems about the exact determination of $T_c$ at atmospheric pressure which are discussed extensively in reference [49]. Under pressure figure 7 the superconducting transition is sharp $\Delta T_c \sim 0.15$ K.

([c]) From reference [51]. $P^*$ is the pressure for the removal of the CDW (PLD) state.

The features of 4 $HbTaS_2$ are most interesting because of the alternating stacking along $c$ axis [49]. To a remarkable extent its properties are a composite of octahedral and trigonal prismatic compounds. The resistivity discontinuity noticed at 315 K corresponds to a lock-in of the CDW in octahedral layers (in 1T-$TaS_2$, $T_d$ = 350 K), and a drop of resistivity at 22 K corresponds to the onset of an incommensurate CDW in trigonal prismatic layers.

The structural aspect of mixed layer compounds has been studied through electron and neutron scattering by Di Salvo *et al.* [27] for 4 $HbTaSe_2$. The behaviour of 4 $HbTaS_2$ is qualitatively very similar [28]. The pressure dependence of $T_c$, $T_0$ (TP layers) and $T_d$ (0 Layers) is given in figure 7. The decrease of $T_d$ can be compared with the analogous decrease of $T_d'$ observed under pressure in 1T-$TaS_2$ [50].

Summarizing, we can say that the PLD (CDW) is removed above 10 kbar (TP layers of 4 $HbTaS_2$).

In 2H-$NbSe_2$ and 4 $HbTaS_2$, $T_c$ increases under pressure until the complete removal of the PLD and then stays nearly constant. It is worth noticing that the maximum $T_c$ = 4.5 K in 4 $HbTaS_2$ is very close to the extrapolation of $T_c$ in 2H-$TaS_2$ up to 44 kbar and not so far away from the 3.80 K value found in $TaS_2(pyr)_{1/2}$, when the PLD-CDW state is removed by intercalation [20].

The experimental situation is not yet clear in 2H-$TaSe_2$ as its low $T_c$ required very low temperature equipment [51]. However its low and presumably weakly pressure dependent $T_c$ is in agreement with the finding of a high and only weakly pressure dependent $T_0$, figure 6. This will be discussed more extensively in section 4.

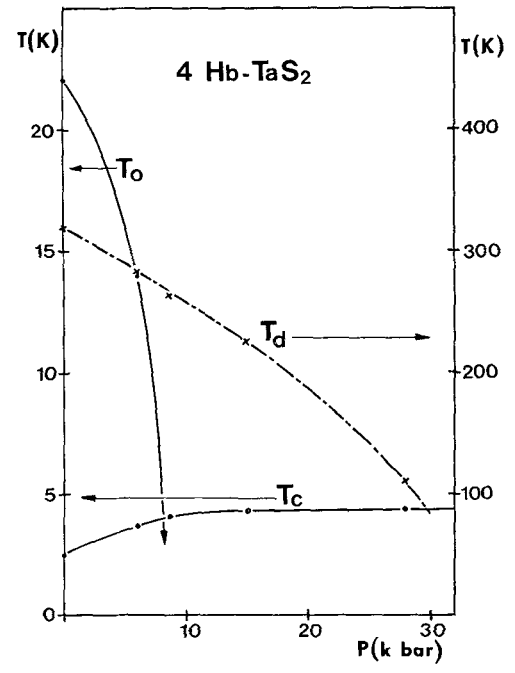


FIG. 7. — Phase diagram of 4Hb-$TaS_2$ after reference [49]. The left temperature scale refers to $T_0$ and $T_c$ in the trigonal prismatic layers. The right temperature scale refers to the lock-in temperature $T_d$ in the octahedral coordinated layers.

We also give some results of $T_c$ pressure dependence in intercalated-$TaS_2$ up to 14 kbar [52]. The zero field $T_c$ was measured by the extrapolation to zero field of $Hc_2$, measured in a high magnetic field on powdered samples. Up to 14 kbar a slight linear increase of $T_c$ is observed for all 3 compounds (amine intercalated-$TaS_2$) (Table II).

