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ON THE NATURE OF THE LOW-TEMPERATURE PHASE OF 1T-TaS₂

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Résumé. — Il paraît que les phases à basse température de 1T-TaS₂ sont complètement isomorphes mais la seconde montre un comportement métallique, tandis que la première une conduction activée. Cela est attribué au fait que la formation de l'onde de densité de charges seule ne produit pas d'écarts sur l'entière surface de Fermi. Le rôle de la courbure de la nappe de soufre dans la formation du super-réseau est mis en évidence qui explique l'épuisement de charges aux centres des amas de 13 sites et qui indique une plus grande probabilité de la localisation de Mott sur les amas que sur les atomes individuels. Les spins impairs associés aux amas peuvent causer l'apparition d'une nouvelle phase magnétique préconisée originalement par Anderson.

Abstract. — We note that the low-temperature phases of 1T-TaS₂ and 1T-TaSe₂ seem completely isostructural, but the second shows metallic behaviour while at lowest temperatures the first has an activated conductivity. This is ascribed to the fact that charge-density wave formation alone does not produce gaps over the entire Fermi surface. We emphasize the role of sulphur sheet buckling in superlattice formation which explains the charge depletion in the centers of the 13-site clusters and suggests that a Mott-localization onto clusters rather than to single atoms is likely to occur. The unpaired spins associated with the clusters may lead to the appearance of a novel magnetic phase first suggested by Anderson.

Group VB transition metal dichalcogenides show an amazing variety of phase transitions [1]. After donating four electrons to bonding orbitals derived mainly from anion p-states, each metal ion is left with one electron to fill d-type states. It is just the situation in which electron localization without an accompanying lattice distortion changing the number of electrons per unit cell could occur [2]. As most of the transitions mentioned above are accompanied by abrupt changes in the resistivity, and sometimes in its temperature coefficient, it might have been tempting to regard at least some of them as Mott-transitions. When more data, especially on structure, became known, this view was abandoned.

Extensive X-ray and electron diffraction investigations [1, 3, 4] revealed that all of the transitions are accompanied with structural changes increasing the number of lattice sites in the unit cell. Most, if not all, of them can apparently be described very satisfactorily in terms of a Fermi-surface driven charge-density-wave [CDW] formation with its concomitant periodic lattice distortion [PLD], or its eventual locking into a commensurate superlattice. Hence, there seems to be no need to invoke localization owing to correlation: the materials are either on the metallic side of the Mott-transition, even if not far removed from it, or they are conventional band semiconductors. When in materials supposed to have a few pieces of Fermi surface [FS] left electrical

behaviour unusual in metals, such as a negative temperature coefficient of resistivity, is found it is usually ascribed to the smallness of some of the gaps.

We would like to point out a possible exception. In our opinion the low-temperature properties of 1T-TaS₂ can be at least equally well described assuming that there the one-electron picture breaks down. We envisage a Mott-transition occurring either simultaneously with the incommensurate to commensurate transition at 200 K, or taking place, without further structural changes, at some lower temperature. Electron localization is certainly *not* the driving force for the emergence of the $\sqrt{13}$ reconstruction; rather superlattice formation establishes the conditions which facilitate a Mott-transition.

According to resistivity measurements [5] two consecutive phase transitions occur in 1T-TaS₂: the first at 350 K from a metallic to a semimetallic, and the second at 200 K from the semimetallic to a semiconducting state. Below 50 K certainly an activated conductivity seems to be present and Thompson *et al.* [5] put the activation energy at about 10^{-4} eV. Structural investigations [3, 4] identified the phases as an incommensurate CDW phase at high, an almost-locked-in incommensurate state at intermediate, and a commensurate superlattice state with 13 Ta atoms in the 2-dim. unit cell at low temperatures. 1T-TaSe₂ is closely analogous in

many respects, but here only one phase transition takes place at 473 K from an incommensurate to the commensurate phase. For all we know, the commensurate phases of the two materials are isostructural. The in-plane atomic displacements for a Ta sheet are shown in figure 33 of reference [1] the two-dimensional unit cell contains 13 atoms. Figure 1

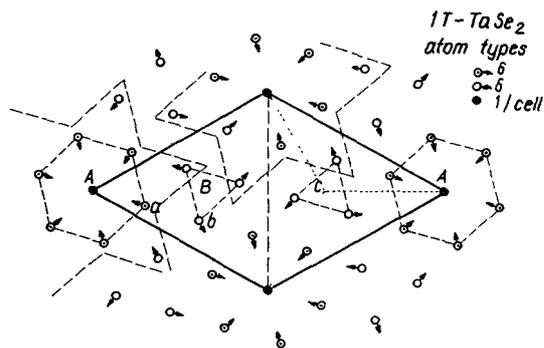


FIG. 1. — Atomic displacements in the commensurate phase of 1T-TaSe₂, after figure 33 of Ref. [1]. Dashed lines indicate the star-shaped clusters which we take as structural units.