TABLE II

| | $T_c$ (K) | $\frac{\partial \ln T_c}{\partial P}$ (%) (kbar$^{-1}$) | $\Delta C$ (Å) |
|---|---|---|---|
| $TaS_2$ (butylamine)$_{0.53}$ | 2.50 | + 0.9 | *h*3.7 |
| $TaS_2$ (decylamine)$_{0.39}$ | 2.60 | + 0.22 | 8.5 |
| $TaS_2$ (hexadecylamine)$_{0.60}$ | 2.58 | + 0.28 | 33.6 |
| 2 H-$TaS_2$ | 0.65 | + 10 | |

The weak pressure coefficient of $T_c$ in intercalated $TaS_2$ contrasts with that of pure 2H-$TaS_2$. If the intercalation of the 2H polymorphs acts to remove the PLD-CDW states [20] the pressure enhancement of $T_c$ in intercalated $TaS_2$ does reveal a striking connection with the absence of the PLD-CDW state.

A correlation between superconductivity and the existence of a PLD-CDW state has been suggested through measurements on $H_x$-$TaS_2$ by Murphy *et al.* [53]. Nevertheless, addition of hydrogen also changes the filling of the conduction band by charge transfer without apparently fully suppressing the PLD-CDW, since resistivity anomalies are still present. As already mentioned the absence of PLD-CDW state in 2H-$NbS_2$ is in agreement with the pressure independence of $T_c$ [9].

In conclusion, the comparative study of $dT_0/dP$ and $dT_c/dP$ in the whole $TX_2$ series (including intercalated compounds) shows that the large pressure enhancement of $T_c$ is due to a removal of the CDW (PLD) state occurring under pressure. This was made evident for 2H-$NbSe_2$ and 4 Hb-$TaS_2$ and was also confirmed by studies of 2H-$NbS_2$ and intercalated layer compounds where the CDW is totally missing and partially removed. One material whose behaviour bears some resemblance to that of 2H-$NbSe_2$ is the A 15 compound $V_3Si$. This material is known to undergo at 22 K a cubic to tetragonal phase transition accompanied by a softening of the sound velocity and of certain phonon modes [54, 55]. The effect of pressure is to decrease the lattice transformation temperature $T_0$ and to increase $T_c$ in the distorted phase.

The measurements of Chu and Testardi [56] on this system, at pressures up to 18 kbar, indicate by extrapolation that $T_0$ and $T_c$ would cross at about 24 kbar and that at higher pressures a different pressure dependence of $T_c$ in the cubic phase would presumably result though not yet directly observed.

4. **Review of the theoretical approaches to the distorted phases.** — The idea that a CDW state could be the fundamental state in some metals was put forward by Overhauser in his 1968 article [57]. The electron density at **R** can be written :

$$\rho(\mathbf{R}) = \rho_0(1 + \alpha \cos \mathbf{Q}.\mathbf{R})$$

where $\rho_0$ is the average electron density, **Q** the wave vector of the charge oscillation and $\alpha$ the relative modulation amplitude. Overhauser has shown that a CDW state can be stabilized by means of the correlation energy, though the electron-phonon coupling is not taken into account. The CDW state is characterized by a one electron potential $V(\mathbf{R}) = -G \cos \mathbf{Q}.\mathbf{R}$ opening gaps in the electron dispersion curves at $\pm$ **Q**/2. Later Chan and Heine [58] taking into account the screened exchange interaction $\bar{V}_Q$, the Coulomb interaction $\bar{U}_Q$ and the electron-phonon coupling $\bar{\eta}_Q^2$, derived the conditions for the stability of a CDW state accompanied by a PLD [59] of same wave vectors, namely

$$\frac{4\,\bar{\eta}_Q^2}{\hbar\omega(\mathbf{Q})} - (2\,\bar{U}_\mathbf{Q} - \bar{V}_\mathbf{Q}) > \frac{1}{\chi_\mathbf{Q}^0} \qquad (4)$$

where $\omega(\mathbf{Q})$ is the *bare* phonon frequency at **Q** and $\chi_\mathbf{Q}^0$ is the wave-vector dependent susceptibility defined as

$$\chi_\mathbf{Q}^0 = \sum_{\mathbf{k},\sigma} \frac{n_{\mathbf{k},\sigma} - n_{\mathbf{k}+\mathbf{Q},\sigma}}{E_{\mathbf{k}+\mathbf{Q}} - E_\mathbf{k}}.$$

A PLD-CDW state would be stable at zero temperature (condition (4)) for given values of $2\,\bar{U}_Q - \bar{V}_Q > 0$ only if the electron phonon coupling is large enough and if there exist some peculiar wave-vectors **Q** for which $\chi_\mathbf{Q}^0$ becomes large.