of this paper has been taken from this source, apart from a minor addition. We feel that the choice of the unit cell does not emphasize the appearance of star-shaped clusters, as indicated by dotted lines in figure 1, having a central atom (A), a surrounding hexagon of atoms moving in radially, and a second shell of atoms still moving into the cluster, but obliquely. These star-shaped clusters will figure in our considerations as the basic structural unit. Structural investigation of the high-temperature phase of 1T-TaS₂ shows ⁽¹⁾ that wherever Ta ions move closer to each other, S atoms in the surrounding sheets move outwards and sink toward the metal sheet where the concentration of Ta atoms decreases. The $\alpha\beta\gamma\alpha\beta\gamma$ stacking seen [4] in the incommensurate phase indicates that the sulphur-sheet-swelling repel each other for steric reasons at least, if no other. In the commensurate phase the repeat distance in the c direction increases to 13 c_0 from the original 3 c_0 , and the new three-dimensional triclinic unit cell has 26 Ta atoms. Both $c + a$, and $c + 2a$ are possible for the "A" position in the next sandwich; Scruby *et al.* [4] favour the former, but consideration of the repulsion of sulphur swellings would rather suggest the latter which would mean smaller departure from the original $\alpha\beta\gamma\alpha\beta\gamma$ stacking. However, the choice between these possibilities does not affect the rest of the argument.

Returning to the electrical properties: while the ground state is obviously non-metallic in TaS₂, TaSe₂ in its low-temperature phase is clearly a metal [6], with a conductivity about 500 times higher

(1) Wigers, private communication.

than the lowest measured value for the sulphide. Also, there is no indication of activation in the selenide.

There being an even number of electrons per unit cell, one might in principle expect a perfect gapping and conventional semiconducting properties. The fact that this does not happen in 1T-TaSe₂, where the transition temperature is quite high, and seems to near completion in 1T-TaS₂ only at temperatures well below 200 K, strongly suggests that the formation of gaps is not the main motivation for the phase transitions considered here. (It seems to play a major role, though, in the appearance of the incommensurate CDW's.) A look at the high-temperature FS derived for 1T-TaSe₂ (figure 34 of reference [1] which for ready reference we reproduce as figure 2)

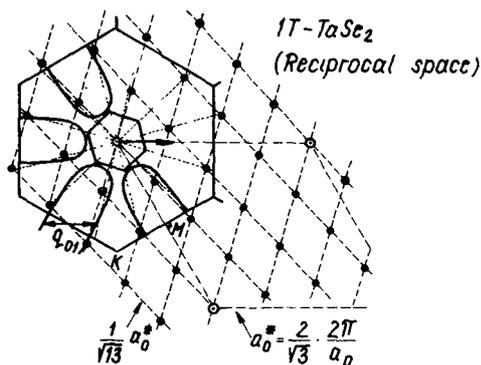


FIG. 2. — The high-temperature Fermi surface of 1T-TaSe₂, after figure 34 of Ref. [1].

shows that the FS cuts across 12 of the 13 new zones, and not at all marginally. Rather than trying to explain the qualitatively different electrical properties of the two materials invoking differences in the details of their Fermi surfaces, we suggest that *locking in of the CDW's would not produce perfect gapping in either of them, and the insulating ground state of the sulphide is to be explained by a Mott-transition.* To see, how this may come about, let us first consider the role played by sulphur sheet buckling in the energetics of the transition, and its effect on electronic charge redistribution.

As we have already mentioned, a CDW in the Ta plane is accompanied by the undulation of the sulphur sheets of the sandwich, i. e. a periodic change of the c/a ratio. The consequences of this can be crudely assessed by examining figures 10a and 10b in Mattheiss' paper [7] on the band structure of dichalcogenides. (Fig. 3 in ours.)