There are mainly two ways for obtaining large values of $\chi_\mathbf{Q}^0$.

i) The Fermi surface contains large areas connected by **Q** with parallel tangent planes : this is the *nesting* criterion presumably responsible for the Peierls distortion of 1 d metals such as KCP [60] and TTF-TCNQ [61].

ii) The band structure exhibits Van-Hove singularities (saddle-points) connected by wave-vectors **Q** and located very close to the Fermi level [62]. This is a situation encountered probably in the A 15 compounds [23, 63].

Both approaches lead, at finite temperatures $T_0$, to the onset of a PLD-CDW state through a second order phase transition. The phase transition temperature depends on a coupling constant $\Lambda_\mathbf{Q}$ by a relation similar to that of $T_c$ in the McMillans' theory of strong coupling superconductivity [64, 65].

$$T_0 \sim T_F \exp -\frac{1 + \Lambda_\mathbf{Q}}{\Lambda_\mathbf{Q}}$$

where $\Lambda_\mathbf{Q}$ can be expressed as

$$N(E_F)\left[\frac{4\,\eta_\mathbf{Q}^2}{\hbar\omega_\mathbf{Q}} - (2\,\bar{U}_\mathbf{Q} - \bar{V}_\mathbf{Q})\right].$$

A phenomenological approach of the PLD-CDW states in layer compounds dichalcogenides has been given recently by McMillan [44] by means of Landau-Ginzburg theory.

The free energy is expanded as a power series expansion in the order parameter and gradients of the order parameter. The order parameter is taken as the amplitude of the CDW.

This purely two dimensional theory predicts a first order transition from the normal state to the ICDW-PLD state. By allowing a further distortion with its cost of elastic energy, the attractive interaction energy between the CDW and the lattice of positive ions can be maximized towards a state where the wave vectors of the distortion becomes comensurate with the high temperature lattice.

McMillan's theory neglecting the interlayer coupling does not describe adequately enough the structural instabilities in the 2H or 1T systems. It was further noticed by McMillan [66] that Coulomb interaction between CDW of neighbouring layers can determine the relative phases of the oscillation and therefore the stacking of the CDW-PLD along the $c$ axis. This coupling appears necessary to explain the second or weakly first order character of the transition at $T_0$ in 2H polytypes. However, the early 2-d model seems quite appropriate to the onset of CDW-PLD in 4 $HbTaS_2$ or 4 $HbTaSe_2$, since for mixed coordinated systems the interlayer interaction between trigonal prismatic layers can be neglected [27]. In fact, a first order transition is observed at the onset of the ICDW-IPLD transition at $T_0$ [27, 30].

Whereas the driving mechanism for the CDW-PLD instability may be the *nesting* (process i) of this section), leading in 1T materials, to the opening of a gap on large portions of the Fermi surface and to a metal to insulator transition at $T = T_d$, it is likely that a Van-Hove singularities (process ii)) would explain better the behaviour of the more complex 2H polytupes for which only a minor fraction of the Fermi surface is removed at $T = T_d$. (See for example the behaviour of the resistivity of 2H-$TaSe_2$ at $T = T_d$ [47].)

5. **The connection between the existence of distorted phases and superconductivity.** — We shall begin by presenting the various possibilities of $T_c$ enhancement in the frame of the strong coupling theory of superconductivity [64] for which $T_c$ is derived by the relation

$$T_c = \frac{\theta_D}{1.45} \exp\left(\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\,\lambda)}\right) \qquad (5)$$

where

$$\lambda = \frac{N(E_F) < I^2 >}{M < \omega^2 >} \qquad (6)$$

$< I^2 >$ is the Fermi surface average of an electronic matrix element and $< \omega^2 >$ is an average of phonon frequencies. $\theta_D$ is the Debye temperature and $\mu^*$ is the Coulomb pseudo potential. We must keep in mind that an unambigous definition of the Debye temperature in strongly anisotropic materials such as layer compounds is open to question.