With the actual value of $c/a = 5.853/3.365 = 1.739$, about 6.2 % larger than what would belong to ideal octahedral coordination, the threefold degeneracy of the lower t_{2g} level is lifted, and a small splitting between the lowermost d_{z^2} and the high-lying ($x^2 - y^2$, xy) level results. From Mattheiss' calculation this

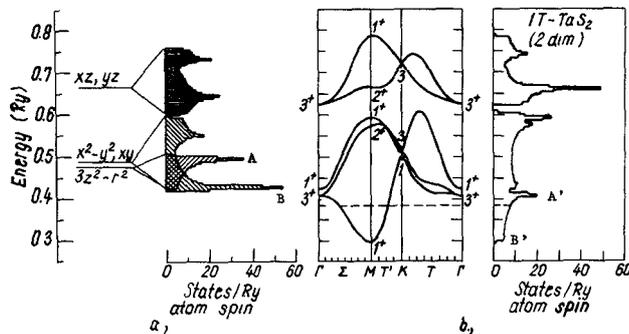


FIG. 3. — Ligand-field levels and density-of-states curves for unhybridized d-bands in high-temperature 1T-TaS₂; b) The two-dimensional results after having taken hybridization into account/after Mattheiss [7]. Notations A, B, A' and B' referred to in the text.

can be estimated as 0.15 eV. Starting from atomic-like orbitals of the corresponding symmetries, and neglecting hybridization, one arrives at the density-of-states figure of figure 3a. The sharp peak B at the bottom of the band of parentage ($x^2 - y^2$, xy), and a higher-lying peak A originating from the $3z^2 - r^2$ states are particularly noticeable. The effect of including hybridization is profound. The peak at the bottom has disappeared, leaving only a relatively sharp shoulder at the bottom (B'), and at the same time the band extended significantly towards lower energies. Decreasing the c/a ratio from its actual value would bring us nearer to cubic symmetry, i. e. to threefold degeneracy and consequently to stronger hybridization: the band would extend farther to deeper energies. Now, if we have a periodic change in the c/a ratio, that would allow in first approximation to keep the Fermi level fixed, and we would get a *lower electron density in the high c/a regions, and charge pile-up in the low c/a regions*. That means smaller electronic density in the centres of our star-shaped clusters, and more electrons on its perimeter. This conclusion is in agreement with recent XPS experiments [8, 9]. We can even get a rough estimate for the numbers: assuming that the B'-A' separation scales with the crystal field splitting which is about 0.15-0.2 eV for 6.2% departure from the ideal c/a value, and noticing that the density-of states curve is relatively flat between the Fermi level and B', we can get bounds by taking $n(E_F)$, and $n(E_B)$, respectively:

$$\Delta n = - (1.8-3.7) \frac{\Delta(c/a)}{(c/a)_0} \frac{\text{electrons}}{\text{atom}}$$

So, a few tens of per cents' change in the local electronic density is not an unreasonable expectation. The figure 0.5 for the amplitude of the CDW that Wertheim *et al.* give, is somewhat higher than what could be expected from our simple argument.

The change in the shape of the band owing to the modulation of c/a is going to have an effect on the

energy balance of CDW formation as well. Taking the simple form

$$\frac{c}{a}(x) = \left(\frac{c}{a}\right)_0 + \delta \cos qx$$

one has to evaluate

$$\Delta E = \frac{1}{L} \int_0^L dx \int_{B'(x)}^{E_F} \varepsilon n_x(\varepsilon) d\varepsilon - \int_{B'_0}^{E_F} \varepsilon n(\varepsilon) d\varepsilon$$

where $B'(x)$ is the shoulder at the bottom of the band as a function of coordinate x . In view of the already mentioned constancy of the density of states near B' , the terms arising from the oscillation of $B'(x)$ cancel and so one expects contributions coming from the neighbourhood of the Fermi level to dominate.

Expanding in powers of δ

$$n_x(\varepsilon) = n_0(\varepsilon) + \frac{\partial A'_0}{\partial \left(\frac{c}{a}\right)} \frac{\partial n}{\partial \varepsilon} \delta \cos qx + \left. \frac{1}{2} \frac{\partial^2 n}{\partial \varepsilon^2} \left| \frac{\partial A'_0}{\partial \left(\frac{c}{a}\right)} \delta \cos qx \right|^2 \right.$$

and integrating over x over the period L of the CDW, one obtains

$$\Delta E = - \frac{\delta^2 E_F}{4} \left| \frac{\partial A'_0}{\partial \left(\frac{c}{a}\right)} \right|^2 \left(\frac{\partial n}{\partial \varepsilon} \right)_{\varepsilon=E_F} \quad (1)$$

The last factor of the expression $\partial n/\partial \varepsilon$ can be quite large if E_F is near to A' ; in fact if we take the formula valid for a two dimensional saddle point singularity

$$\frac{\partial n}{\partial \varepsilon} = \frac{\text{const}}{|\varepsilon - A'|}$$

is divergent at A' .