The logarithmic derivative of (5) becomes

$$\frac{\partial \ln T_c}{\partial P} = \frac{\partial \ln \theta_D}{\partial P} + \varphi(\lambda) \frac{\partial \ln \lambda}{\partial P}. \qquad (7)$$

We can imagine different channels for the pressure dependence of $T_c$.

*a*) A usual change of the electron-phonon coupling constant as observed in transition metals.

*b*) An anomalous change of $\lambda$ coming either from a low value of $< \omega^2 >$ in (6) or from a large pressure dependence of $N(E_F)$ under pressure.

In the region where the undistorted metallic state is stable, down to $T_c$, namely $P > 36$ kbar for 2H-$NbSe_2$, $P > 10$ kbar for 4 $HbTaS_2$ and all pressures for 2H-$NbS_2$ the experimental pressure dependence of $T_c$ is

$$\left.\frac{\partial \ln T_c}{\partial P}\right|_{exp} = + 0.04\ \%\ \text{kbar}^{-1}\ [9, 32]\,.$$

The pressure dependence of $\lambda$ can be derived in 2H-$NbSe_2$ by (7). Specific heat data [67] give $\lambda = 0.9$ at $P = 0$ kbar. In the following we shall take for $\lambda$ the values derived from the low temperature specific heat measurements. This is presumably a reasonably good assumption in 2H-$NbSe_2$ since the PLD-CDW state disturbs only weakly the Fermi surface. However such a simple analysis should not be made for 2H-$TaSe_2$, a situation where the onset of the PLD-CDW presumably removes a larger fraction of the density of states therefore decreasing $\lambda$ significantly.

We take

$$\frac{\partial \ln \theta_D}{\partial P} = -\frac{1}{2}\frac{\partial \ln \rho \perp c}{\partial P} = 0.1\ \%\ \text{above 30 kbar [11].}$$

Therefore from (7) we find with $\varphi(\lambda) = 1.62$ and $\mu^* = 0.1$, $\partial \ln \lambda / \partial P = -0.04\ \%\ \text{kbar}^{-1}$. An estimate of the pressure dependence of $\lambda$ can also be directly performed using the electron-phonon coupling theory of transition metals [68] applied to a single layer

$$\frac{\partial \ln \lambda}{\partial P} = -a q_0 K_a - \frac{\partial \ln < \omega^2 >}{\partial P} \qquad (8)$$

$a$ is the distance between niobium atoms in the planar hexagonal lattice, $q_0$ is the Slater parameter of d wave-functions.

Assuming that

$$\frac{\partial \ln < \omega^2 >}{\partial P} = \frac{\partial \ln \theta_D}{\partial P},$$

with the previous value for $\partial \ln \theta_D / \partial P$, $q_0 = 1\ \text{Å}^{-1}$, $a = 3.4$ Å and $K_a = -4 \times 10^{-4}$ kbar$^{-1}$ [11], we derive $\partial \ln \lambda / \partial P = -0.07\ \%\ \text{kbar}^{-1}$ which does not show a large discrepancy with the previous derivation based on the McMillan's formula (5).

Around 10 kbar

$$\frac{\partial \ln \rho \perp c}{\partial P} \approx -0.5\ \%\ \text{kbar}^{-1},$$

then, with (8) and (7) we obtain

$$\frac{\partial \ln \lambda}{\partial P} = -0.37\ \%\ \text{kbar}^{-1}$$

and

$$\frac{\partial \ln T_c}{\partial P} = -0.35\ \%\ \text{kbar}^{-1}$$

whereas the experimental value is

$$\left.\frac{\partial \ln T_c}{\partial P}\right|_{exp} = + 0.7\ \%\ \text{kbar}^{-1}$$

is the pressure range 0 to 25 kbar.