Formula (1), of course, indicates an energy gain growing indefinitely with δ ; the amplitude will be determined by taking into account the elastic energy term as well. A notable feature is that (1) does not depend on q , the wave vector of the CDW; that will have to be determined by other considerations. One can briefly comment on the effect of pressure: under pressure there will be a *uniform* decrease in c/a , and as the bottom of the band recedes from A' , so will E_F ; this leads to a decrease in $n(E_F)$, and in $(\partial n/\partial \varepsilon)_{E_F}$ as well, consequently, pressure acts to suppress CDW formation — just as found experimentally.

Presently we do not follow this course of investigation further; for our present purposes suffice it to say that c/a alternation does play an essential role in the energetics of CDW formation, and one of its concomitants is electron density depletion in regions where c/a is locally bigger than average.

In view of the sizeable atomic displacements both

towards the cluster centres in the Ta sheets (see Fig. 1) and perpendicularly to the layers in the S sheets, one expects an essential modification of the electronic structure with respect to what could be expected for the undistorted material. As the star-shaped clusters surrounded by dotted lines in figure 1 form easily distinguishable structural units, a good starting point seems to be to solve the problem of the electronic structure of the individual clusters first. This would lead to Cluster-Wannier orbitals, presumably quite well localized. The nature of the result can be guessed from what we said about the effect of varying c/a . Because of crystal field effects, the low-lying orbitals will be found in the regions of Ta rarefaction, i. e. at the borders of the clusters. These are the least tightly bound orbitals, for which interaction between clusters would be essential, but we do not have to deal with this problem, because the associated bands will be filled, anyway. Cluster Wannier orbitals of higher energies will be more centred on the clusters.

Having 13 electrons per cluster, we can fill up the six low-lying orbitals associated with the border sites, and will be left with a single electron to be put on an inner orbital. Restricting our attention to the bands which would derive from the partially filled higher orbitals, the first question we can ask is whether band formation will really occur, or a localized picture will be valid. As the clusters are well separated, and the orbitals rather localized onto the clusters, we can reasonably expect *intra-cluster Coulomb interaction to be large enough compared to the intercluster transfer integral for a Mott-transition to occur*. As the value of the Mott-Hubbard gap that can be derived from resistivity data [5] is merely a few times 10^{-4} eV, Mott-transition turns out to be marginally possible, and it is understandable that the larger anionic polarizability of the Se ions will prevent a Mott-localization from occurring in 1 T-TaSe₂.

In lack of a detailed calculation for the electronic structure of commensurate phases we cannot actually demonstrate that the criterion of Mott-localization

for the *thirteenth* electrons in the clusters will be satisfied. Instead, we guess the validity of this statement from experiments and proceed to explore the consequences.

It should be noted that the susceptibility begins to deviate from its temperature-independent value below 50 K, i. e. in the same temperature regime where an Arrhenius plot fits the resistivity. As 12 out of the 13 electrons will be paired in the low-lying orbitals, one has to *associate one unpaired electron, i. e. $S = \frac{1}{2}$ with each cluster*. We expect that the localized moments of the clusters will interact *antiferromagnetically* via a superexchange mechanism — experiments in any case exclude a ferromagnetic coupling. Now, let us notice that though the original triangular lattice is severely distorted, *the 13-atom clusters, and their unpaired spins will form another undistorted triangular lattice*. Neglecting all but nearest neighbour interactions (which looks a much better approximation for the clusters than it would be for the ions) one is faced just with the problem that Anderson considered [10]: with the problem of the isotropic triangular $S = \frac{1}{2}$ antiferromagnetism. Anderson was the first to point out that this may be a very special case inasmuch as this system can be suspected to have a purely singlet, so-called resonating valence bond (RVB) ground state rather than a conventional Néel-type ground state. Subsequent work [11, 12] added further circumstantial evidence supporting this guess, but the properties of the as yet hypothetical RVB ground state (or, rather, low-temperature phase) still remain largely unknown. However, comparison [12] with the other *anomalous* antiferromagnet, the $S = \frac{1}{2}$ Heisenberg linear chain, suggests that we should expect a (probably rounded) maximum in the susceptibility in the neighbourhood of $T \sim J/k$, where J is the antiferromagnetic coupling. As experiments show the susceptibility starts increasing at about the same temperature where the resistivity does; if our picture is valid, this corresponds to the Mott-Hubbard gap, which is expected to be much larger than J , so we are still on the rising side of the susceptibility maximum.

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