If a similar analysis is performed for 2H-$TaS_2$ with the parameter $K_a \approx -1 \times 10^{-4}$ kbar$^{-1}$ and $\partial \ln \rho \perp c/\partial P = -0.12\ \%$ kbar$^{-1}$ (around 10 kbar from our resistivity data), we obtain

$$\partial \ln \lambda/\partial P = -0.07\ \%\ \text{kbar}^{-1}\ .$$

With $\lambda = 0.41$ [67] we derive

$$\partial \ln T_c/\partial P = -0.5\ \%\ \text{kbar}^{-1}$$

from (7), a value which is also very far from the experimental determination in the 10 kbar region

$$\left.\frac{\partial \ln T_c}{\partial P}\right|_{exp} = + 10\ \%\ \text{kbar}^{-1}\ ,$$

A larger value of $\lambda$ would lead to an even smaller value of $\partial \ln T_c/\partial P$. Summarizing, one can say :

5.1 The large pressure enhancement of $T_c$ in the trigonal prismatic compounds cannot be understood in terms of the variation of the electron-phonon coupling constant such as in transition metals [69].

However, the latter process can account fairly well for the much weaker (by one order of magnitude) positive pressure coefficient observed as the PLD-CDW state is removed under high pressure.

Assuming that for layer compounds with strong electron-phonon interactions the contribution $4\,\bar{\eta}_Q^2/\hbar\omega_Q$ is dominant upon Coulomb and exchange contributions in the criterion for the stability of the PLD-CDW state we derive

$$\frac{\partial \ln T_0}{\partial P} \approx \varphi(\lambda_Q)\frac{\partial \ln \lambda_Q}{\partial P} \quad \text{with} \quad \lambda_Q = \frac{N(E_F) < \omega_Q^2 >}{M\omega_Q^2}$$

where $\omega_Q$ is now a bare phonon frequency.

Then assuming a

$$\varphi(\lambda_Q)\frac{\partial \ln \lambda_Q}{\partial P} \approx \varphi(\lambda)\frac{\partial \ln \lambda}{\partial P}$$

we obtain the pressure dependence

$$\frac{\partial \ln T_0}{\partial P} = -0.6\ \%\ \text{kbar}^{-1}$$

and $-0.56\ \%$ kbar$^{-1}$ for 2H-$NbSe_2$ and 2H-$TaS_2$ respectively. These latter values approach the experimental pressure dependence of $T_0$ in 2H-$NbSe_2$ and 2H-$TaS_2$, see table I.

It must be kept in mind that the previous estimates are very tentative. In particular a comparison of the experimental data with theory awaits a proper derivation of the phase transition temperature in terms of electron-phonon, Coulomb and exchange interactions.

It is likely that the pressure dependence of $T_0$ cannot be explained solely either by a change of the amplitude of Van Hove singularities or by a change in the nesting characteristics occurring under pressure. The previous estimates suggest that the decrease of the interaction itself is a major factor.

5.2 The next possibility namely, a small value of $< \omega^2 >$, has been proposed by Testardi [70] to account for the pressure dependence of $T_c$ in A 15 superconductors. The existence of a soft phonon mode connected with a structural instability at $T_0$ may decrease the average $< \omega^2 >$, provided the wave vector of the PLD is large. As long as $T_0 > T_c$ and $dT_0/dP < 0$ pressure makes $dT_c/dP > 0$. However a maximum of $T_c$ is expected for $T_c \approx T_0$ in this model, a feature which is in contradiction with the experimental results in the layer compounds.

5.3 A large increase under pressure $N(E_F)$ in the CDW-PLD state is conceivable according to an argument suggested by Friedel [71].

At the onset of the CDW-PLD state, gaps open at the Fermi surface in the direction of the star of $\mathbf{K}_i$ vectors. This will decrease the density of states at the Fermi level, and accordingly, reduce $T_c$ (Fig. 8).

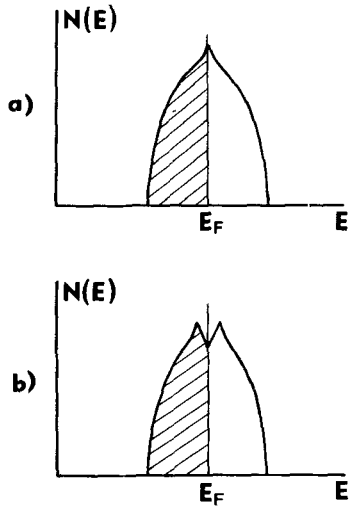


FIG. 8. — Density of states of the $dz^2$ band (schematic) in 2H polytypes) *a*) normal undistorted phase ; *b*) CDW(PLD) phase.

When pressure is applied, both the fraction of Fermi surface, removed by the phase transition (nesting hypothesis) and the amplitude of the gaps decrease. Our NMR data at 21 kbar in 2H-$NbSe_2$ show that the amplitude of the CDW is reduced by the same am ount as $T_0$. It follows as pressure increases, that the reduction of $N(E_F)$ will be smaller and $T_c$ will increase. This interpretation for $T_c$ suggests that in the various compounds, the larger the $T_0$ the smaller the $T_c$. This is in complete agreement with the observations, table I in the 2H family.

Since it seems that electron-phonon coupling is weaker in S compounds than in Se compounds of Ta, it is conceivable that the Chan-Heine criterium is not

fulfilled in 2H-$NbS_2$, although its Fermi surface may not differ from that of 2H-$NbSe_2$ [38].

6. **Conclusion.** — We have presented an extensive report of the structural instabilities on the trigonal prismatic layer dichalcogenides.

The pulsed NMR experiments on $^{93}Nb$ in 2H-$NbSe_2$ have revealed the unambiguous existence of three CDW-PLD below a temperature $T_0 = 33$ K. These three waves correspond to the star of 3 wave vectors incommensurate with the reciprocal lattice vectors. The NMR technique led also to results concerning the pretransitional behaviour. Namely that the structure factor $S(Q, \omega)$ exhibits two components : the first which extends up to a finite energy $\approx$ 0.01-0.1 meV probably due to critical fluctuations above $T_0$ and which provides an additionnal contribution to the nuclear spin lattice relaxation rate, the second, which is entirely static and is due to charged impurities. High pressure experiments give $dT_0/dP < 0$ for all members of the trigonal prismatic family and for $T_0$ of the trigonal prismatic layers in the mixed-compound 4 $HbTaS_2$.

Both the examination of the NMR line shape in 2H-$NbSe_2$ under pressure and the increase of the lock in temperature in 2H-$TaSe_2$, under pressure, enable us to establish that the spanning vectors in the ICDW-IPLD state tend towards commensurateness under pressure. Our NMR results and $T_d(P)$ in 2H-$TaSe_2$ confirm a picture of the ICDW state in terms of large commensurate domains separated by walls in which the phase of the order parameter rotates by $2\pi/3$ [66].

The two dimensional phenomenological theory of McMillan applies very well to the weakly coupled trigonal prismatic layers of 4 $HbTaS_2$, predicting in these a 1st order transition at the onset of CDW's, in agreement with the experiments. Simultaneous studies of $T_c$ and $T_0$ in the 2H series have shown that the modification of the electron-phonon coupling constant occuring under pressure could explain a large contribution to the pressure depressed $T_0$, the other contribution originating possibly in either a denesting effect or in the modification of Van-Hove singularities of the band structure. The salient result of our study is that the large pressure enhancement of $T_c$ existing as long as $T_0 > T_c$ can only be understood by the reduction of the density of states at Fermi level in the PLD state. This reduction of $N(E_F)$ is proportional to the amplitude of the CDW and therefore a removal of the CDW state can significantly increase $T_c$.

Layer compound dichalcogenides are very appealing materials for various reasons :

*a*) Pure and rather large crystals can be grown.

*b*) Their structure is relatively simple.

*c*) Through the 2-d character, the electronic structure can be made exhibit some of the features extensively studied at present, namely, electronic metal-insulator transitions (Peierls transitions in 1-d systems).

It appears from this high pressure study that the mechanism for enhancement of $T_c$ in the layer compounds is now well established and understood by the Friedel model. It is also likely that similar explanations could be valid for the A 15 superconductors.

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